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Nano-enabled environmental products and technologies – opportunities and drawbacks

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Title:

Nano-enabled environmental products and technologies – opportunities and drawbacks

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Preface

The previous Danish government and the Red-Green Alliance (in Danish, Enhedslisten) signed an agreement for four years (2012-2015) that focuses on the use of nanomaterials in products on the Danish market and their consequences to consumers and the environment. The Danish Environmental Protection Agency (EPA) has initiated a series of projects with the aim of further clarifying possible risks to consumers and the environment.

The current project complements previous activities by investigating the benefits for health and environment that the use of nanomaterials in products and technologies may have.

The project was carried out from August to November 2015.

The project activities have been overseen by the following steering group members:

- Katrine Bom (Danish EPA)
- Flemming Ingerslev (Danish EPA)
- Frans Christensen (COWI A/S).

Executive summary

Under the Agreement "Better Control of Nanomaterials" ("Bedre styr på nano"), the Danish EPA has commissioned a number of projects aiming to investigate and generate new knowledge on the presence of nanomaterials in products on the Danish market and assess the possible associated risks to consumers and the environment.

The current project on nano-enabled environmental products and technologies aims to investigate the benefits for health and environment that the use of nanomaterials in products and technologies may have. More specifically, the project aims at providing an overview of:

- Relevant nano-enabled environmental technologies.
- Types of products and technologies on the (Danish) market, as well as products and technologies, which are still in R&D.
- Provide a qualitative overview of health and environmental pros and cons of these technologies.

The project has focused specifically on solutions where the properties of nanomaterials are used more or less directly in addressing health and environmental problems: solutions often referred to as nano-enabled environmental technologies. These include nano-enabled products and technologies applied in: 1) purification of water and wastewater, 2) remediation of soil and groundwater, 3) cleaning of air, 4) reduction of energy consumption and 5) for improving hygiene in the health care sector by utilizing the antibacterial properties of certain nanomaterials.

The report does not profess to provide an exhaustive overview of all technologies but rather gives an overview of the most well-known and widely applied technologies based on literature review and dialogue with stakeholders.

Water treatment

Treatment of water for removal of chemical substances, pathogenic microorganisms, smell or taste issues has been undertaken for millennia. However, the use of nanotechnology for large-scale treatment of drinking water and wastewater still appear to be limited largely to the lab-scale and the pilot-scale, in Denmark and worldwide. There are three primary methods by which nanomaterials can be utilized in water treatment:

- Adsorption/filtration, where the materials selectively target and up-take pollutants by sorption to remove them physically from the water being treated.
- Disinfection, where the materials can physically/chemically attack a pathogen in the water and kill it completely or render it inactive to the extent that it is no longer a threat.
- Chemical or photocatalytic reaction by which the materials are capable of degrading a pollutant into less harmful compounds.

Some of the nanomaterials found to be among the most promising in relation to water treatment are reviewed in the current report. Carbon nanotubes (CNT) comprise one of the materials, which acts as a highly efficient sorbent for a range of pollutants and therefore can potentially replace the traditional use of activated carbon for water purification in some situations, although it is much more costly. Zeolite is another possible nano-sorbent, which is robust to mechanical and chemical stresses and therefore is used in a variety of industrial applications, although not much within the water sector.

Among the more reactive nanomaterials nano zero-valent iron (nZVI) should be mentioned, which can be used in particular to degrade a variety of organic contaminants but also to remove arsenic from drinking water. Silver in nano-form has prominent anti-bacterial properties and is currently the most utilized nanomaterial for disinfection and other anti-microbial applications as it can be incorporated into membranes, immobilised on various support materials, used in coatings etc. It is used e.g. in small, portable water purifiers.

The main hindrances to more widespread use of nanomaterials for water treatment are the possible risks these materials pose to human health and the environment, as well as the high cost of the technologies compared to accepted standard treatment methods.

Soil and groundwater remediation
In practice, the current use of nano-based technology for soil and groundwater remediation is confined to *in situ* remediation, preferably under saturated conditions, i.e. in the groundwater environment. Nanotechnology does not appear to be used for clean-up of contaminated surface or near-surface soils where cheaper, well-proven methods are available. The dominating nanomaterial used in practice for *in situ* remediation is zero valent iron in the nano-form (nZVI), sometimes combined with palladium or another catalytic metal (so-called bimetallic nanoparticles or BNPs) to further increase the reaction rate of nZVI. nZVI has attracted attention for *in situ* remediation of sites contaminated with metals and/or chlorinated solvents because of its higher reactivity compared to traditional (macro) ZVI and potentially higher mobility.

Technically, nZVI is injected as a slurry directly into the zone where remediation is required either to create reactive treatment zones in an aquifer or into so-called DNAPLs (dense non-aqueous phase liquids), also known as "free phase" contaminations. Likely, application of nZVI-based techniques are most well suited to tackle source zones rather than dilute plumes.

Important factors hampering more widespread use of nZVI (and other nanomaterials) within this field are partly:

- technical, such as the strong tendency of nanoparticles to agglomerate, thus reducing the reactivity and mobility of the iron, and passivation (deactivation) due to oxidation of the iron before the remediating action is completed,
- economical, as the cost-effectiveness compared to micro/macro-scale ZVI in many cases has been found to be dubious, and
- reluctance in many countries to fully accept this use of nanomaterials because the potential risks to human health and the environment are not considered sufficiently elucidated.

Hence, the early high expectations surrounding this technology have decreased somewhat, or have become more realistic, and nZVI is no longer perceived as being a universal solution but rather a supplementary tool that can be advantageous to use for certain contaminants under certain conditions. There are currently no indications that the use of nZVI for remediation will increase much in Denmark in the near future.

Air pollution reduction/air purification
Air pollution and air quality issues that can be addressed by use of nano-based technology relate to both outdoor air pollution, including emissions to air, and to improvement of indoor air quality. Two main categories of systems are known:

- Active systems requiring power supply to run a reactor or air transport system, and

- Passive systems exerting their action via nano-treated or nano-coated surfaces just exploiting the energy from natural ventilation and solar irradiation or general room illumination.

The active systems include well-proven large-scale industrial applications aimed to reduce emissions of noxious air pollutants (e.g. NO_X, sulphur and/or volatile organics (VOC)) in exhausts from industrial facilities, not least from coal-fired power plants and incineration plants. These systems are based on nano-enabled catalytic converters typically utilizing vanadium oxide immobilised on a support matrix, sometimes in combination with a noble metal to increase performance. Similar systems are widely applied in diesel-driven vehicles to reduce emissions of NO_X and other air pollutants in the exhaust gases. Small-scale indoor air purifier devices for domestic use are also available. They can contain a photocatalytic titanium dioxide (TiO_2) unit for removal of NO_X and VOCs as well as a filter with nanosilver for disinfection of the air.

Examples of passive systems include the outdoor application of coatings or films with a photocatalytic nanomaterial, in practice predominantly TiO_2, most often in the form of treated/coated building facades, roofs, pavement slabs or road surfaces that can degrade NO_X and VOCs in the ambient air, in particular considered relevant in dense urban environments. Indoor systems (treated walls and/or flooring materials) are also being developed that can reduce VOCs and malodour in indoor air in particular. These are also often based on the use of nano-TiO_2. Commercial products exist within this category of air cleaning system; however, they are currently considered niche products and, overall, the area seems still to be in its infancy.

Some issues related to nanotechnology use for air pollution reduction remain to be fully clarified, e.g. the implications of the emission to air of nano-metals from catalysts and fuel additives and the possible generation of harmful substances when nano-TiO_2 photocatalytically degrades VOCs.

Reduction of energy consumption
The application of nanotechnology within the area of production, storage and use of energy can provide environmental benefits by resulting in reduced energy consumption either by

- shifting from a more energy-consuming technology to a nano-based, more energy efficient technology,
- refining existing technologies through improving the properties, or
- reducing the quantity of material needed given the higher reactivity of the nanomaterials.

The possible applications of nanotechnology within the energy area are wide-ranging but have been confined to the following products and technologies in this study: photovoltaic devices, hydrogen fuel cells, nanotechnology-based catalysts, energy storage devices, insulation materials/technologies, LED/OLED lighting, self-cleaning coatings and fuel additives.

Photovoltaic devices. Nanotechnology is used here to increase the performance of existing solar cell technology where the market is currently dominated by first generation cells. The efficiency can be enhanced using gold and silver nanoparticles. Efficiencies of thin-film solar cells (second generation) may be improved by coating the surface with e.g. metallic or silicon dioxide (SiO_2) nanoparticles.

Hydrogen fuel cells show promising potential as an alternative to carbon-based energy sources. However, several technological challenges currently prohibit fuel cells from wide scale implementation, and nanotechnology is likely to play a key role in overcoming some of these. Use of nano-based catalysts may for example help to increase the speed and efficiency of these processes or to address hydrogen storage challenges; several nano-based solutions have been proposed, e.g. light metal hydrides, core-shell sodium borohydride ($NaBH_4$) nanoparticles and carbon nanotubes.

Nanotechnology-based catalysts. Nanotechnology may be used in industrial catalytic systems to provide nanostructures inside and on the surface of the catalyst, increasing the ratio between the surface area and volume, and thereby increasing the efficiency of the catalytic reaction. Examples of use areas are in oil refineries and for production of a variety of high-volume chemicals (e.g. ammonia or styrene).

Batteries and supercapacitors where use of nanomaterials can improve the properties of batteries in terms of increasing the available power and decreasing the time needed for recharging, e.g. by coating the surface of the electrode with nanomaterials. Using metal-oxide nanomaterials or carbon-based nanostructures on the surface of electrodes in supercapacitors may also result in increased capacity of these devices.

LED (light emitting diodes) *and OLED (organic LED) lighting* represent energy-efficient alternatives to the conventional light bulb and have many different applications. Nanotechnology may be used to optimise the performance of these devices and utilization of so-called *quantum dots* in LED may optimise this technology further by improving efficiencies and light yield.

Insulation of buildings. In Denmark, about 40% of total energy consumption is used for buildings, so proper thermal insulation may lead to great environmental benefits. Silica aerogel for example is a nanostructured porous material showing excellent potential as thermal insulating material. Energy consumption for buildings may also be reduced using glazing materials based on nanotechnology, which respond to changes in temperature or solar radiation.

Self-cleaning coatings. Use of self-cleaning nano-based coatings may result in energy reductions in several ways, e.g. by providing an easy-to-clean surface whereby the amount of water and energy needed for cleaning is reduced. Self-cleaning windows may increase the amount of sunlight entering a room, reducing the need for heating and artificial light; as well, self-cleaning solar cell surfaces may increase the amount of light that penetrates the solar cell, thus increasing the energy yield.

Fuel additives. Nanoporous catalysts or nanoparticles (e.g. CeO_2) can enhance efficiencies of combustion processes and reduce emissions when used as fuel additives. Friction-reducing nano-products used as fuel or motor oil additives may also reduce fuel consumption of vehicle engines.

Due to the wide range of different applications of nanotechnology within the energy area, the market potential for the different applications is highly dependent on the specific technology area. Nano-based catalysts, batteries, self-cleaning coatings, silica aerogel insulation materials and nano-based fuel additives are currently on the market, but the presence of these products on the Danish market is assumed to be limited at present.

Hygiene improvement
The current project has focused on biocidal nanoproducts relevant for the healthcare sector, which is known to be challenged with infections. These products can be divided into the following sub-categories, depending on their applications:

- General surface coatings applied on-site, which are all-purpose coatings and antibacterial paints used on general surfaces e.g. wall, floors and furniture;
- Biocidal purging or fuming, applied at locations of high risk by units that disperse the nanomaterial in a room;
- Articles pre-treated with biocidal products with the purpose of avoiding spread of microbes, and
- Articles used to disinfect other articles such as cleaning cloths or nano-functionalized washing machines.

Anti-microbial coatings and paints often contain nano-TiO_2, which upon radiation and contact with the humidity in the air can release free oxygen radicals capable of killing microbes. Certain nano-polymers which kill microbes due to electrostatic mechanisms may also be applied.

Purging/fuming solutions on the market are based on hydrogen peroxide, possibly in combination with nanosilver. The release of silver ions from silver produces well-known disinfectant properties. Use of nanosilver with larger surface area per weight is more efficient than products containing larger silver particles.

A range of articles/products used in the health care sector might be pre-treated with a disinfectant. This includes e.g.:

- Hospital room inventory (chairs, beds, tables, wheel chairs, bed-side lighting, cupboards);
- Contact surfaces (light switches, alarm buttons, hand rails, taps, toilet flush buttons), and
- Mobile patient monitors & machines (e.g. respirators, various devices for measuring blood pressure/ECG/heart rate, as well as various ECG, BP & HR monitors).

The surface treatment agents might e.g. be nano-TiO_2, nanosilver, so-called *liquid glass Si*, which provides an anti-adhesive surface and electrostatic anti-microbial activity.

Finally, cloths and washing machines used to clean other articles might be treated with nanosilver to disinfect the articles cleaned.

These products are all on the market today, but their possibly high potential for improving hygiene in the health care sector has not yet been fully realised, as it takes some time to enter this sector due to pre-assessment procedures and perhaps due to some hesitation towards the possible health and safety issues associated with the term "*nano"*.

Use of disinfectants might also have some derived health and environmental benefits, including:

- Less need for cleaning; lower water consumption and less need for harsh cleaning agents;
- Less use of antibiotics if infection frequency drops, and
- Improved indoor environment as e.g. the free oxygen radicals released from nano-TiO_2 will not only kill microbes, but also react and degrade volatile organics possibly leading to better quality indoor air etc.

Market considerations for Danish industry

The current project has not performed market analyses as such, but based on the information gathered and dialogue with a range of stakeholders, it is concluded that Danish industry could establish a competitive edge in relation to applying nano-enabled environmental technologies in the following fields:

- Photovoltaics/solar cells
- Aerogel insulation materials
- Hydrogen fuel cells
- Tailor-made air purification solutions (applying existing nano-technologies)
- General disinfectants for the health care and other sectors.

Opportunities and drawbacks - life-cycle considerations

The current report highlights how nano-enabled technologies might reduce health and environmental problems. However, use of nanomaterials and nanotechnologies may also be associated with drawbacks. As indicated above, some concerns exist as to whether the nanomaterials themselves might trigger health and environmental problems during use due to their inherent toxicity. This aspect is thoroughly covered in other reports from the "Better-control-of-nano" initiative, and has not been elaborated in detail in the current project.

Beyond risk assessment of (eco-)toxicity, there appears to be broad consensus among stakeholders that life cycle considerations are relevant to provide an overall view of health and environmental pros and cons of nanoproducts. The review activities conducted in this project have, however, revealed that considering the wide applications area of nanomaterials in environmental technologies, surprisingly few life cycle assessments (LCAs) of such technologies have been conducted and published to date. The few existing studies indicate that one of the main trade-offs with the use of nanomaterials is whether the sometimes energy-intensive nanomaterial production phase (e.g. for carbon based nanomaterials) and the use of sometimes scarce metals are outweighed by the benefits obtained in the use phase, where a considerably lower amount of material and more energy-efficient solutions are often applied, as compared to conventional technologies. The use of highly toxic metals (such as cadmium and lead based compounds in some technologies exploiting the improved electrical properties of nanomaterials) is also flagged as a concern by some authors, although the amounts used are often limited.

Sammenfatning

Som en del af aftalen "Bedre styr på nano" har den danske Miljøstyrelse iværksat en række projekter, der sigter på at undersøge og generere ny viden om forekomsten af nanomaterialer i produkter på det danske marked og vurdere potentielle risici for forbrugerne og miljøet.

Nærværende projekt om nano-baserede miljøteknologier og -produkter har til formål at undersøge de miljø- og sundhedsmæssige fordele, som anvendelsen af nanomaterialer i produkter og teknologier kan give. Mere specifikt sigter projektet på at give et overblik over:

- Relevante nano-baserede miljøteknologier og -produkter
- Typer af produkter og teknologier på markedet (herunder det danske), samt produkter og teknologier, som stadig er under forskning og udvikling
- Miljø- og sundhedsmæssige fordele og ulemper ved disse teknologier.

Projektet har fokuseret specifikt på løsninger, hvor egenskaberne af nanomaterialer mere eller mindre direkte indgår i løsningen af miljø- og sundhedsmæssige problemer; løsninger der ofte omtales som nano-baserede miljøteknologier. Disse omfatter nano-baserede produkter og teknologier, der anvendes til: 1) rensning af vand og spildevand, 2) rensning af jord og grundvand, 3) rensning af luft, 4) reduktion af energiforbruget og 5) at forbedre hygiejnen i sundhedssektoren ved at udnytte de antibakterielle egenskaber af visse nanomaterialer.

Rapporten foregiver ikke at give en udtømmende oversigt over alle teknologier, men snarere at give et overblik over de mest kendte og bredt anvendte teknologier, baseret på information fra litteraturen og dialog med aktører.

Vandrensning

Rensning af vand for at fjerne kemiske stoffer, sygdomsfremkaldende mikroorganismer, lugt eller afsmag har været foretaget i årtusinder. Anvendelsen af nanoteknologi til rensning af drikkevand og spildevand i større omfang synes dog stadig i høj grad at være begrænset til laboratorie- og pilotforsøg, både i Danmark og på verdensplan. De tre væsentligste metoder, hvormed nanomaterialer kan anvendes til vandrensning, er:

- Adsorption/filtrering, hvor materialerne er selektivt målrettet mod at optage forurenende stoffer via sorption, hvorved stofferne fysisk kan fjernes fra det vand, der renses
- Desinficering, hvor materialerne fysisk/kemisk angriber en sygdomsfremkaldende organisme i vandet og enten dræber det helt eller inaktiverer det, hvorefter det ikke længere udgør en trussel
- Kemisk eller fotokatalytisk reaktion, hvorved materialerne er i stand til at nedbryde et forurenende stof til mindre skadelige stoffer.

Rapporten gennemgår nogle af de nanomaterialer, der anses for at være blandt de mest lovende i forhold til vandrensning. Kulstof-nanorør (CNT) er et af de materialer, der fungerer som en meget effektiv sorbent for en række forurenende stoffer, og det kan derfor i nogle situationer potentielt erstatte den traditionelle brug af aktivt kul til rensning af vand til trods for, at det er meget dyrere end aktivt kul. Zeolit er en anden mulig nano-sorbent, som er robust over for mekaniske og kemiske påvirkninger, og som derfor bruges i en lang række industrielle anvendelser, dog stadig ikke ret meget inden for vandsektoren. Blandt de mere reaktive nanomaterialer bør nul-valent nano-jern (nZVI) nævnes. Nul-valent nano-jern kan især anvendes til at nedbryde en bred vifte af organiske forureningsstoffer, men kan også anvendes til at fjerne arsen fra drikkevand. Sølv i nano-form har fremtrædende anti-bakterielle egenskaber, som indtil nu har været det mest brugte nanomateriale til desinfektion og andre antibakterielle anvendelser, da det kan inkorporeres i membraner, immobiliseres på forskellige bærematerialer, indlejres i coatninger m.v. Det anvendes bl.a. i transportabelt vandrensningsudstyr.

De største hindringer for en mere udbredt anvendelse af nanomaterialer til vandrensning er den mulige risiko disse materialer udgør for menneskers sundhed og miljøet samt de høje omkostninger ved disse teknologier sammenlignet med gængse vandrensningsmetoder.

Rensning af jord og grundvand
Den nuværende brug af nano-baseret teknologi til rensning af jord og grundvand er i realiteten begrænset til såkaldt *in situ* remediering, fortrinsvis under mættede betingelser, dvs. i grundvandsmiljøet. Nanoteknologi synes ikke at blive anvendt til oprensning af forurenet overfladejord, hvor billigere, velafprøvede metoder er til rådighed. Det dominerende nanomateriale til *in situ* remediering er nul-valent nano-jern (nZVI), der somme tider kombineres med palladium eller et anden katalytisk metal (såkaldte bimetalliske nanopartikler) for at øge reaktionshastigheden af nZVI. nZVI har særligt tiltrukket opmærksomhed til *in situ* oprensning af lokaliteter forurenet med metaller og/eller klorerede opløsningsmidler på grund af dets højere reaktivitet og potentielt højere mobilitet i forhold til traditionelt (makro) nul-valent jern.

Rent teknisk injiceres nZVI som en opslemning ind i zonen, hvor rensning er påkrævet, enten for at skabe reaktive rensningszoner i et vandførende lag eller for at nedbryde forureningskomponenter i ikke-vandige zoner, såkaldte "fri fase" forureninger. nZVI-baserede teknikker er formentlig mere velegnede til at håndtere forureninger nær kilden frem for mere fortyndede forureningsfaner.

Vigtige faktorer, der begrænser en mere udbredt anvendelse af nZVI (og andre nanomaterialer) inden for dette område er:

- Tekniske faktorer, såsom nanopartiklers stærke tilbøjelighed til at agglomerere, hvilket reducerer jernets reaktivitet og mobilitet, og passivering (deaktivering) på grund af oxidation af jernet før den ønskede reaktion er tilendebragt,
- økonomiske faktorer, fordi omkostningseffektiviteten i forhold til mikro-/makro-skala ZVI i mange tilfælde har vist sig at være tvivlsom, og
- modvilje i mange lande til fuldt ud at acceptere denne anvendelse af nanomaterialer, fordi de potentielle risici for menneskers sundhed og miljøet ikke betragtes som tilstrækkeligt belyst.

Derfor er de tidligere høje forventninger til denne teknologi aftaget noget - eller blevet mere realistiske - og nZVI opfattes ikke længere som en universel løsning, men snarere som et supplerende værktøj, der med fordel kan anvendes til at rense for visse forurenende stoffer under visse betingelser. Der er for øjeblikket ingen tegn på, at anvendelsen af nZVI til remediering vil vokse meget i Danmark i den nærmeste fremtid

Nedbringelse af luftforurening/luftrensning
De luftforurenings- og luftkvalitetsproblemer, der kan løses ved brug af nano-baseret teknologi, relaterer sig både til luftforurening udendørs, herunder emissioner til luft, og til forbedring af luftkvalitet indendørs. Der findes to overordnede kategorier af systemer:

- aktive systemer, som kræver strømforsyning for at drive en reaktor eller et luft-transport system, og
- passive systemer som udøver deres virkning ved hjælp af nano-behandlede eller nano-coatede overflader, udelukkende ved brug af energi fra naturligt luftskifte og solindstråling eller generel belysning.

De aktive systemer omfatter velafprøvede industrielle anvendelser, der har til formål at reducere udledningen af skadelige luftforurenende stoffer (f.eks. NOx, svovl og/eller flygtige organiske stoffer (VOC)) i udstødninger fra industrianlæg, ikke mindst kulfyrede kraftværker og forbrændingsanlæg. Disse systemer fungerer ved hjælp af nano-baserede katalysatorer, typisk vanadiumoxid immobiliseret på et bæremateriale, eventuelt i kombination med et ædelmetal for at øge ydeevnen. Lignende systemer er almindeligt anvendt i dieseldrevne køretøjer for at reducere udledningen af NOx og andre luftforurenende stoffer i udstødningsgassen. Små indendørs luftrensningsapparater til husholdningsbrug er også velkendte. Disse består normalt af en enhed med fotokatalytisk titandioxid (TiO_2) til fjernelse af NOx og VOC samt et filter med nanosølv til desinfektion af luften.

Passive systemer omfatter udendørs belægninger indeholdende et fotokatalytisk nanomateriale, i praksis hovedsageligt TiO_2. Der er eksempelvis tale om overfladebehandlede/coatede bygningsfacader, tage, fortovsfliser eller vejbelægninger, der kan nedbryde NOx og VOC i den omgivende luft, hvilket især anses for relevant i bymiljøer. Derudover findes der indendørs systemer (behandlede vægge og/eller gulvmaterialer) til at mindske mængden af især VOC og ubehagelige lugte i indeluften. Disse er oftest også baseret på nano-TiO_2. Der findes kommercielle produkter inden for denne kategori af luftrensningssystemer, men disse betragtes i øjeblikket som nicheprodukter, og samlet set synes området stadig at være på udviklingsstadiet.

Der mangler stadig afklaring af visse spørgsmål i forbindelse med anvendelsen af nanoteknologi til at reducere luftforurening. Spørgsmålene knytter sig eksempelvis til konsekvenserne af udledning af nano-metaller til luften fra katalysatorer og brændstofadditiver, samt til den mulige dannelse af skadelige stoffer når VOC bliver nedbrudt af fotokatalytisk nano-TiO_2.

Reducering af energiforbrug
Anvendelsen af nanoteknologi inden for området produktion, opbevaring og anvendelse af energi kan give miljømæssige fordele som følge af et reduceret energiforbrug. Dette sker ved at

- skifte fra en mere energiforbrugende teknologi til en nano-baseret, mere energieffektiv teknologi, at
- optimere eller raffinere eksisterende teknologier ved at forbedre egenskaberne, eller ved at
- reducere den påkrævede materialemængde, muliggjort af nanomaterialets højere reaktivitet.

De mulige anvendelser af nanoteknologi inden for energiområdet er meget vidtrækkende, men er i denne undersøgelse begrænset til følgende produkter og teknologier: Fotovoltaiske enheder, brintbaserede brændselsceller, nanoteknologi-baserede katalysatorer, energilagringsenheder, isoleringsmaterialer/-teknologier, LED/OLED belysning, selvrensende belægninger og brændstofadditiver.

Fotovoltaiske enheder. Nanoteknologi bruges i denne sammenhæng til at øge effektiviteten af eksisterende solcelleteknologi, hvor markedet i øjeblikket er domineret af første-generations solceller. Effektiviteten kan forbedres ved hjælp af guld- og sølvnanopartikler. Effektiviteten af tynd-film solceller (anden generation) kan forbedres ved at coate overfladen med f.eks. nanopartikler bestående af metaller eller siliciumdioxid (SiO_2).

Brintbrændselsceller viser lovende potentiale som alternativ til kulstofbaserede energikilder. Dog er der flere teknologiske udfordringer, som i øjeblikket forhindrer implementering af brændselsceller, og det forventes, at nanoteknologi vil spille en central rolle i at overvinde nogle af disse. Nano-baserede katalysatorer kan for eksempel benyttes til at øge hastigheden og effektiviteten af processerne eller til at håndtere udfordringerne omkring lagring af brint. Til sidstnævnte er flere forskellige nano-baserede løsninger blevet foreslået, f.eks. lette metalhydrider, core-shell natrium borhydrid ($NaBH_4$) nanopartikler og kulstof-nanorør.

Nanoteknologi-baserede katalysatorer. Nanoteknologi kan anvendes i industrielle katalytiske systemer til at give nanostrukturer inden i og på overfladen af katalysatoren, således at forholdet mellem overfladeareal og volumen forøges, og effektiviteten af den katalytiske reaktion øges. Eksempler på anvendelsesområder er i olieraffinaderier samt til produktion af en bred vifte af kemikalier med stort produktionsvolumen (f.eks. ammoniak og styren).

Batterier og superkondensatorer, hvor anvendelse af nanomaterialer kan forbedre egenskaberne ved at øge den tilgængelige effekt og reducere den nødvendige tid til genopladning, f.eks. ved at coate overfladen af elektroden med nanomaterialer. Brug af metaloxid-nanomaterialer eller kulstof-baserede nanostrukturer på overfladen af elektroder i superkondensatorer kan også resultere i øget kapacitet af disse enheder.

LED (light-emitting diodes/lysdioder) og OLED (organiske LED) belysning repræsenterer energieffektive alternativer til den konventionelle elpære og har mange forskellige anvendelser. Nanoteknologi kan bruges til at optimere ydeevnen for disse enheder og anvendelse af såkaldte *quantum dots* (kvantepunkter) i LED kan optimere denne teknologi yderligere ved at forbedre effektiviteten og lysudbyttet.

Isolering af bygninger. I Danmark anvendes omkring 40% af det samlede energiforbrug til bygninger, og ordentlig varmeisolering kan således give store miljøfordele. Silica aerogel er et nanostruktureret porøst materiale, der synes at have stort potentiale som termisk isoleringsmateriale. Energiforbruget i bygninger kan også reduceres ved hjælp af materialer til vinduesglas baseret på nanoteknologi, som reagerer på ændringer i temperatur eller solindstråling.

Selvrensende overfladebelægninger. Anvendelse af selvrensende nano-baserede belægninger kan medføre energibesparelser på flere måder, f.eks. ved at skabe en rengøringsvenlig overflade, hvorved mængden af vand og energi, der kræves til rengøring, reduceres. Selvrensende vinduer kan øge mængden af sollys, som kommer ind i et rum, hvilket reducerer behovet for opvarmning. Kunstigt lys og selvrensende overflader på solceller kan øge mængden af lys, der trænger ind i solcellen, hvilket øger energiudbyttet.

Brændstofadditiver. Nanoporøse katalysatorer eller nano-additiver til brændstoffer (f.eks. CeO_2) kan øge effektiviteten af forbrændingsprocesser og reducere emissionerne af problematiske stoffer. Friktionsnedsættende nano-produkter, der anvendes som brændstof- eller motorolieadditiver, kan også reducere forbruget af brændstof i køretøjer.

På grund af den brede vifte af forskellige anvendelser af nanoteknologi inden for energiområdet, afhænger det potentielle marked for de forskellige anvendelser meget af det specifikke teknologiområde. Nano-baserede katalysatorer, batterier, selvrensende overfladebelægninger, silica aerogel isolationsmaterialer og nano-baserede brændstofadditiver er på markedet nu, men det formodes, at anvendelsen af disse produkter på det danske marked er begrænset for nærværende.

Hygiejneforbedring

Det nærværende projekt har fokuseret på biocidholdige nanoprodukter af relevans for sundhedssektoren; en sektor hvor risikoen for infektioner via smitteoverførsler er velkendt. Disse produkter kan inddeles i følgende underkategorier, afhængigt af deres anvendelse:

- Generelle overfladebehandlinger/coatings, f.eks. all-round-coatinger og antibakteriel maling, som anvendes på overflader f.eks. vægge, gulve og møbler
- Gasning med biocidholdige produkter, som anvendes på steder med høj smitterisiko ved hjælp af enheder, der spreder nanomaterialet i et rum
- Varer/artikler forbehandlet med biocidholdige produkter, med det formål at undgå spredning af mikroorganismer.

- Varer/artikler, som bruges til at desinficere andre artikler, såsom klude eller nano-funktionaliserede vaskemaskiner.

Antimikrobielle coatings og malinger indeholder ofte nano-titandioxid, som ved belysning og kontakt med fugt i luften kan frigive frie oxygenradikaler, som dræber mikroorganismer. Visse nano-polymerer, som dræber mikroorganismer på grund af elektrostatiske effekter, kan også anvendes.

De markedsførte løsninger, som indebærer gasning, er alle baseret på hydrogen peroxid, eventuelt i kombination med nanosølv. Frigivelse af sølv-ioner fra sølv er et velkendt desinfektionsmiddel. Anvendelse af nanosølv, med større overfladeareal, er mere effektiv end anvendelsen af større sølvpartikler.

En række af produkter, der anvendes i sundhedssektoren, kan forbehandles med et desinfektionsmiddel. Dette omfatter eksempelvis:

- Inventar til hospitalsværelser (stole, senge, borde, kørestole, sengebelysning, skabe)
- Kontaktoverflader (lyskontakter, alarmknapper, gelændere, haner, toilet-skylleknapper)
- Mobile patientmonitorer og maskiner (f.eks. respiratorer, diverse udstyr til måling af blodtryk/EKG/puls, samt diverse EKG-, blodtryks- og hjertefrekvensskærme).

Overfladebehandlingsmidlet kunne eksempelvis være nano-titandioxid, nanosølv, eller såkaldt "liquid glass Si" ("flydende glas silicium"), som giver en anti-klæbende overflade og en elektrostatisk antimikrobiel aktivitet.

Endelig kan aftørringsklude og vaskemaskiner, som benyttes til at rengøre andre artikler, være behandlet med eksempelvis nanosølv, for at desinficere de artikler der rengøres.

Disse produkter er alle på markedet i dag, men deres potentiale for at forbedre hygiejnen i sundhedssektoren er ikke eller endnu ikke fuldt realiseret, da det tager noget tid at få adgang til denne sektor på grund af forhåndsgodkendelsesprocedurer og muligvis på grund af en vis betænkelighed omkring de mulige sundheds- og sikkerhedsmæssige problemer, som kan være associeret med ordet "*nano*".

Anvendelsen af desinfektionsmidler kan også have nogle afledte miljø-/sundhedsgevinster, som for eksempel:

- Mindre behov for rengøring, lavere vandforbrug og mindre behov for skrappe rengøringsmidler.
- Mindre forbrug af antibiotika, hvis infektionsfrekvensen falder.
- Forbedret indeklima, da de frie oxygenradikaler, som frigives fra nano-titandioxiden, ikke kun vil dræbe mikroorganismer, men også reagere med og nedbryde flygtige organiske stoffer, hvilket muligvis fører til forbedret indeklima.

Markedsovervejelser for dansk industri

Der er i nærværende projekt ikke foretaget markedsanalyser som sådan, men baseret på de indsamlede oplysninger og dialog med en række aktører, vurderes det, at dansk industri kunne etablere en konkurrencefordel i forhold til anvendelsen af nano-baserede miljøteknologier på følgende områder:

- Fotovoltaiske enheder/solceller
- Aerogel isoleringsmaterialer
- Brintbaserede brændselsceller
- Skræddersyede luftrensningsløsninger (ved hjælp af eksisterende nanoteknologi)
- Generelle desinfektionsmidler til sundhedssektorer og andre sektorer.

Muligheder og ulemper - livscyklus overvejelser

Nærværende rapport har fokuseret på, hvorledes nano-baserede teknologier kan være med til at reducere sundheds- og miljømæssige problemer under brug. Dog kan anvendelse af nanomaterialer og nanoteknologi også være forbundet med ulemper. Som anført ovenfor er der nogen bekymring om, hvorvidt nanomaterialer i sig selv kan medføre sundheds- og miljømæssige problemer under brug på grund af deres iboende farlighed. Dette aspekt er grundigt belyst i andre rapporter fra "Bedre styr på nano"-indsatsen, og er ikke blevet uddybet i detaljer i dette projekt.

Ud over risikovurdering af stoffernes iboende farlighed, synes der at være bred enighed blandt interessenter om, at livscyklusovervejelser er relevante for at give et samlet overblik over miljø- og sundhedsmæssige fordele og ulemper ved nanoprodukter. Den litteratur-gennemgang, som er gennemført i forbindelse dette projekt har dog vist, at i betragtning af det meget brede anvendelsesområde af nanomaterialer i miljøteknologi er der til dato blevet gennemført og offentliggjort overraskende få livscyklusvurderinger (LCA) af disse teknologier.

De få eksisterende undersøgelser viser, at én af de vigtigste afvejninger ved anvendelsen af nanomaterialer er, hvorvidt den til tider meget energikrævende produktionsfase af nanomaterialer (f.eks. kulstof-baserede nanomaterialer) opvejes af de fordele, der kan opnås i brugsfasen ved at mere energieffektive løsninger anvendes. Ligeledes skal brugen af sjældne metaller afvejes mod de betydeligt lavere mængder af materiale, der anvendes for at opnå de ønskede effekter i forhold til konventionelle teknologier. Brugen af meget giftige metaller (såsom cadmium og bly-baserede forbindelser i nogle teknologier, der udnytter forbedrede elektriske egenskaber af nanomaterialer) bliver også markeret som en bekymring af nogle forfattere, selv om de mængder, der anvendes, ofte er meget begrænsede.

1. Introduction

1.1 Background

A range of products and technical solutions exploit unique or enhanced properties of nanomaterials. These properties include specific electrical and optical properties, enhanced reactivity of smaller particles because of larger surface areas, and enhanced strength/weight ratio of some carbon-based nanomaterials.

Simultaneously, an increasing concern for possible health and environmental impacts of nanomaterials has been raised as the small size and large surface area, and thus greater reactivity, might lead to increased risks for humans and the environment.

1.2 Scope

1.2.1 Health and environmental opportunities and drawbacks

The starting point for the current project is an investigation of where the use of nanomaterials in products and technologies may provide health and environmental benefits. Such products and technologies are marketed and applied as they are considered to provide health and environmental benefits in the use phase.

However, there might also be some concerns associated with the use of nanotechnology in the addressed technologies and products. Furthermore, these technologies might cause health and environmental concerns in other phases of the life cycle, e.g. workers' exposure to dusty materials, as well as energy and scarce metal consumption during the manufacturing/production phase. While there seems to be broad consensus among stakeholders that such life cycle considerations are needed and relevant to provide an overall view of pros and cons, the review activities conducted in this project have revealed that surprisingly few life cycle assessments (LCAs) of such technologies have been conducted and published to date, considering the wide applications area of nanomaterials in environmental technologies. A summary of these LCAs is provided in Appendix 1. That review indicates that one of the reasons for the limited number of LCAs might be the lack of inventory data (i.e. data indicating consumption of energy and materials, and emissions from relevant life cycle stages). Another reason seems to be that researchers hesitate to conduct LCAs due to the lack of inherent property data (e.g. on toxicity) of the applied nanomaterials.

The few studies reviewed indicate that one of the main trade-offs with the use of nanomaterials is whether the occasionally energy-intensive nanomaterial production phase (e.g. for carbon nanotubes and some other carbon based nanomaterials) and the use of sometimes scarce metals are outweighed by the benefits obtained in the use phase, where a lower amount of material and more energy-efficient solutions are often applied, as compared to conventional technologies. A few studies suggest that this trade-off may often occur, whereas it is questioned by others. The use of highly toxic metals (such as cadmium and lead based compounds in some technologies exploiting the improved electrical properties of nanomaterials) is also flagged by some authors, although the amounts used are usually limited. See appendix 1 for details.

The amount and properties of the material used will therefore form a crucial parameter in LCAs. A situation where markedly less material is consumed is the use of nanosilver, which has a high specific surface area and thus a higher rate of release of anti-microbial silver ions, as compared with larger sized silver particles. Clearly, this lower material use should be weighed against potential other drawbacks associated with nanosilver, such as energy demand during production and increased toxicity of the nano-form.

The project will not go into detail in relation to assessment of exposures and (eco-)toxicological risks associated with the nanomaterials involved in the addressed products and technologies, as this aspect is thoroughly covered in other reports from the "Better-control-of-nano" initiative as e.g. summarised in Christensen *et al.* (2015, in prep.).

1.2.2 Technologies in focus

Nanomaterials are applied in products and processes for improving, for example, efficiency, strength or surface properties, as compared to more conventional solutions. Nanomaterials are therefore often used to obtain a technical benefit.

In the broad context, one could argue that many of these solutions provide benefits for the environment and health during use; strong materials, for example, increase durability and thereby potentially reduce the need for resources and smooth surfaces might reduce the need for manual cleaning and thereby improve health. Such nano-enabled solutions which indirectly lead to benefits (such as stronger and lighter materials) are not considered to be within the scope of this project.

The project will, however, more specifically focus on solutions where the properties of the nanomaterials are used directly in addressing health and environmental problems, solutions which are often referred to as nano-enabled environmental technologies.

This includes how nano-enabled technologies are applied in remediation: cleaning of air and soil, as well as ground, drinking and wastewater.

Another area subject to great attention is application of nano-enabled technologies to reduce or optimise energy consumption. This group of technologies will also be addressed in the project.

Finally, the project will focus on the (increased) antibacterial properties of some nanomaterials which are or could be used for improving hygiene in different fields. In this part of the project, it has been decided to focus on the health care sector, known to be challenged with the spread of infections due to the presence of resistant bacteria and contagious viruses.

Focusing on these technologies does not imply that the project will provide an exhaustive overview of all possible solutions. The project attempts to give an overview of the most well-known technologies based on literature and dialogue with stakeholders.

1.2.3 Nanomaterials and nano-technologies

The project will aim to focus on products, solutions and technologies where nanomaterials are either directly used in the application or where nano-structures on surfaces such as catalysts and membranes are used in these techniques. It should be noted that the latter are not in themselves considered nanomaterials according to the EU definition of a nanomaterial[1]. However, membranes where "nano" solely refers to the pore size of membranes will not be included. It is acknowledged that the distinction between what to include and what not to include is subtle.

1 Commission Recommendation of 18 October 2011 on the definition of nanomaterial. (2011/696/EU). Official Journal L 275/38.

1.3 Objective

The project shall aim at providing an overview of:

- Relevant nano-enabled environmental technologies in relation to remediation, energy optimisation and hygiene in the health care sector;
- Types of products and technologies on the (Danish) market, as well as products and technologies which are still in R&D, and
- Provide a qualitative overview of health and environmental pros and cons with these technologies.

These objectives will be addressed based on the activities outlined in Chapter 2.

2. Approach and Methodology

In order to meet the objectives of the project, the project has been divided into a number of simultaneous activities for each of the identified technology groups: water, soil and air remediation, as well as energy optimisation and hygiene improvement.

2.1 Information gathering

Information has been gathered via literature searches, the internet and consultations with experts in academia and relevant Danish companies. Given the scope of the project, the literature focus has been on identifying reviews and overview reports describing relevant technologies.

The activities in the project revealed that depending on the technology area addressed, information was available from different sources. The details of the specific searches and information sources for the relevant technologies are given in Appendix 2.

2.2 Overview of technologies

The relevant collected information has been reviewed and assessed, and for each of the five technology groups, the more specific nanoproducts/nano-enabled solutions have been described briefly in terms of functionality and involved chemistry. Where possible and relevant, comparing the nano-enabled technologies with conventional technologies in terms of efficiency was attempted.

2.3 Market considerations

It has not been the main purpose of the current project to study market developments and trends.

However, based on the literature reviewed and the expert interviews, the project attempts to provide an overview about which products/technologies are currently on the market and which are in the research pipeline. Based on the information collected, the project has also assessed whether Danish companies might have a competitive edge within the technology groups assessed.

2.4 Health and environmental pros and cons

As noted in the introduction, nano-enabled environmental technologies may be associated with health and environmental disadvantages during use and in other life cycle phases, e.g. during production/manufacturing and disposal of the nanomaterials.

The life cycle considerations have been assessed based on relevant identified literature. The review of this information is presented in Appendix 1 and summarised in section 1.1.

Given the limited number of relevant LCAs, it was decided that the pros and cons considerations in the individual chapters (chapters 3 to 6) should mainly focus on the use/use phase of the technologies, where generally more information is available. As noted in section 1.1, it shall however be emphasised that life cycle based assessment would be needed to examine the overall benefits and drawbacks associated with these technologies.

3. Water treatment

Although widely used in other environmental remediation operations, the use of nanotechnology in drinking water, wastewater, and groundwater treatment systems is primarily limited to the lab-scale and pilot-scale, both in Denmark and in the rest of the world. Tests on nanoproducts have so far shown very promising results, and if some major safety concerns can be overcome, then nanoproduct use may eventually proliferate. These major concerns are the not yet fully clarified toxicological effects that nanomaterials may have on humans and the environment, and the relatively high cost of water treatment with nanomaterials compared to established and cheap methods, such as activated carbon or biological treatment.

More specifically, however, this chapter aims to describe the various materials being researched and employed for different types of water treatment. These materials range from highly expensive novel compounds like carbon nanotubes to nano-sized materials of common compounds like silver and iron. Moreover, this chapter will go on to describe how each material can be used, whether it be for adsorption of certain environmental pollutants, disinfection of pathogens in water sources, chemical oxidation/reduction and photocatalysis of chemicals, or how the material is used when incorporated into a membrane system.

It should be noted that the *in situ* treatment of contaminated groundwater is not described in this chapter but rather in the following chapter (4) on soil and groundwater remediation.

3.1 Overview of nanoproducts and technologies

Water of different categories such as groundwater, drinking water, industrial process water and wastewater have undergone treatment for various purposes for numerous years, primarily involving removal of nutrients, undesirable substances or disinfection to prevent spreading of diseases. Many different approaches and technologies have been developed and implemented over the years such as filters, membranes, degradation in bioreactors, chemical oxidation, UV-irradiation, etc.

For the purpose of water and wastewater treatment using nanoproducts, there are three primary methods with which these materials can be utilized:

1. Adsorption/filtration, where the materials are selectively targeting and up-taking pollutants to remove them physically from the bulk solution of water being treated.
2. Disinfection, where the materials can physically/chemically attack a pathogen in the water and kill it completely or render it inactive to the extent that it is no longer an anthropological threat.
3. Chemical or photocatalytic reaction by which the materials are capable of degrading a pollutant into subsequent compounds that are more benign in nature.

The following sections aim to cover the more commonly used and widely available nanomaterials, and to describe how they work as well as how they are employed in the current market.

3.1.1 Carbon Nanotubes

Activated carbon has been applied for decades as a sorbent material to clean drinking water, as well as wastewaters of industrial, petrochemical, residential, and commercial operations. This usage occurs primarily because it is extremely cheap, contains a wide variety of various surface functional groups (including carboxyl, quinone, phenol, and lactone), and has a high surface area for adsorption (up to 2000 m^2/g), stemming from the nano-porous nature of the material itself, with pores as small as 2 – 50 nm.

Activated carbon systems are usually made in the form of cartridges or columns where water is passed through via gravity or a pressure-driven method. As the water flows through the carbon, contaminants found in the water come into contact with the carbon and are adsorbed by the carbon material. Furthermore, this carbon can be regenerated simply by repeating the original production process, where the heat and oxidizing gas drive off any sorbed contaminant. However, the further development of carbon into carbon nanotubes (CNTs), whose usage has exploded onto the market in the past two decades (Savage and Diallo 2005), with the promise that they can eventually lead to at least partial substitution of activated carbon in the marketplace.

Studies have already proven that CNTs can vastly outperform typical activated carbon with the adsorption of various organic pollutants, as much as 99% greater in certain cases (Pan and Xing, 2008), and 3-4 times higher for heavy metals, such as Pb^{2+}, Cu^{2+}, and Cd^{2+} (Li et al., 2003). Furthermore, CNTs provide a sustainable approach, in that as the metals sorb to the surface functional groups found on the carbon, the metals can subsequently be released and collected simply by adjusting the pH of the solution (Rao et al., 2007). In short, these CNTs consist of graphitic cylinders made up of networks of hexagonal carbon linkages that can be as small as 2 nm in diameter (Iijima 1991), and in spite of their small diameter, CNTs can have extremely high length/diameter ratios. The advantage that CNTs possess over traditional activated carbon is that while retaining their high surface area, the structure is easily controllable and well-defined, offering fine-tuning of the compound for application purposes. It is these abilities to control size and length of the CNT, to open/close the ends of the CNT, and to functionalize the surface of the CNT with various metals, functional groups (e.g. alcohol, carboxylic, or carbonyl groups) that provide for extremely effective adsorption properties.

Hence, water treatment with CNTs can be very effective and is used primarily as an adsorbent material, applied to a wide range of compounds such as various heavy metals (As, Cd, Pb, etc.), organic pollutants (benzene, toluene, halogenated solvents, herbicides, etc.), and inorganic contaminants, as well as chlorinated organics like 1,2-dichlorobenzene and trichloroethylene, polycyclic aromatic hydrocarbons, phenolic compounds, surfactants, herbicides like atrazine, antibiotics like tetracycline, and many others (Liu et al., 2013). However, being that CNTs are to date quite expensive, effective use of this technology has been limited to the adsorption of more complex molecules (e.g. polar aromatics, pharmaceuticals, and pesticides) that are not as readily adsorbed using traditional methods. Regardless, the market is seeing a shift into CNT-based water treatment technologies. Foremost is their incorporation into membrane materials, not only to adsorb contaminants, but also to provide mechanical strength. Current research has also seen a shift into using CNT-incorporated membranes for lower-cost seawater desalination purposes; however, realization of this remains yet to be determined. Some companies have also introduced prototype portable water filters containing CNT meshes or sheets in to the market, capable of treating polluted water sources. These portable water CNT water filters have been targeted mainly for military use, disaster relief, remote-area travelling, and also as an attachment at the tap for residential use.

Given the high cost of CNTs, some focus has been diverted towards a similar, but cheaper material: graphite oxide nanosheets, which have exhibited similar adsorption characteristics towards organics and metals (Gao et al., 2011). There has been a great deal of recent advancement in the production of CNTs that have made them more affordable; whereas in the past CNTs have cost as much as $700 USD (4700 DKK) per gram, in recent years, prices have fallen to as low as $15-35 USD (100-250 DKK) per gram. However, this is still drastically more expensive than standard activated carbon, which can cost as low as $1 USD (6 DKK) per *kilogram*.

3.1.2 Chitosan

Chitosan is a polysaccharide compound derived from naturally occurring peptides called chitin, which is very similar to cellulose and the next most abundant naturally occurring fibre after cellulose. It comes from a wide range of sources in the environment, most notably the shells of crustaceans, insects, and mushrooms. Being that it can be made cheaply from already naturally occurring sources, chitosan has an advantage that it can be operated at low costs in a low-tech manner. This ability also draws the appeal of chitosan towards rural areas and developing countries.

In addition to being an appealing bio-sorbent, chitosan also displays antimicrobial properties. The particular antimicrobial mechanism is the formation of tight nanoscale pathways that allow for molecular transport across cell membranes, which ultimately can lead to the collapse of a cell (Gazit, 2007). It is also for this reason that nanoscale chitosan is so widely used in the biomedical and drug delivery markets. More specific to water disinfection, however, this process can lead to cell membrane damage as well as chelation of trace metals within the cell that are necessary for life. Given this phenomenon, it was made possible to custom-make these nano-structures for specific applications, whether that be for removal bacteria, viruses, or fungi (Gazit, 2007).

Chitosan, due to its high hydrophilicity, presence of surface functional groups, and flexible nature, is also used as a bio-sorbent for many different contaminants, namely heavy metals, dyes, phenols, and certain anions (Bhatnagar and Sillanpaa, 2009). Some of the adsorption rates for various compounds include numbers in the range of hundreds of mg of dye for each gram of chitosan and reaching as high as 1000 mg dye per gram chitosan, 100 – 200 mg of phenol per gram chitosan, or as much as 100 mg of nitrate per gram chitosan (Bhatnagar and Sillanpaa, 2009). The unique nature of these particles gives chitosan the ability to be used in applications like flocculation in water and wastewater treatment as well as the disinfection of drinking water. Use of nanoscale chitosan for disinfection remains slightly elusive for large-scale operations, unless incorporated into a membrane; however, its use in coagulation and flocculation operations is increasing and appears to be the most promising use for it. It is promising because it is extremely efficient at coagulating organic and inorganic compounds and chelating highly toxic heavy metals; and in the process, the particles grow in size to a point where the unknown risks coming from their nano-size become irrelevant.

3.1.3 Zeolites

Natural zeolites are found in regions all over the world, coming primarily from minerals in volcanogenic sedimentary rock. Zeolites, which can be generally defined as highly crystalline and highly porous inorganic materials, are comprised primarily of silicon and aluminium and oxygen, for example $Na_6Al_6Si_{10}O_{32}$ (Breck 1974). There are at least 50 natural zeolites and there are well over 150 synthetic versions of zeolites being produced for various purposes.

Natural zeolites and conventionally synthesized zeolites typically range from 1-10 µm; however, zeolites can be synthesized on the nanoscale, from 5-100 nm (Ding and Zeng 2007), most often by grinding e.g. using a ball-milling procedure in a wet environment. When synthesized in this and other similar manners, these nanoscale zeolites can have targeted and uniform crystal structures, depending on the application. These nanoscale versions of zeolites have substantially higher surface areas and smaller diffusion path lengths than non-nano zeolites (Vogel et al. 2006, Song et al. 2005). It is their robustness towards mechanical and chemical stresses that gives zeolites such proliferation in the catalysis, separation, and ion-exchange markets (Theron et al., 2008). Specifically, what makes zeolites so great for sorption and ion exchange is the high density of ion exchange sites (e.g. Na^+) and porosity. Due to this phenomenon, nanoscale zeolites have been given much attention to their incorporation into various types of membranes to aid in the desalination process of seawater and brackish water sources within the past decade.

For example, this ion exchange mechanism was applied towards heavy metal removal in acid mine drainage (Itskos et al., 2015) and electroplating wastewaters (Alvarez-Ayuso et al., 2003). Furthermore, it has been established that nanoscale zeolites are also capable of removing radioactive elements from liquid nuclear waste streams, providing an extremely cheap alternative to current treatment practices (Yeritsyanet al., 2013). Recent large-scale applications incorporating the use of zeolites include operations targeting the removal of inorganic ions such as ammonium, heavy metals, organic pollutants, dyes, humic substances, and radioactive elements. However, outside of the use in membrane technologies, in particular those designated "mixed-matrix membranes," introduction of nanoscale zeolites into these operations is still in its infancy.

3.1.4 Iron oxides and zero valent iron

Iron, and iron based particles, are by far the most prolific nanoparticles used in the field of water treatment due to iron being ubiquitous in the earth's crust, cheap to manufacture, environmentally safe, and also a very effective contaminant reductant when converted to its zero valent form (Fe^0).

Hence, the uses of iron-based nanoparticles cover various sorption applications and reductive decontamination applications. Sorption of contaminants stems from the complexation of the dispersed metals and the oxygen in the corresponding metal oxides (Koeppenkastrop and DeCarlo, 1993). Furthermore, as the particle size of these iron-based particles is reduced, the adsorption capacity has the potential to drastically increase. To date, applications involving the use of (nano) iron oxides for the adsorption and subsequent magnetic removal of pollutants include removal of bacteria, arsenic, and organic contaminants, among others (Liu et al., 2006; Yavuz et al., 2006; Auffan et al., 2008). Perhaps most notably, drinking water treatment by use of magnetic iron oxide nanoparticles to adsorb arsenic and subsequently be removed by a simple magnet was named one of Forbes Magazine's "Top Five Nanotech Breakthroughs of 2006." This could prove to be one of the cheapest and most effective techniques to remove arsenic from drinking water, which could drastically improve the quality of life for tens of millions of people around the world that suffer from arsenic-laden water, in places like India and Bangladesh, for example.

In addition to iron being an extremely successful adsorbent material, when converting it into Fe^0, it becomes highly reactive. The basic mechanism is that as the Fe^0 particle oxidizes from an iron-oxide shell, electrons are released and water is broken down into hydroxyl radicals and protons, which creates an environment capable of degrading many pollutants (see Figure 1 below).

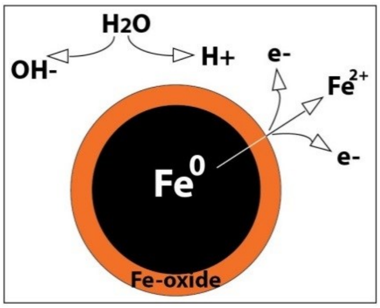

FIGURE 1
BASIC REACTION MECHANISM OF NZVI PARTICLES IN WATER TO FORM POLLUTANT-REDUCING CONDITIONS.

Therefore, nano-Fe^0 (nZVI) technologies must take great care in that the reactivity of the particles is not lost before the particles themselves are oxidized and more or less inert. Nonetheless, in 2014, papers dealing with nZVI accounted for 15.8% of all the papers mentioning ZVI (Fu et al., 2014). Although the bulk of work performed has to deal with the use of *in situ* applications of nZVI in the form of soil and groundwater remediation (discussed in Chapter 4), there are plenty of applications in industrial wastewater, drinking water, or "pump-and-treat" operations for groundwater. For example, when combing nZVI onto a kaolin support, these particles were able to remove 98.8% of Pb^{2+} and 99.8% of total chromium in electroplating wastewater streams (Zhang et al., 2010).

Moreover, there are many companies on the market, like NanoIron s.r.o. in the Czech Republic, which make nZVI powders and slurries that are designed to not only be injected into the ground for soil remediation, but also for the pump-and-treat applications and treating industrial sewage loaded with dyes and various other contaminants. Therefore, although not totally commercial at this point, the future nZVI for pump-and-treat operations lies in one of two forms, that involve attaching the nZVI to some other base material. The first is maintaining nZVI in the form of a slurry and adding that to an already existing treatment operation. The second is by attaching nZVI to a larger particle or granule (e.g. kaolin or activated carbon) and forcing contaminated water through a column as a flow-through system.

3.1.5 Silver and gold nanoparticles

Silver (Ag) has been used to improve human health and conditions for centuries and its toxicity towards various microorganisms has been extensively studied since the 1970s (Spadaro et al. 1974), resulting in the use of silver antimicrobials in many bio-medical applications (Liau et al. 1997). This notion led the United States National Aeronautics and Space Administration (NASA) to develop a lightweight device that released silver ions in the water supply of a spacecraft that would keep the drinking water bacteria-free, thus eliminating the need for chlorine. Building on this technology, many companies later used similar methods to deliver silver ions into swimming pool waters, keeping them free of bacteria. Such devices are now frequently used in private pools all over Denmark and the rest of the world.

This history has led to the development of silver being engineered as nanoparticles, and is currently the most utilized nanomaterial for disinfection and anti-microbial applications. Most notably available on the commercial market is the use of silver nanoparticles (AgNPs) for small-scale personal water purifiers, the type typically used by hikers and backpackers in the wilderness. Using AgNPs this way (usually as part of a membrane system in combination with activated carbon) eliminates the need for more toxic and foul-tasting disinfection methods like iodine tablets. The idea driving the use of (AgNPs) is that there is a release of biocidal silver ions (Ag^+) that attach to and alter the membrane permeability of a cellular organism, which can subsequently attack the thiol groups in proteins or the phosphates in DNA (Xiu et al., 2011). In this process, these AgNPs then break down the respiratory chain and cell division, which eventually leads to the death of the cell (Rai et al., 2009).

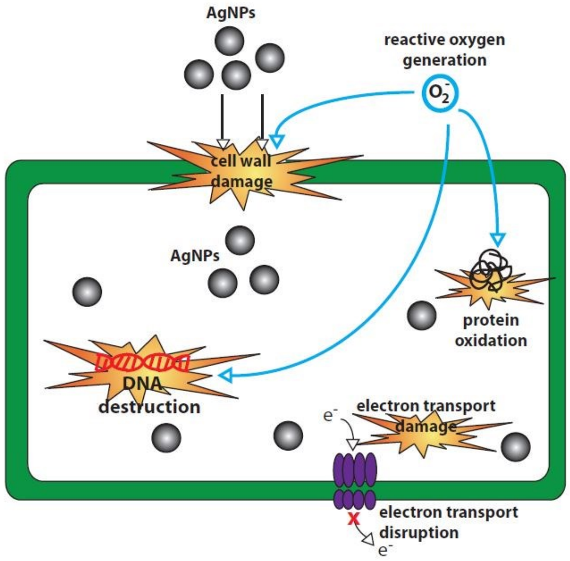

FIGURE 2
VARIOUS ANTIMICROBIAL ACTIVITIES USING SILVER NANOPARTICLES.

In this context, AgNPs have been used as a disinfectant for Gram-negative organisms (e.g. *E. coli, V. cholerae, Salmonella*), Gram-positive organisms (e.g. *Staphylococcus*), and many other pathogens in drinking water and wastewater treatment (Jain and Pradeep, 2005; Li et al., 2008; Theron et al., 2008). Furthermore, the versatility of AgNPs comes with their ability to be incorporated into a plethora of different materials. These materials include zeolites, dendrimers, and membranes, among others, which are then incorporated into disinfection treatment systems as particles in bulk solution or as a means of filtering.

Although the incorporation of AgNPs into other materials makes them substantially cheaper, the particles themselves remain quite expensive; a price of nearly 180,000 DKK per kg for a 5% dispersion of AgNPs has been quoted. This number is obviously extremely high, and further optimization of the technology, primarily incorporation into other particles or membranes, remains the only practical method of treatment technologies.

Even though AgNPs are very effective and can be sufficiently immobilized in many materials, the problem of re-dissolution of the particles remains, and consequently that of silver release control and further replenishment of AgNPs. This last statement is important in the further implementation of silver for water treatment purposes, as it is that the Danish Ministry of the Environment has set a limit of only 10 μg/L of silver at the tap (BEK no 292). However, even if silver is released into the water treatment and distribution network from any of these sources, it is usually effectively removed during the municipal wastewater treatment process as silver can be readily transformed into non-dissolvable silver sulphide (Ag_2S).

Although the current price of gold (Au) makes the notion of using gold nano-particles (AuNP) for water treatment purposes seem daunting at first, the unique properties that gold exhibits on the nanoscale make the idea more plausible, although the economics may make the use of gold nanoparticles (AuNPs) unrealistic in the long run. Even so, given that AuNPs have the ability to remove such extremely harmful compounds like mercury or trichloroethylene (TCE), they may be economically justified. For example, when combining AuNPs with a simple citrate molecule, it is possible to adsorb and remove mercury from contaminated river water (Ojea-Jiménez et al., 2012). This works in a multi-step process where the citrate reduces the AuNPs, which then act as a catalyst to reduce mercury and allow for it to be trapped by other metals (e.g. copper or iron) in solution. Moreover, when combined with another noble metal, such as palladium, AuNPs exhibit extremely high catalytic reduction capacity towards some hazardous compounds, such as trichloroethylene (Fang et al., 2011) and nitrite (Qian et al., 2014). Various other operations employing AuNPs are proving effective for removal of certain halocarbons, BTEX compounds, and sulphur-containing organic contaminants (i.e. pesticides). However, as with AgNPs, the problem of cost remains with AuNPs. Addition of catalytic noble metals and/or a stabilizing agent into which to incorporate the gold remains the only current method to ensure AuNPs can be used at an appropriate cost level.

3.1.6 Metal oxides of titanium, magnesium, and zinc

The use of metal oxide nanomaterials for treating water is not limited only to iron oxide (as mentioned in Ch. 3.2.4). Although used for various purposes and effects, metal oxides of magnesium (Mg), zinc (Zn), and titanium (Ti) are also the subject of much attention.

Of all the metal oxides, titanium dioxide (TiO_2) is perhaps the most versatile, and possibly the most widely used with the exception of iron oxides. TiO_2, by means of photocatalysis, is capable of adsorbing metals, organic contaminants, and various other compounds, disinfecting water contaminated with a wide range of bacteria, and degrading certain pollutants. An ideal example of how TiO_2 can adsorb metals is in the treatment of arsenic (As) by Pena et al., 2005. They demonstrated how it is possible to oxidize, and subsequently adsorb, As(III) to As(V) with TiO_2 acting as a photocatalyst by producing various reactive oxygen species such as the H^+ ion, hydroxyl radical (OH^-), superoxide (O_2^-), and hydrogen peroxide in the presence of UV-light. Going even further, single crystal nano TiO_2 particles have been developed to a point where nearly the entire face of the particle has a reactive surface, enabling one of the most efficient treatment mechanisms in the nanoproduct market (Yang et al., 2008).

Moreover, when targeting disinfection purposes, TiO_2 is also extremely effective, whether it be in the form of thin films (Kikuchi et al., 1997), as TiO_2 nanorods (Joo et al., 2005), doped with ferric iron (Egerton et al., 2006), or combined with silver nanoparticles (Sokmen et al., 2001). These and many other studies report a killing efficiency of TiO_2 of at least 50%, but most often upwards of 80-90%, meaning that this may not be capable of being the final disinfection agent for drinking water treatment purposes. However, if it were coupled with other treatment steps (i.e. advanced oxidation processes, membranes, etc.), it could act as an efficient cost-reducing measure to reduce chemical addition and inhibit biofouling of a membrane system.

Similar to the use of iron oxides as a means to adsorb contaminants, and particularly heavy metals, zinc oxide nanoparticles are also used as a nanomaterial adsorbent. Similarly as with iron nanoparticles, zinc oxide does not adsorb metals well as a bulk commodity, but becomes quite effective when reduced to the nanoscale. Zinc oxide nanoparticles, in various forms, have been effective as an adsorbent for arsenic and other metals. Although the mechanism is not completely understood to date, zinc oxide nanoparticles' main advantage is their use as an antimicrobial agent against a wide range of bacteria, which has been proven in many situations (Sawei et al., 2003; Adams et al., 2006).

One of the suggested mechanisms has been that since zinc oxide is known to have a high affinity to absorb UV-radiation, this will in turn lead to a photocatalytic production of hydrogen peroxide (H_2O_2), a well-known agent capable of destruction of microorganisms (Sawei et al., 2003). Another suggested mechanism for the antimicrobial power of zinc oxide is that zinc oxide nanoparticles are capable of penetrating the cell and consequently causing the unravelling of the cell membrane (Brayner et al., 2006; Huang et al., 2008). In the end, though, zinc in significant concentrations can be toxic to humans and aquatic life, and the Danish Ministry of the Environment recommends no more than 3-5 mg/L in drinking water at the tap (BEK no 292).

Magnesium based nanoparticles are primarily used in the disinfection of water. For example, Stoimenov et al., 2002, demonstrated that magnesium oxide (MgO) can be extremely effective for treatment against various bacteria (e.g. *E. coli* and *B. megaterium*). This ability as a biocide comes from an unusually high surface area of MgO in nano-form and a unique crystalized structure that allows for many reactive surface sites (Klabunde et al., 1996). In addition to the very structure of the particles themselves, these MgO nanoparticles also possess a unique ability to uptake high amounts of halogens, and in particular chlorine gas, which further contributes to the biocidal activity (Sun and Klabunde, 1999). However, this poses a problem as the halogen needs to be introduced to the particle. Therefore, although there is much interest in MgO as an antimicrobial agent in water, further progress in this as a treatment mechanism appears limited.

3.1.7 Overview of nanotechnologies for water treatment/purification

There are three main categories for the treatment of water: groundwater treatment, industrial and/or wastewater treatment, and drinking water treatment. Although many of the treatment targets overlap in all three of these categories, each category tends to have its own problems that need to be solved.

Groundwater is nearly free of pathogenic contamination, so disinfection of groundwater is irrelevant; treatment of groundwater focuses primarily on heavy metals and possible industrial source pollution, such as halogenated organics, dyes, or pesticides. Treatment of groundwater may be carried out for environmental purposes or for purification prior to use for drinking or for sensitive industrial applications.

Industrial/wastewater treatment is similar to that of groundwater treatment in terms of compounds to treat, except that in industrial/wastewater the compounds usually occur in much higher concentrations, as would be the case in smelting operations or electroplating operations, for example.

Drinking water treatment focuses much more on disinfection, and on some of the same industrial compounds at much lower concentrations. However, drinking water operations need to be capable of removing a much higher percentage of contaminants in order to be fit for human consumption. For example, the Danish Ministry of the Environment has set drinking water limits at the tap at 10, 20, and 10 µg/L for bromate, nickel, and arsenic, respectively (BEK no 292).

Therefore, it is clear that these various treatment targets overlap significantly with the nanoproduct technology employed for treatment. Therefore, it is necessary to organize these technologies with respect to the method of treatment, which is one of three methods: pollutant removal by adsorption, disinfection of water (i.e. toxic action), and pollutant degradation by chemical reduction or photocatalysis. Certain nanoproducts can often be applied in more than one category, as is the case with TiO_2, which is effective at both disinfection and photocatalytic degradation of contaminants.

Table 1 presents an overview of the nano-technologies identified for water and wastewater treatment and purification including nanomaterial involved, functionality, application areas and stage of development.

TABLE 1
OVERVIEW OF THE USE OF NANOTECHNOLOGY FOR WATER/WASTEWATER TREATMENT/PURIFICATION

Application/product	Involved "nano" (material, surface etc.)	Why is "nano" applied?	Development stage
Pollutant removal by adsorption	CNTs (membranes, portable water filters), zeolites (membranes, desalination), metal-oxides and chitosan (powders in water treatment for adsorption or coagulation)	High surface area, high accessible adsorption sites, fine-tuning of compound to pollutant, easy to reuse	Primarily lab-scale and pilot-scale. Prototype commercial products.
Disinfection for drinking water or wastewater	Chitosan (membranes), Ag (membranes, portable water filters), TiO_2 and MgO (powders, thin films, membranes), CNTs (membranes, portable water filters)	Cell membrane damage, metal chelation in cells, reactive oxygen species (ROS) production, chemical stability	Primarily lab-scale and pilot-scale. Prototype commercial products.
Pollutant degradation by chemical reduction or photocatalysis	nZVI (flow-through columns, slurries), Au (membranes, slurries), TiO_2 (powders, thin films, membranes)	Catalytic reduction and photocatalysis not seen in bulk materials, unique quantum effects	Primarily lab-scale and pilot-scale

Additionally, it must be noted that many of these nanoproducts are actively being developed into membranes and membrane processes. Primarily, these are zeolites, silver, carbon nanotubes, TiO_2, and magnetite. The addition of these nanoproducts to membranes can aid in a wide variety of operational concerns, of note by acting as anti-biofouling agents, antimicrobial agents, or having tuneable chemistry to filter out particular compounds. A general overview of how and why these nanoproducts are used is summarized by Qu et al. (2013) as shown in in Table 2.

TABLE 2
OVERVIEW OF THE USE OF NANOPRODUCTS BEING INCORPORATED INTO MEMBRANE TECHNOLOGY

Application/product	Involved "nano" (material, surface etc.)	Why is "nano" applied?
Membranes and membrane processes	Zeolites	Filtration, molecular sieve, hydrophilic, high permeability, tunable chemistry
	Silver	Antimicrobial, anti-biofouling
	CNTs	Antimicrobial, high mechanical strength, tunable chemistry for filtration, chemical stability, anti-biofouling
	TiO_2	Photocatalysis, hydrophilic, chemical stability, reactivity addition to membrane
	Magnetite	Tunable chemistry, superparamagnetic

3.2 Market considerations – today and in the future

The research world and academic market are flooded with reports on the use of nanotechnologies for various water treatment purposes: everything from drinking water treatment to contaminated groundwater treatment to severely polluted industrial wastewater and acid mine drainage treatment. Results in the lab and in certain pilot studies have proven that these materials can be extremely effective in the adsorption, disinfection, or degradation of contaminated water. Furthermore, there are plenty of commercially available nanomaterials/-products available to the consumer. However, the commercial market for the full-scale, widespread use of these technologies for environmental/water treatment purposes remains nearly absent.

The first hindrance for widespread use of nanotechnologies is that the effect of nanoproducts on the human body and environment are insufficiently studied to date. Therefore, both governments and companies are extremely reluctant to employ nanotechnology in water treatment systems, especially drinking water treatment systems. It becomes a liability risk to use these nanoproducts for water treatment.

The second hindrance for nanoproduct use in water treatment is the cost. Unlike many other treatment targets (i.e. carbon dioxide capture, acid mine drainage, oil spills, etc.), the treatment of water for the public use needs to be extremely cheap. For reference, Dansk Vand- og Spildevandsforening (DANVA) reported in 2013 that the average operating costs for Danish drinking water companies were 4.65 DKK per cubic metre. To utilize many of these nanoproducts for standard water treatment practices can be costly: a one to three log increase in the price per cubic metre. These kinds of prices are not sustainable for typical water treatment operations, whether that be for drinking water, wastewater, or groundwater. That being said, the current situation in Denmark regarding the use of nanoproducts in mainstream water treatment is for all intents and purposes non-existent. This has the potential to change though, if the technology cost could drastically reduce and if the technology could be developed in a way assessed to be safe for the end users. However, there are potential “niche” markets where the use of nanoproducts in water treatment could be feasible, even if the costs remain high.

Certain compounds, perfluorinated compounds (PFCs) in particular, have the potential to be treated with nanoproducts. PFCs are used for many applications, including coatings for cookware and other common consumer items and the use as a fire-fighting chemical. The use of, and subsequent environmental contamination, of PFCs at airfields in Denmark is a particular problem in certain areas. Certain studies have shown the potential of nanomaterials to be able to treat and degrade these extremely recalcitrant chemicals. If the further development of nanomaterials in this particular context could be optimized to a point where sufficient degradation could take place, then this nanoproduct market has great potential in Denmark, and the world.

It is difficult to put an exact number on operations that currently employ nanotechnology in the water and wastewater treatment market, especially since many developers/manufacturers of systems using nanoparticles incorporated into membranes or other compounds are very reluctant to disclose their exact product make-up. Although, according to the Organisation for Economic Co-operation and Development (OECD), the global market for water and wastewater treatment was approx. $1.6 billion USD in 2007, and was expected to reach $6.6 billion USD by the end of 2015. Most of that market (43%) is the incorporation of nanomaterials into filtration operations (Helmuth Kaiser Consultancy, 2006). Between those years of 2007 and 2015, the highest growing sector was expected to be the disinfection market.

However, we can still attain a general idea of the scope of research and the market from certain projects funded by the EU, in particular initiatives like the Nano4water cluster. This group started with five collaborations co-funded by the Research DG of the European Commission following a Joint Call on nanotechnologies for water treatment (FP7-ENV-NMP-2008-2). These five collaborations are CleanWater, MONACAT, Nametech, NewED, and WATERMIM. This group of projects expanded to 17 projects only four years later: 17 projects focusing on nanotechnology in water treatment, with the expectation to further expand in the near future. One of the main goals of this coalition is to continue to develop nanotechnology in the real-world market, by up-scaling lab and bench scale operations into pilot and full scale operations by the year 2020. A particular goal is to focus on technologies centred around CNTs, titania nanostructures, nano-photocatalysts, nanoparticle incorporated membranes, and antimicrobial nanoparticles (Helmut Kaiser, 2006).

3.3 Health and environmental pros and cons during use

Benefits from the use of nanomaterials in the water and wastewater treatment sector vary widely, depending on the material and application, whether that be pollutant adsorption, antimicrobial disinfection, or chemical degradation of a pollutant. Nanomaterials present a unique range of benefits due to their size, ranging from exponentially higher surface area for adsorption, fast dissolution, extremely high reactivity in many cases, and even exhibit certain quantum effects not seen in the bulk materials.

For adsorption purposes, properties like the extremely high surface area for attachment, nanoporous nature, and quantity of binding sites on these materials make them extremely efficient per unit of material being used.

For disinfection purposes, the nanosized nature of the material allows the use of certain compounds like silver and chitosan that normally do not exhibit the same degree of disinfection properties.

For chemical degradation purposes, these nanomaterials offer a much higher efficiency compared to when considered as a larger bulk material. In a world with an exponentially increasing population with an equally exponentially increasing demand for raw materials, nanomaterials use a fraction of that raw material, hence potentially offering an economically- and material usage-friendly direction into the future.

However, these advantages do not come without any disadvantages; namely, the effects that nanomaterials can have on the environment and human health. The knowledge about these risk aspects is still limited, outside of a narrow range of lab-scale studies. In particular, compounds like silver that are used in disinfection need a great deal more study on their ecotoxicological and human health effects. Possible consequences can be further magnified when being put into place for drinking water operations, as reiterated in discussions in this chapter. Although most nanoparticles used in bulk solution tend to agglomerate together and fall out of solution and most nanoparticles incorporated into membranes and other compounds tend to be stable in those composites, the risk of these particles being released back into the treated water is judged to be real.

4. Soil and groundwater remediation

Systematic identification and remediation of contaminated soil and groundwater at polluted industrial sites, petrol stations etc. has taken place for more than two decades in Denmark, implying costs to society of billions of Danish kroner. The remediation technologies have evolved steadily during this period and in this chapter one of the emerging approaches, the use of nano-technology and nanomaterials for soil and groundwater contamination clean-up, is reviewed.

With regard to groundwater there is an interface with technologies for (drinking) water purification and clean-up, but this chapter only looks at *in situ* remediation of groundwater as an unexploited potential water resource, whereas chapter 3 on water cleaning focuses on the final treatment of already extracted raw groundwater at the waterworks prior to distribution to the consumers. The techniques described in chapter 3 for the latter purpose are also considered to cover techniques where contaminated groundwater is treated *ex situ* (i.e. in a reactor on the surface).

4.1 Overview of nanoproducts and technologies

Whenever possible, soil contamination should be addressed at or near the source. Typically, surface-near soil contamination is excavated and treated off site by chemical, thermal and/or biological methods (or simply disposed of at a special designed dump site) depending on the character and magnitude of contamination. However, based on the literature review (e.g. Mueller and Nowack, 2010) and general experience, the use of nanotechnology for these soil remediation techniques appears to be of minor importance, if any at all. This is probably because the use of nano-technology has technical constraints and is less cost-effective compared to traditional methods.

Other *in situ* techniques such as removal of heavy metals from contaminated soil by uptake in certain plant species (that are subsequently harvested) are also known and several reports on full-scale implementation of such techniques exist; however, they do not involve use of nanotechnology.

If the contamination cannot be addressed directly at the source, or the contamination has moved by leaching to deeper soil layers or to the groundwater, other technologies such as *in situ* remediation using chemical, thermal or microbiological techniques come into the picture. It is here that nano-based technology has attracted interest as an alternative to more well-known chemical treatment methods due to the anticipated higher efficiency of the nanoparticles. In the case of soil and groundwater remediation the nano-based product applied is the nanomaterial itself.

Above all, the interest has concentrated on nano-zero valent iron (nZVI) as the reactive material but also the potential of other nanomaterials is being explored, e.g. bimetallic nanomaterials (e.g. nZVI + Pd (palladium) as a catalyst), self-assembled monolayers on mesoporous supports (SAMMS), dendrimers, carbon nanotubes (CNT) and metalloporphyrinogens. The particle size of nZVI used in practice for *in situ* remediation typically ranges from 10-100 nm (US EPA, 2008).

4.1.1 *In situ* groundwater remediation with nZVI and modified nZVI

Chemical methods for *in situ* remediation of groundwater have been known and applied in practice since the early 1990s, not least in the USA, e.g. using the properties of metallic substances such as elemental iron to degrade chlorinated solvent plumes in groundwater (CLU-IN, 2012). An example of this is installing a trench filled with macro-scale zero-valent iron (ZVI) to form a permeable reactive barrier (PRB) where the solvent is degraded when the polluted plume flows through.

However, nano-scale ZVI has attracted attention as a promising emerging technology for *in situ* remediation because of the expected higher reactivity than macro-scale ZVI due to the much higher surface area of nZVI as well as a potential higher mobility in the aquifer due to the much smaller particle size. A number of reviews on the chemical and physical properties of nZVI and its applicability (including limitations, risks and research needs) for soil/groundwater remediation have been identified and used for this summary (e.g. CLU-IN (2012), Crane and Scott (2012), Fu et al. (2014), Grieger et al. (2010), Karn et al. (2009), Kharisov et al. (2012), Mueller et al. (2012), O'Carroll et al. (2013), Taghizadeh et al. (2013), Tratnyek and Johnson (2006), US EPA (2008), Watlington (2005)).

The functionality of nZVI can be exploited in approaches to *in situ* remediation other than PRB, such as creating reactive treatment zones in an aquifer by a series of nZVI injections or injecting nZVI at so-called DNAPL (Dense Non-Aqueous Phase Liquid) contamination zones (also known as "free phase" contamination). These two different approaches are illustrated Figure 3.

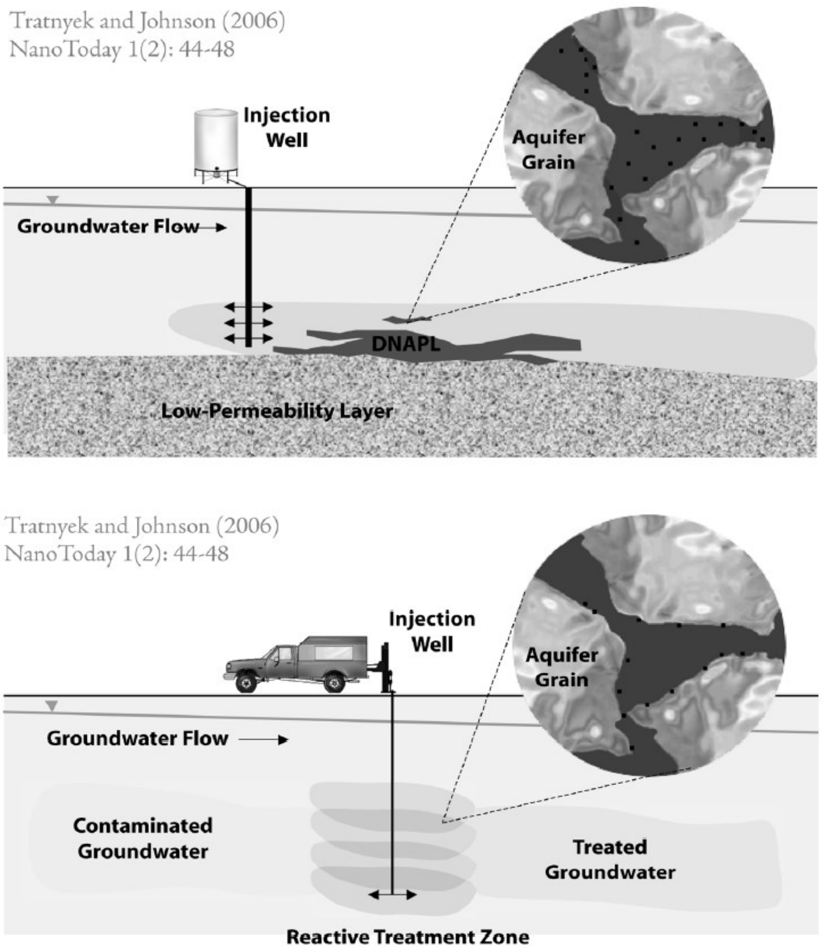

FIGURE 3
OVERVIEW OF IN SITU METHODS FOR GROUNDWATER REMEDIATION USING NANO-BASED ZVI TECHNIQUES (REPRODUCED FROM CLU-IN, 2012)

The advantage of using nano-scale ZVI instead of macro- or micro ZVI is the increased reactivity, which can be 10 to 10,000 higher than for granular iron, and higher reaction rate with the target contaminants, which has been found to be 25-30 times faster than for ZVI in the µm-mm size range (Mueller and Nowack, 2010). The much higher surface area per mass unit is found to be the most important factor for the higher reactivity and reaction rates (Tratnyek and Johnson, 2006). Many reviews indicate particularly the potential of nZVI for remediation of contamination with chlorinated organic substances (chlorinated solvents, PCB etc.) and its higher mobility in saturated subsurface soil as important (CLU-IN (2012), Bardos et al. (2015b, Fu et al. (2014), Mueller et al. (2012), Mueller and Nowack (2010), O'Carroll et al. (2013)).

Among factors affecting remediation performance, a disadvantage of nZVI is the strong tendency of the nanoparticles to **agglomerate** to each other or to soil particles, which significantly reduces the potential mobility and reactivity of the particles. Therefore, modifications of the nano-iron particles have been introduced, e.g. coatings with polyelectrolytes or triblock polymers or encasing in emulsified vegetable oil droplets (emulsified nZVI or just EZVI) to improve stability and contact with the contaminant (especially relevant for treatment of DNAPL contaminations) (CLU-IN, 2012). Carboxy-methyl-cellulose (CMC) has also been used successfully as a stabilizing material for nZVI, e.g. for the removal of arsenic (As) from groundwater by reduction of As(III) and As(V) to As(0) (Fu et al. (2014), Habuda-Stanic and Nujic (2015) and Kanel et al. (2006)).

Another disadvantage is **passivation**, or deactivation, which occurs because the high surface energy of nanoscale iron (and other nanomaterials) makes it susceptible to oxidation in air, thus decreasing the reactivity of the material as oxides are formed from the zero-valent parent material. Finally, site-specific conditions such as soil matrix composition or geochemical properties can affect the performance of a nanomaterial by reducing its mobility and/or "eating" some of its reaction potential due to groundwater constituents reacting with the elemental iron (CLU-IN, 2012).

Fu et al. (2014) discuss immobilization of nZVI onto a number of supports e.g. carbon, bentonite, kaolinite and zeolite, which can facilitate practical operation of nZVI while at the same time maintaining the high reduction ability of this nanomaterial. Doping with other metals, i.e. creating bimetallic nanoparticles (BNP) by coating iron (Fe) as the principal metal with a thin layer of transition metals such as palladium (Pd), platinum (Pt), copper (Cu) and nickel (Ni) has proved effective especially for the reductive dehalogenation of chlorinated organic compounds. Fe/Pd bimetal has generally been found to outperform the other bimetallic combinations. Fu et al. (2014) also summarizes several studies and tests using nZVI for the removal or retainment of soil/groundwater pollutants such as arsenic, various chlorinated organic compounds (COCs), nitroaromatic compounds (NACs), heavy metals, nitrate, phenol and dyes.

Crane and Scott (2012) report that in the US approximately 40% of all nZVI remediation projects deploy bimetallic nZVI, while no such field applications have yet taken place in Europe.

O'Carroll et al. (2013) suggest that nZVI technology may be better suited to source zones than dilute plumes (other authors have also made this observation). They found that modifications of the nanoparticles are necessary to improve stability, reaction life-time and selectivity. This is in agreement with Tratnyek and Johnson (2006), who underline that high reactivity tends to correlate with low selectivity, thus requiring either repeated injections (and thereby higher costs) or surface modifications to improve selectivity and transport distances.

4.1.2 Nanomaterials other than nZVI for *in situ* remediation

CLU-IN (2012) lists the following nanomaterials, which have also been investigated for *in situ* remediation of soil and groundwater[2]:

- **Bimetallic nanoscale particles (BNPs)** that consist of iron or other metals in conjunction with a metal catalyst, such as palladium (Pd), platinum (Pt), gold (Au)

[2] CLU-IN (2012) also mentions that nanoscale TiO_2 is being pilot tested for *ex situ* treatment of contaminated groundwater as part of a pump and treat system. This *ex situ* use of nano-TiO_2 is described in chapter 3 as one of the methods applicable for water purification.

or nickel (Ni). The combination of metals increases the kinetics of the oxidation-reduction reaction. Iron/palladium BNPs are commercially available and currently the most common.

- **SAMMS**, self-assembled monolayers on mesoporous supports, consist of a nanoporous ceramic substrate coated with a monolayer of functional groups tailored to preferentially bind to the target contaminant, most typically metals or other elements.
- **Nanotubes**, which are most often made from carbon (carbon nanotubes, CNT) but also have been made from other materials such as TiO_2. They are electrically insulating, highly electronegative and easily polymerized and act primarily as sorbents.
- **Ferritin**, a photocatalytic iron storage protein that can potentially reduce the toxicity of e.g. chromium and technetium.
- **Dendrimers**, hyper-branched polymer molecules with three components: core, branches and end groups (tree structure). Their surfaces have several functional groups that can be modified to enhance specific chemical activity and they could be used to construct permeable reactive barriers.
- **Metalloporphyrinogens**, naturally occurring, organic porphyrin molecules complexed with metals. These have the capability to reduce chlorinated solvents such as TCE, PCE and carbon tetrachloride under anoxic conditions.

However, with the exception of bimetallic NPs, in particular the Fe/Pd-based ones, none of these materials appear to be used commercially or at full scale anywhere today.

4.1.3 Overview of nanotechnologies for soil/groundwater remediation

The table below presents an overview of the nano-technologies identified for *in situ* soil/groundwater remediation, including nanomaterial involved, functionality, application areas and stage of development.

TABLE 3
OVERVIEW OF THE USE OF NANOTECHNOLOGY FOR SOIL AND GROUNDWATER REMEDIATION

Application/product	Involved "nano" (material and/or surface...)	Why is "nano" applied?	Development stage
In situ remediation (1) (by injecting a slurry with the nano-material directly into the subsurface soil or aquifer)	nZVI, possibly surface modified to avoid agglomeration and/or passivation	To increase reaction rate and mobility compared to ZVI	Commercial use primarily in the USA; in Europe only experimentally, and a few full-scale applications. More than 50% of the US market
In situ remediation (2) (ditto)	nZVI + other metal (e.g. Pd) (bimetal)	To further increase reactivity compared to nZVI	As above. Approx. 40% of the US market
In situ remediation (3) (ditto)	Other nano-materials, e.g. nanotubes, dendrimers	Primarily to increase active lifespan and optimize substance-specific reactivity	Research/development stage

4.2 Market considerations – today and in the future

Bardos et al. (2015a) report from the EU-funded NanoRem project (Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment) that they have identified around 70 projects worldwide documenting use of nZVI for remediation at the pilot or full scale while another 60 field applications have been reviewed by others. Most deployments of nZVI have focused on degradation of chlorinated solvents for plume management but a number of pilot studies have also demonstrated successful treatment of small aromatic compounds (BTEX), perchlorates, chromium (VI), diesel fuel, PCBs and pesticides. Mueller et al. (2012) mention in their review of nZVI use for remediation in Europe that while use of nZVI is an established treatment method in the USA, only three full-scale remediations have been carried out so far in Europe. In Europe, the focus has been on treatment of chlorinated hydrocarbon contamination.

In 2006, 80,700 contaminated sites in Europa had been remediated while another 245,900 sites with positively identified contamination awaited remediation and yet more than 1.8 million sites were identified as potentially contaminated. Thirty-seven percent of the sites were contaminated with heavy metals, almost 34% with mineral oil, 13% with PAHs and the remainder with BTEX (6%), phenols (3.6 %), chlorinated hydrocarbons (2.6%) and other substances (3.6%) (Caliman *el al.* (2010)).

According to CLU-IN (2012), concerns about possible human health and/or environmental effects of nanomaterials in general has also affected the use of such materials in soil and groundwater remediation in the USA. CLU-IN (2012) mentions that e.g. DuPont has ruled out the use of nZVI for remediation at its sites until issues concerning fate and exposure have been more thoroughly researched, and the Continental Western Group of insurance companies has announced *that it will no longer cover injury or damage arising from nanotubes or nanotechnology, as used in products or processes*.

In 2001, when field demonstrations of nZVI technology first took place, the cost of the material was high, about 500 USD/kg, but had reduced to 50-100 USD/kg by 2006. In some cases this is still not cost-effective but in others the total costs of deploying the technology can be quite competitive in the life cycle cost perspective compared to traditional *ex situ* solutions (CLU-IN, 2012).

The US Navy conducted full scale field demonstrations with nZVI at three military sites around 2005: Hunters Point shipyard, NAS Jacksonville and NAES Lakehurst. Although the efficiencies of the treatments differed for different reasons, it was nevertheless concluded that nZVI injection is a promising option for treatment of source zones (Gavaskar et al., 2005). Prices of nZVI material were obtained from numerous vendors and varied at the time of reporting (2005) from $20 to $77 per pound depending on the quantity. The prices also vary depending on whether the product is unsupported and non-catalysed or it is supported and catalysed (i.e. bimetallic).

Crane and Scott (2012) mention that in 2004 the price for nZVI varied between £15 and £100 per kg while the price for micro or granular zero valent iron was less than £1 per kg. At the time when the article was written, the price of nZVI was in the range of £ 50-150 per kg; it was assessed that it must reduce to <£ 10 to be competitive for *in situ* chemical oxidation. Crane and Scott (2012) report that "*the competiveness of nZVI against other in situ treatments such as chemical oxidation is still widely disputed*". Further, they find that "*The universal acceptance of nZVI as a remediation technology may well occur, but not until a fundamental understanding of behaviour, interactions and impact has been demonstrated*".

Karn et al. (2009) review and discuss benefits and potential risks of nanotechnology, not least nZVI, in relation to *in situ* remediation. Information from 45 project sites was aggregated. The authors found that nanoremediation, in particular the use of nZVI, has site-specific requirements that must be met in order for it to be effective related e.g. to geology, hydrogeology and geochemistry of the site. These site-specific requirements would determine if the particles can actually infiltrate the remediation zone and whether the conditions are favourable for reductive transformation of contaminants. According to Mueller et al. (2012) it is generally agreed that remediation with nZVI in dense geological formations is less efficient and that unsaturated media are more difficult to treat.

With regard to remediation costs, Karn et al. (2009) refer to a case study from New Jersey with removal of TCE and PCE where the use of nZVI could lead to cost savings of about 80-90% compared to the traditional pump-and-treat method. They also roughly estimate that using nano-remediation, potential savings of $87-98 billion can be realised to clean up the nation's (i.e. the USA's) waste sites over the next 30 years although they note that not all sites have conditions suitable for nanoscale remediation methods. The time required for clean-up would also be reduced significantly compared to pump-and-treat where nanotechnology could be applied (pump-and-treat methods 18 years on average against 1-2 years for nZVI treatment). Karn et al. also mention that the potential risks need to be addressed before the technique is used on a mass scale.

Mueller et al. (2012) state that the German Institute for Geosciences and Natural Resources, which conducted one of the few field-scale remediations in Europe, decided to discontinue their project in 2008 due to technical difficulties of disseminating the iron below ground and a cost-benefit analysis indicating that the technology was not yet ready for large-scale application, despite the widespread application in the USA and three successful projects in Europe. Thus, the advantages and viability of nZVI compared to traditional ZVI treatments remain controversial.

In Denmark the use of nanotechnology for groundwater remediation is still at the research and development stage. At DTU Environment, lab scale experiments with nZVI have been conducted during the last decade, as part of the INWAT (INtegrated WAter Technology) project among others, where the use of coated nZVI particles for remediation of free phase (DNAPL) contamination with chlorinated solvents was examined. Recently, GEO (Hindrichsen et al., 2015) reported results of field scale remediation trials at three sites in Denmark with stimulated reductive dechlorination by direct nZVI slurry injection. At one location where molasses was preinjected, a considerable degree of full degradation of PCE and TCE was observed while at another site, not prestimulated with molasses, the degradation was only partial. Before that, the only proven field demonstration project in Denmark using nZVI was performed in Taastrup in 2011 by COWI and Geosyntec Consultants (USA) on behalf of the Capital Region of Denmark. nZVI was injected under high pressure into a basal clay till to test the feasibility of jet injection of nZVI into low permeable glacial clay moraine deposits, which prevail in the shallow subsurface in Denmark. Overall the project succeeded in distributing ZVI into glacial clay till; however, a number of challenges related to bypassing natural vertical fractures remain.

Thus, the overall impression from our literature review and interviews is that the early high expectations related to the applicability of nanotechnology for soil/groundwater remediation have decreased somewhat, or perhaps are becoming more realistic; i.e. nZVI is no longer perceived as a universal solution to the challenges in soil/groundwater remediation but rather as a supplementary tool, which can be applied advantageously under certain conditions for certain contaminants but in other situations would not be cost-effective compared to other approaches such as use of micro-/macro-scale ZVI. The largest potential for nZVI use seems to be for removal of chlorinated organics, in source zones rather than in dilute plumes, and maybe more advantageously in sandy rather than in clayey aquifers (Durant, pers. comm. (2015); various review articles e.g. O'Carroll et al. (2013), and own experience).

The need for a study on the use of nano-technology (nano-iron) was mentioned in the 2007 version of the Danish EPA's programme for development of new technology for soil/groundwater remediation (Miljøstyrelsen, 2007). However, for unknown reasons, it was never implemented and it has not been mentioned in later revisions of the programme. Hence, there are currently no signs that application of nano-technology for soil remediation will be increasing in Denmark in the near future. The technology is currently not considered to be sufficiently "mature" and/or cost-effective compared to other existing *in situ* methods. There is no national policy in Denmark preventing application of nZVI or other nano-technology; however, specific permission to inject substances (also non-nano) must always be obtained locally (at the municipal or regional level) on a case-by-case basis. If cost-effectiveness of nZVI can be documented, it is assessed that there will be a market for this technology in Denmark.

4.3 Health and environmental pros and cons during use

According to Bardos et al. (2015), the principal potential benefits of nZVI use are the extent and speed of contaminant degradation. Furthermore, there may be an extension of the range of treatable contaminants to include types traditionally perceived as recalcitrant. In addition, as the active lifespan of nZVI is likely to be limited due to agglomeration and passivation, the impacts on the environment are likely to be lower than for other *in situ* remediation options (Bardos et al. (2015). However, as the human health and environmental risks are not yet fully clarified and documented, many countries have taken a precautionary principle approach to the use of nanomaterials (including nZVI), which in reality prevents the implementation of this technology for groundwater remediation.

Another aspect in relation to the above, mentioned by Crane and Scott (2012), is the possible reversible nature of the remediation of metal and/or radionuclide contamination in complex and/or natural waters using nZVI. For example, a change in the groundwater conditions (pH, redox potential etc.) could in principle reverse the original fixation of the metals, thereby unexpectedly re-remobilising them and thus reintroducing the pollution problem. Clarification of this potential issue is needed.

Grieger et al. (2010) also discuss risk aspects of nZVI use for in situ remediation. They conclude preliminarily that "*at present there are no significant grounds on which to form the basis that nZVI currently poses a significant, apparent risk to the environment, although the majority of the most serious criteria (i.e. potential for persistency, bioaccumulation, toxicity) are generally unknown*".

Some pros and cons related to health/environment/resource aspects of the application of nanotechnologies in soil/groundwater remediation are summarized below.

Pros:

- Iron (ZVI) is not a limited/scarce resource.
- nZVI can, in principle, decontaminate a significantly larger volume than micro-/macro-ZVI per weight unit of material.
- nZVI offers superior degradation rates and limited production of undesirable degradation intermediates.
- Potentially, the range of treatable soil/groundwater contaminants can be extended.
- Contaminated sites can be remediated (removal of source) faster than by traditional methods.
- Injection of nZVI with known, commonly applied techniques is relatively cheap and injection can be performed at significant depths.

Cons:

- Not fully mature as treatment technology and presently not considered a cost-effective method (except perhaps in special cases).
- Catalytic bimetals (to be used in combination with nZVI) will often be noble metals such as Pt, Pd or Au (i.e. limited/scarce resources).
- The active lifespan of nZVI is rather short and therefore several injection rounds are typically needed.
- Possible risks to the environment are not fully clarified.

5. Air pollution reduction/air purification

Applications of nanomaterials and nano-technologies for reducing indoor or outdoor air pollution/improving indoor or outdoor air quality are addressed in this chapter. However, some technologies and materials serve more than one purpose, e.g. some materials are used as catalysts in engines for vehicles to improve combustion, thus resulting in both lower energy consumption and cleaner exhaust gases. Therefore, some small overlaps occur with the descriptions in chapter 6 of technologies for reduction of energy consumption, although the focus in the current chapter is on air quality aspects while chapter 6 focuses on energy aspects of the technology.

Only aspects related to the intended use of nanotechnology/-materials for air cleaning and air quality improvement are described in this chapter, while indirect impacts of the technologies in a life cycle perspective, e.g. carbon foot-print/climate change aspects related to the manufacturing of nanomaterials, are not addressed here.

5.1 Overview of nanoproducts and technologies

The nano-based technologies and materials for reduction of air pollution/improvement of air quality can be divided into two main groups based on area of application, namely uses targeting outdoor air pollution/quality issues and uses targeting indoor air quality issues.

Within each of these categories, a distinction can be made between active and passive technologies. Active technologies or systems require a power supply to run a reactor or an air transport system, while passive systems simply exert their action via treated or coated surfaces exposed to natural light or general room illumination and available ambient air flow.

Identified areas where nanotechnology/-materials are already being implemented commercially have been tested at the full scale or are currently being developed include:

- Passive air cleaning systems for outdoor applications utilizing photocatalytic properties of certain nanomaterials on treated surfaces to degrade air pollutants;
- Industrial exhaust/emission cleaning with catalytic systems;
- Catalytic systems to improve combustion efficiency of automobile engines;
- Passive photocatalytic air cleaning systems for indoor air quality improvement;
- Active photocatalytic air cleaning systems for indoor air quality improvement, and
- Sorption-based systems with nano-particles to clean indoor air.

In the following, a number of examples of such technologies and materials are described with regard to purpose, air quality issues/pollutants addressed, technology ("how does it work?"), efficiency, state of development as well as implementation and cost aspects (where possible).

5.1.1 Passive outdoor air cleaning by photocatalytic action on treated/coated surfaces

This technology works by coating walls, roofs, pavements or other outdoor surfaces with the nano-material (in some cases in the form of a nano-treated film) and exploiting the ability of anatase TiO_2 to absorb ultraviolet (UV) radiation from the sun and acting as a catalyst to form reactive hydroxyl (OH) radicals in the presence of atmospheric moisture. The OH radicals subsequently react with (oxidise) and thereby degrade a number of different air pollutants including nitrogen oxides (NO_X)

and various volatile organic compounds (VOCs). In principle, other photoactive nanomaterials could serve the same purpose; however, the reality seems to be that currently only TiO_2 is being used in practice. This is partly because of its high oxidative ability and chemical stability, and partly because of its low cost and availability compared to other potential materials (Rickerby and Morrison, 2007).

In a recent review of nanotechnology innovations for the construction industry, Hanus and Harris (2013) also present an overview of air purifying surfaces and mention, among others, that the EU currently funds a project known as LIGHT2CAT. The project aims to develop highly efficient visible light-activated TiO_2 for inclusion in concrete for the improvement of ambient air quality, in particular with regard to reduction of NO_X levels by conversion to nitrate. Incorporation into other materials (e.g. asphalt roads, paints) or surface coatings are also mentioned as possible areas of nanotechnology use. However, some uncertainty exists as to whether the photocatalysts will degrade not only NO_X, but also result in the generation of various potentially harmful by-products due to incomplete degradation of VOCs.

Hanus and Harris (2013) mention three main application techniques that have been suggested for producing catalytic concrete pavements: i) application of a thin, photocatalyst-containing cementitious layer, ii) application of a photocatalyst-containing solution onto the concrete surface, or iii) application by sprinkling the photocatalyst onto the fresh concrete. Each method has its advantages and disadvantages in terms of reactivity and durability. The use of such concrete surfaces has in particular attracted interest in dense, heavily trafficked urban areas, including so-called street canyons. Trials in a model street canyon in France treated with nano-TiO_2 have shown significantly reduced levels of NO_X (36-82 %) compared to an untreated reference. Other trials in a number of other countries have also shown promising results. When incorporating nano-TiO_2 in paint it is important to select an appropriate paint/coating formulation to achieve both reactivity and durability and to avoid formation of unwanted by-products (Hanus and Harrris, 2013).

Rickerby and Morrison (2007) mention that in street canyon tests, NO_X concentrations were reduced by 40-80 % depending on differences in emission sources, wind direction and orientation of the walls. While nitrate is the transformation product of photocatalysis of NO_X, aldehydes are the main transformation products of organic pollutants.

The California Energy Commission (CEC, 2008) has published a report prepared by the Lawrence Berkeley National Laboratory where the use of TiO_2 as a photocatalyst for removal of air pollutants was evaluated. In particular, the potential for passive cleaning of outdoor air using films or plates treated with anatase TiO_2 was studied. The main pollutants to be removed by this technique (photocatalytic oxidation) were anticipated to be NO_X and VOCs. In laboratory experiments conducted as part of the study, it was shown that a high-quality TiO_2 catalyst had an activity of roughly 200 m/day for NO_X and 60 m/day for typical VOCs (explanation of unit used: if 1 m^2 of catalytic surface can clean an air volume of 100 m^3/day, it has an activity of 100 m/day) (CEC, 2008).

While active air cleaning systems exploiting the photocatalytic properties of TiO_2 to clean indoor air, e.g. for malodourous compounds, are commercially available, the practical feasibility of passive outdoor systems remains controversial. While some claim that air pollution could be halved with this technique, others question this assertion (CEC, 2008). In the report it is concluded that air pollution reduction by this method is technically feasible, but accomplishing it in a cost-effective way would be challenging.

Chen and Liu (2010) studied the removal of NO_X originating from vehicle emissions by functionality enhanced asphalt roads, i.e. roads where a TiO_2 photocatalyst had been immobilised on the surface. Experiments showed that 6 % to 12 % of the produced NO_X could be removed by this technique depending on the actual conditions. Dylla et al. (2011) studied the effects of roadway contaminants such as general dirt, de-icing salt and motor oil on the NO_X removal efficiency of TiO_2 treated concrete pavements and found that such contaminants had a strong negative impact on the efficiency. As well, parameters such as increasing the air flow rate and the relative humidity had a significant negative impact on NO_X removal.

The Danish weekly professional magazine for engineers, "Ingeniøren" ("The Engineer"), recently published an article describing a technique developed by the Danish Technological Institute as part of the EU supported research project Light2CAT. In this project a modified form of catalytic TiO_2 is incorporated into the concrete of paving slabs (instead of coating the slab, which is considered too vulnerable to tear and wear), where it would still able to exhibit a reasonable photocatalytic activity even under normal Danish outdoor conditions (Ingeniøren, 08.09.2015). "Ingeniøren" has previously reported on large-scale tests conducted by the Danish company Photocat on a parking lot in Copenhagen Airport with paving slabs impregnated with photocatalytic TiO_2 (Ingeniøren, 15.11.2013). According to the article in "Ingeniøren", 24% of the NO_X produced on the parking lot in the busiest hours from 10 am to 8 pm was removed. The company points out that the technology is probably most efficient on roofs where, according to the company, 5-35% of the NO_X present in the ambient air can be removed.

5.1.2 Industrial exhaust/emission cleaning with catalytic systems

Catalytic converter systems are proven, well-established environmental technologies being commercially applied worldwide. The catalytic converter is installed as an integrated part of the exhaust systems/chimneys at industrial facilities to remove air pollutants, primarily NO_X, from the emissions to air. The so-called deNOx system, based on Selective Catalytic Reduction (SCR), typically uses a vanadium oxide catalyst immobilised on a support matrix and ammonia (or urea) as the reducing agent to convert NO_X to N2 and water. The catalyst material may be nano-sized but this is often not clearly stated by the vendors/manufacturers of deNOx systems of which several exist worldwide, including in Denmark.

As an example, Kristensen et al. from the Technical University of Denmark (DTU) have presented a deNOx system for cleaning of flue gases based on anatase TiO_2 particles coated with a monolayer of amorphous V_2O_5. Systems based on active monolayers of other oxides, such as Fe_2O_3 and CuO on a ZrO_2 support base, were also presented and found to be highly competitive in terms of efficiency and selectivity compared to a commercial reference catalyst (Kristensen et al., 2009).

More recently, the Danish Innovation Fund (2014) announced that a Danish company, Dinex A/S, with 50 % support from the Innovation Fund, would join forces with two Danish universities (DTU and AU) and the Danish Technological Institute to develop nano-based catalysts for NO_X removal. The intention is that the catalysts shall be developed with reduced use of noble metals, which are a limited, non-renewable resource, without compromising the catalytic efficiency.

According to industry, catalytic systems based on the use of nanotechnology also exist for other potential air pollutants, e.g. molybdenum- or silicon/vanadium-based systems for removal of sulphur at refineries or power plants (thereby reducing the potential for generation of sulphur dioxide), and aluminium oxide or TiO_2 with a noble metal catalyst for VOC reduction. Generally, the catalysts used for these purposes consist of a metal oxide carrier material with a metal surface or coating.

The use of photocatalysts for reduction of industrial emissions to air, and in particular use of nano-scale catalytic material such as e.g. anatase nano-TiO_2, is an emerging technology still in its infancy. Apart from the catalyst material in itself, it requires an active (UV) photoreactor system to support the catalytic process.

Kwon et al. (2008) reviewed the literature on current research at that time on applications of micro- and nano-TiO_2 for pollutant removal/degradation in photocatalytic systems for air (and water) purification. Most research on gas-phase catalytic reactions has been carried out in glass continuous-bed reactors; fluidized-bed reactors have been used. In such systems the uniform distribution of the catalyst material inside the reactor is essential for a uniform and efficient performance. Significant removal of air pollutants such as NO_X and organics such as benzene, toluene and xylenes (VOCs) by gas-phase photocatalysis has been demonstrated in a number of research reports. Kwon et al. (2008) concluded that photocatalytic nano-TiO_2 appears to be a promising material for use in environmental engineering applications, being attractive in terms of photoreaction efficiency, ease of usage, and potential for economically efficient contaminant reduction.

5.1.3 Catalytic systems to reduce emissions from automobile engines

Catalytic converter systems installed in diesel vehicle exhaust systems to reduce harmful substances in the emissions to ambient air have been known since the 1970s but have become widespread since the 1990s. They are formed of a catalyst, typically in the form of a precious metal such as platinum, palladium, or rhodium, a catalyst support material, and a wash-coat designed to disperse the catalytic materials over a wide surface area. However, only few examples have been identified of full-scale implementation officially claimed to be nanotechnology by automobile manufacturers.

For instance, the Royal Society of Chemistry (2007) reported as follows on a nano-based system introduced by the Japanese automotive manufacturer Mazda Motor Corp.:
Mazda Motor Corporation has unveiled a new generation of catalytic converters that use 70 to 90 per cent less of the precious metals which help to purify exhaust emissions. The converters rely on nanoparticles of the catalytic metal, each less than five nanometres across, studded onto the surface of tiny ceramic spheres. The Japanese firm claims this is the first time 'a catalyst material has been achieved that features single, nanosized precious metal particles embedded in fixed positions.' Automotive catalysts use platinum, rhodium and palladium to speed up chemical reactions of pollutants such as nitrogen oxide, carbon monoxide and hydrocarbons, to create non-toxic emissions.

Mazda claims to have overcome the typical practical problems such as migration of the nano particles resulting from exhaust heat leading to agglomeration and thereby reduced efficiency, but have not provided further details on how this has been overcome.

Nanowerk, an international Internet portal informing about advancements in nanotechnology, reported recently (2015a) on developments within the area by another Japanese manufacturer of automobiles, Toyota:
Toyota Central R&D Labs. Inc. in Japan are involved in research to develop catalysts that are controlled at the quantum-level. With this level of control, "we can expect an extreme reduction of precious metal usage in automotive exhaust catalysts and/or fuel cells," says Dr. Yoshihide Watanabe, chief researcher at the Toyota Central R&D Labs in Japan.

Another recent example from Nanowerk (2015b) is the news that now, after nearly half a century of R&D on the topic, *"researchers at Case Western Reserve University have shown that an inexpensive metal-free catalyst performs as well as costly metal catalysts at speeding the oxygen reduction reaction in an acidic fuel cell*" and that the catalyst also corrodes less than metal-based materials and has proved more durable.

An American manufacturer of catalytic converters for cars, SDCmaterials (2015), states that "*SDCmaterials has developed a unique materials processing & integration capability that delivers active-catalyst materials with superior reaction properties. Our NanoParticle Synthesis System* *and Integration technologies have enabled us to create a high performance composite Nano-on-Nano™ catalyst specifically designed for automotive applications"*.

To support the development of "greener" cars, i.e. cars based on fuel cells rather than the traditional combustion engines based on fossil fuels, the EU is funding the so-called Nano-Cat Project (2015), with focus on Fuel Cells (FC), considered to be a promising but challenging technology aimed to replace the combustion engine. The Nano-CAT project intends to propose alternatives to the use of pure Pt as catalyst and promote Pt alloys or even Pt-free innovative catalyst structures with good activity and enhanced lifetime because of improved resistance to degradation. The Nano-CAT project will focus on the development of new supports such as functionalized Carbon NanoTubes and conductive carbon-free Metal Oxide as these supports offer better resistance towards degradation than the carbon black commonly used.

Catalysts that are not fixed to and supported by a solid matrix, i.e. fuel additives, are also known in the transport industry; these include primarily nano-scale cerium oxide as well as oxides of other metals such as aluminium, magnesium and cobalt. As an example, Energenics Europe Ldt. (2015) markets the product Envirox™ based on cerium oxide, a common industrial oxidation catalyst widely used in catalytic converters. According to Energenics, cerium oxide would normally be incompatible with diesel fuel but by using nanotechnology, it has been re-engineered into a liquid dispersion which mixes in easily. The company concludes that *"cerium oxide nanoparticles may be added to fuel and improve performance by promoting clean fuel and soot burn within the combustion cycle, and by gradually oxidising carbon deposit build within the engine resulting in more efficient performance and improved fuel economy"*.

5.1.4 Passive photocatalytic air cleaning systems for indoor air quality improvement

Passive indoor photocatalytic systems work in principle like their outdoor parallels, i.e. by coating a wall, floor or other indoor surface directly with the active nano-material (e.g. by spraying) or a film or other product (e.g. a table top material) in which the photocatalytic material is embedded. However, in their review of nanotechnology for the construction industry, Hanus and Harris (2013) mention that there are only few studies on photocatalyst-based indoor air purification under unsupplemented indoor lighting conditions. Some studies exist of trials in real enclosed environments supplemented with UV lamps, resulting in NO_X reductions of between 20 % and 50 %.

Zaleska (2008) has presented a review where various metallic and non-metallic materials and methods for preparation of doped-TiO_2 are presented that, among others, can be used for photocatalytic oxidation of indoor air pollutants and for disinfection even under poor indoor lighting conditions (mainly the visible part of the light spectrum). Among other products, a Danish developer and vendor of various nano-based solutions markets an indoor flooring material with nano-TiO_2 aimed to reduce VOCs and odour in indoor air while utilizing only natural light and normal room illumination as energy sources.

Similar systems aimed primarily at disinfection exist and are described in chapter 7 on hygiene improving technologies. However, they may also concurrently improve general indoor air quality.

5.1.5 Active photocatalytic air cleaning systems for indoor air quality improvement

Active nano-based systems for purification of indoor air (elimination of malodour or removal of organic contaminants, VOCs) rely on photocatalytic oxidation (PCO) and utilise nano-semiconductor catalysts and ultraviolet (UV) light to convert the compounds into water and carbon dioxide. Most frequently, the nano-catalyst used is anatase TiO_2 but because of a number of unsolved issues, the technology is still primarily at the research/development stage. However, a couple of suppliers of nano-based photocatalytic air purification devices have been identified, see e.g. Whirlpool (2015). These are typically small stand-alone consumer products that are simply placed in a room and plugged into a socket for power to run the UV light source and a small fan to pass the air through the UV-reaction unit in the device. Often these devices also comprise a variety of filters for different purposes, which are not necessarily based on nano-technology.

Mo et al. (2009) reviewed the literature on photocatalytic materials and systems for purification of VOCs in indoor air and found that PCO reactors had promising features in relation to lowering the ventilation rates with the aim to reduce energy consumption of HVAC (heating, ventilation and air conditioning). PCO systems can in principle deliver the necessary improved indoor air quality, which is typically the crucial issue in relation to operating HVAC systems at low flow rates. According to Mo et al. (2009), PCO technology may be integrated into new and existing HVAC systems due to its modular design, room temperature operation, negligible pressure drop, low power consumption and low maintenance requirements. The authors also present a number of different configurations of UV reactor systems that are potentially applicable in this context.

However, Mo et al. (2009) also found that there are still problems to be solved, e.g. with regard to potentially harmful intermediates formed by the PCO reactions when VOCs are being oxidised, as well as some practical aspects related to kinetics parameters that need to be solved to ensure stable and efficient operation under varying temperature and humidity conditions.

Sharmin and Ray (2012) presented the use of ultraviolet light-emitting diodes as a new concept in the field of PCO systems for removal of VOCs from indoor air, demonstrating the effectiveness of this technology as compared to traditional UV-light sources. The authors showed that UVLEDs with 360 nm wavelength and a total energy of 72,000 µW (60 LEDs) were able to activate five different types of photocatalysts to remove benzene and xylene from air in a pilot-scale continuous reactor. Removal efficiencies ranged from 7-32 %.

Sung et al. (2011) conducted experiments in a museum and a nursing institution and demonstrated that a PCO system based on a nano-Ag/TiO_2 catalyst and UV-light was able to effectively disinfect air by removing airborne bacteria.

5.1.6 Other systems for air purification/pollution reduction

Nanoparticles can also, due to their high surface area to mass ratio, be used to adsorb various indoor air pollutants, both harmful and malodorous. In addition to sorption onto nano-treated walls, the nanomaterials (e.g. nanosilver) can also be attached to or embedded e.g. in ventilation system filters and retain volatile organics from the air passing through the systems. For example, the British company EcoAir (EcoAir, 2015) is marketing a system for domestic use with an anti-bacterial nanosilver filter.

In a review, Wang et al. (2013) describe the potential of graphene-based nanomaterials for adsorptive remediation of environmental pollutants e.g. in air. Graphene oxide possesses several functional groups and strong acidity, exhibiting high adsorption for basic compounds while graphene shows hydrophobic surface qualities and presents high adsorption to chemicals. Modifications with metal oxides or organics can produce various nanocomposites with enhanced adsorption capacity and separation efficiency. The technology is still at a research/development stage and most studies related to purification of indoor air have focused on removal of ammonia and to some extent on sulfur compounds and VOCs.

5.1.7 Overview of nanotechnologies for air purification/pollution reduction

The table below presents an overview of the nano-technologies identified for reduction of air pollution and/or improvement of indoor or outdoor air quality including nanomaterial involved, functionality, application areas and stage of development.

TABLE 4
OVERVIEW OF THE USE OF NANOTECHNOLOGY FOR AIR POLLUTION REDUCTION/AIR QUALITY IMPROVEMENT

Application/product	Involved "nano" (material, surface etc.)	Why is "nano" applied?	Development stage
Air pollution reduction by nano-treated surfaces (e.g. coated walls, roofs or pavement slabs, treated road surfaces, film materials with nano-TiO_2 embedded etc.)	TiO_2, at least commercially	Photocatalyst for NO_X and VOC removal	Commercially available, but not widespread
Catalytic industrial emission reduction (e.g. deNOx converter systems for power plants or incineration plants	Vanadium (V) (above all) Molybdenum	Catalyst for NO_X removal Removal of sulfur	Widely used for NO_X reduction, especially at coal-fired power plants. Used at e.g. refineries
Catalytic car exhaust emission reduction (catalysts for diesel cars)	Platinum (Pt), palladium (Pd), rhodium (Rh)	Catalyst primarily for NO_X removal	Widely used in diesel-fueled automobiles
Indoor air purification by nano-treated surfaces (treated/coated indoor walls, floors, desk tops)	TiO_2	Catalyst primarily for removal of VOCs and bacteria/viruses	Barely on the market as yet
Indoor air purification by photocatalytic reactors (domestic stand-alone electrical devices)	TiO_2	Catalyst primarily for VOC removal	A few commercial products exist
Indoor air purification by nano-treated filters (filters to be incorporated in centralised ventilation systems)	Silver (Ag)	Anti-bacterial biocide	A few commercial products exist

5.2 Market considerations – today and in the future

Nanowerk (2015) reports that researchers at Case Western Reserve University have shown that an inexpensive metal-free catalyst performs as well as costly metal catalysts at speeding the oxygen reduction reaction and that the catalyst also has proved more durable. These findings are considered major steps toward making low-cost catalysts commercially available, which according to the authors could, in turn, reduce the cost to generate clean energy from PEM fuel cells.

SDCmaterials (2015) states that the automotive industry spends over $10B annually on platinum group metals (PGMs) for catalytic converters. A key objective in catalyst design is to lower the exhaust temperature at which the conversions of pollutants take place — the so called light-off temperature. Higher catalyst activity and stability result in lower light-off temperatures and an improved overall emissions profile. Catalyst design can also have a direct impact on fuel economy.

The EU-funded Nano-Cat Project (2015) focuses on development of the Proton Exchange Membrane Fuel Cell (PEMFC), which has been widely and extensively researched and developed for many years; however, a number of issues such as high cost, low reliability and low durability must still be overcome.

Hanus and Harris (2013) mention in their review that some TiO_2 nanoparticle-based products for indoor air purification are commercially available. The authors consider that the market is currently in its infancy, but that a mature market is expected to emerge within the next few years.

Kwon et al. (2008) conclude that photocatalytic nano-TiO_2 appears to be a promising material for use in environmental engineering applications, being attractive in terms of photoreaction efficiency, ease of usage, and potential for economically efficient contaminant reduction.

Based on the industry interviews, it is the authors' impression that nano-based air pollution reduction technologies are widely applied internationally for removal of gaseous pollutants, primarily NO_X but also CO and VOCs, from industrial emissions within a range of sectors. Danish companies are also operating on the Danish and international markets within these areas.

It is assessed that the potential for new companies and SMEs would be rather in relation to tailor-making air cleaning solutions applying current (nano)technology than e.g. developing new types of catalysts, which require a larger set-up.

Manufacturers within the automotive industry apply nanotechnology to produce efficient catalyst systems for diesel engines to reduce emissions, particularly of NO_X. These systems are considered to be twice as efficient as non-catalyst based cleaning systems, e.g. filters. Catalyst-based removal of sulphur from fossil fuels is an indirect way of reducing air pollution, which typically involves use of nanotechnology.

Other systems, such as passive or active systems based on the photocatalytic activity of TiO_2 (and some other metal oxides, e.g. ZnO), appear to be in their infancy from a commercial point of view although some products (e.g. nano-treated concrete slabs or indoor wall coatings or flooring products) are commercially available in countries including Denmark, even at the retail level (e.g. Johannes Fog). It has not been possible to obtain enough information to assess the future market potential, but today such products are considered to be niche products.

5.3 Health and environmental pros and cons during use

Currently, nanotechnology for reduction of air pollution or improvement of indoor air quality appears mainly to be exploiting the catalytic properties of certain nanomaterials, mainly metallic materials based on vanadium, molybdenum and nickel etc., to reduce pollutants in industrial emissions and diesel car exhaust, and photocatalytic TiO_2 to clean indoor air. Many catalyst systems also utilize scarce noble metals to increase catalytic efficiency.

While the use of catalysts based on nanotechnology for reduction of industrial emissions seems to work and is well established, a report by CEC (2008) concludes that reduction of ambient air pollution by use of passive photocatalysis based on nanomaterials (primarily TiO_2) is technically feasible; however, accomplishing it in a cost-effective manner would be challenging. Some claim that air pollution can be halved with this technique, while others question this assertion (CEC, 2008). Some products based on "passive action" of photocatalytic TiO_2, e.g. surface coatings, are commercially available today and appear to be able to reduce e.g. NO_X to some extent.

However, the efficiency of such systems in practice, i.e. over an extended period of time, is generally not well documented and little information has been identified addressing critical issues such as possible life-time reduction due to tear-and-wear and lower efficiency under unfavourable weather conditions, saturation or shielding of active sites by dirt or specific substances etc. Some studies report roadway contaminants such as dirt, de-icing salt and motor oil to have a strong negative impact on the efficiency of the NO_X removal efficiency of TiO_2 treated concrete pavements. In addition, parameters such as increasing air flow rate and relative humidity have been found to have a negative impact on the performance of treated pavements.

Furthermore, some uncertainty exists as to whether the photocatalysts would not only degrade NO_X but also result in generation of various potentially harmful by-products during degradation of VOCs.

Catalytic converter systems in cars emit some fraction of the catalyst metals (e.g. Pt and Pd) to the air environment with the exhaust gases, possibly as nanoparticles, which then can be inhaled by humans if emitted in streets/urban areas. They may also accumulate in the environment, in particular along roadsides or in sediments if released to the aquatic environment with road runoff. Fuel additives in the nano-form, such as e.g. cerium oxide, would be released to air in a manner similar to catalyst materials and would also lead to some degree of exposure to humans and the environment with unknown risks and impacts.

6. Products/technologies reducing energy consumption

This chapter addresses applications of nanoproducts and nanotechnologies, which can be used in the energy value chain in order to reduce energy consumption or provide other environmental benefits related to the consumption of energy.

6.1 Overview of nanoproducts and technologies

Nanotechnology has broad-reaching applications within the area of production, storage and use of energy, where the application of nanotechnology may lead to energy reduction/optimisation as a result of shifts to new technologies, or refinement of existing technologies through improved properties, or reduced materials use. Nanotechnology may be applied to the whole value chain of the energy sector, i.e. energy sources, energy conversion, energy distribution, energy storage and energy use (see Figure 4). In the following, identified nano-based products and technologies are divided into groups according to their place within the energy sector, as laid out in Figure 4.

As can be seen, applications for energy use have a wide scope. This chapter should therefore not be seen as a thorough review of all possible applications.

The focus of this chapter is on those technologies and products most frequently referred to in the reviewed literature, believed to have the greatest potential as regards providing environmental benefits, as well as those closest in development to commercialisation. Furthermore, focus is on applications where the nanomaterials actively contribute to energy saving/optimisation mechanisms.

Thus, the focus is not on applications where nano-enabled technologies more indirectly reduce energy consumption due to use of nanomaterial-based, stronger and lightweight material, or materials with smoother surfaces. Such applications are e.g. the use of carbon nanotubes (CNT) as a material in airplanes and vehicles, which makes them lighter and thus reduces fuel consumption. Other examples are CNT used as coating on rotor blades of wind turbines, making these lighter and increasing the energy yield, and the incorporation of carbon black into automotive tires in order to reinforce the material and reduce rolling resistance, which may lead to fuel savings of 10% (Greßler and Nentwich, 2012).

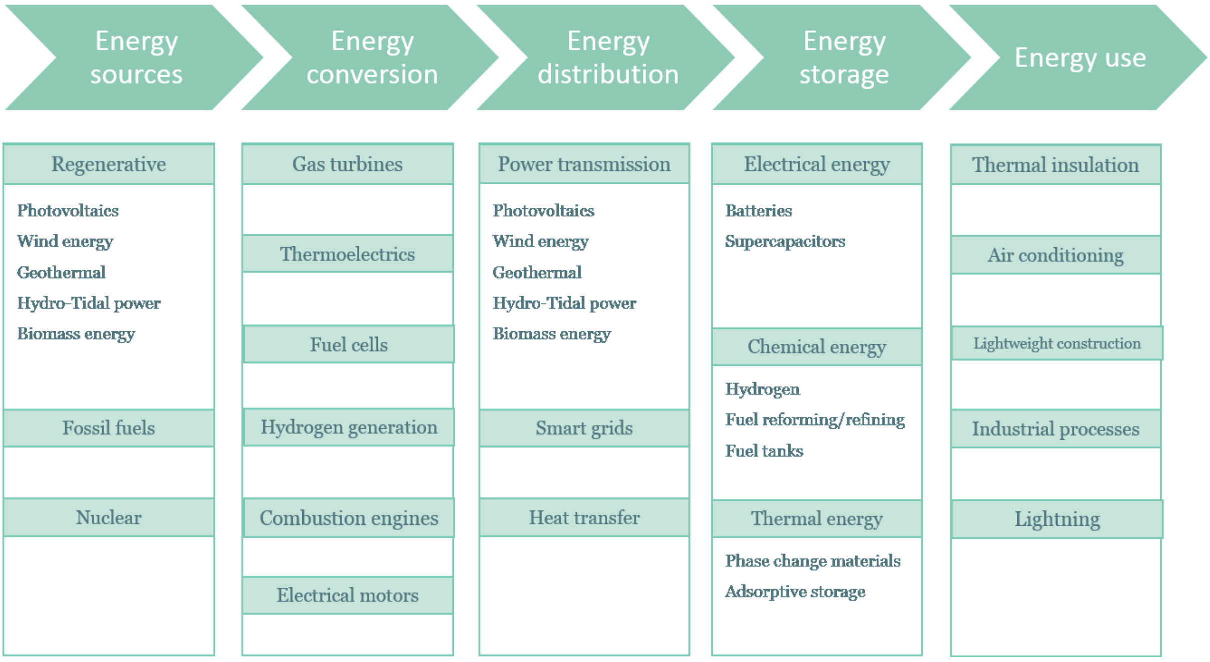

FIGURE 4
EXAMPLE OF AREAS FOR POTENTIAL APPLICATIONS OF NANOTECHNOLOGY ALONG THE ENERGY VALUE CHAIN (INSPIRED BY LUTHER, 2008)

Based on the above focus, it was found relevant to focus on the following technology areas:
Energy sources:
- Photovoltaic devices:
  - Solar cells and solar collectors

Energy change/conversion
- Hydrogen fuel cells (including hydrogen storage)
- Nanotechnology based catalysts

Energy storage
- Batteries and supercapacitors

Energy use
- Insulation of buildings:
  - Aerogels
  - Window coatings
- LED and OLED
- Self-cleaning coatings
- Fuel additives.

6.1.1 Photovoltaic devices

6.1.1.1 Solar cells

Photovoltaic (PV) devices, such as solar cells, present a renewable method of supplying energy. The photovoltaic devices already represent a multi-billion dollar industry, which continues to grow. However, the relatively high costs of photovoltaics currently inhibit their wide scale commercialization, and solar energy is only likely to become truly mainstream when the associated costs are significantly decreased and comparable to that of other energy sources. Nanotechnology is envisaged to play a vital role in progressing towards these aims (Hanus and Harris, 2013; DEFRA, 2007). Besides reducing the cost, nanotechnology may help to improve the efficiency of the photovoltaic devices (Hussein, 2013; Lamont, 2013).

Advances within the field of solar cells have led to three distinct generations of solar cells. First generation solar cells are wafer-based cells mainly made of bulk (mono- or polycrystalline) silicon, which are costly but relatively efficient (Wong et al., 2014; Hanus and Harris, 2013). The first generation solar cells currently account for the largest market share (Wong et al., 2014; Hanus and Harris, 2013; Lamont, 2013). Second generation devices are amorphous silicon thin-film cells, which attempt to reduce costs by using less material, without compromising efficiency. In theory second generation solar cells should have the same efficiency as the first generation devices, but in practise the efficiency is much lower (around 14% compared to 27%, which is the maximum efficiency of first generation devices) (Hanus and Harris, 2013; Abdin et al., 2013). Third generation photovoltaic devices, in theory, combine the best of both the first and second-generation technologies, i.e. high efficiency and low cost, but they are still at the research stage.

Nanotechnology is used within the field of photovoltaics in order to increase the performance of the existing technologies (Wong et al., 2013).

First generation silicon solar cells dominate the market, but they are still not cost efficient for large applications, although Chinese suppliers have marketed relatively low cost alternatives in recent years. Currently solar cells are not able to absorb all incoming light; 20% of the incoming solar radiation is not absorbed as the conventional solar cells are not able to utilise the long-wavelength part of the sunlight. Nanotechnology may be used in order to increase the efficiency of conventional solar cells. Up-conversion of two low-energy photons into one high-energy photon able to generate current may be a solution for increasing efficiencies. Gold and silver nanoparticles may be used to enhance this up-conversion process (Nylandsted Larsen pers. comm. (2015)). This research in up-conversion might also be used in second and third generation solar cells described in the following.

Second generation solar cells, i.e. thin-film solar cells, are made of material combinations of copper/indium/gallium/sulphur/selenium (CIGS- cells) as well as III-V semiconductors (e.g. gallium arsenide) apart from silicon. These cells currently allow for efficiencies of up to 20% (Luther, 2008). Nanotechnology may help to improve the efficiency of these cells by reducing reflection and thereby increasing the coupling of light into the solar cell, which can be achieved by coating the surface of the solar cell with metallic nanoparticles such as gold, silver and platinum, and to a certain degree also copper and aluminium (Nylandsted Larsen pers. comm. (2015)). Note that this effect is not needed for the first generation solar cells, which are thicker and therefore can be manufactured with a structurized surface, decreasing reflection.

Similarly, Lambauer et al. (2012) reported on the use of antireflective coatings of porous SiO_2 nanoparticles (20-50nm) which are applied at a thickness of 150 nm on the glass. By doing so, surface reflection may be reduced and thereby a larger amount of the solar radiation may be energetically used. Indium-tin-oxide (ITO) nanowhiskers on the surface of solar cells also provides an antireflective layer with a reflectivity of 5% (Wong et al., 2013). By applying antireflective coatings consisting of SiO_2 nanoparticles, the efficiency of photovoltaic panels can be increased by 3.5-4 percentage points (Hofmann 2006, as reviewed by Lambauer et al., 2012). Application on the ITO nanowhiskers improved the optical transmission in the 700-1000 nm range and improved the conversion efficiencies of solar cells from 13.93 to 14.37% (as reviewed by Wong et al., 2013).

The use of nanoparticles coatings on thin-film solar cells is still in the research phase.

Another type of solar cell in which nanotechnology also may serve to advance technology is the dye-sensitized solar cell. As stated by Wong et al. (2013): "*Dye-sensitized Solar cells (DSSC) work by sensitizing materials to a different part of the electromagnetic spectrum so that more of the energy being received by the sun may be used by the cell. Nanocrystalline dye-sensitized solar cells are a completely new type of cell. The new development with these cells is that the absorption material is completely separate from the charge carrier transport. This method seems to only be* *effective in transferring the electrons to the charge carrier transport material, when the two are in contact. An attempt to minimize this problem is to have a nonporous micro layer. This method is based on an increased contact between the dye and the charge carrier transport material. Current research is using this design to make the absorption range of titania closer to the visible region of the electromagnetic spectrum increasing the percentage of the energy from the sun. Since the advent of the dye-sensitized solar cell architecture, cells have now reached efficiencies of up to 11%*" (Wong et al., 2013).

A general problem with solar cells is that some of the solar energy is lost, as the solar cells cannot convert the excess energy in high-energy photons. This energy is lost as heat, which is furthermore a disadvantage as efficiency is also affected by the temperature of the solar cells. Research involving semiconductor nanomaterials (quantum dots) to address this issue is on-going, but evaluated as being relatively far from commercialisation (Nylandsted Larsen pers. comm. (2015)).

6.1.1.2 Solar collectors

Solar collectors are a particular sort of heat exchangers, where absorbed incident solar radiation is converted to heat, which is transferred to a fluid (the working fluid). The working fluid conveys this generated heat for different applications (Kasaeian et al., 2015). Solar heat can, for example, be utilised for tap water heating, space heating in buildings or on an industrial scale for power generation in solar power plants (Lambauer et al., 2012). In order to advance the efficiency and output temperature of the solar collectors, several methods have been proposed, including replacing the absorbing medium (water) with high thermal conductivity fluids, so called nanofluids (Abdin et al., 2013). Nanofluid is defined as a fluid containing nano-sized particles, and these fluids enhance the rate of heat transfer compared to base fluids (Kasaeian et al., 2015). In a review of applications of nanotechnology for solar energy harvesting, Abdin et al. (2013) reports on several studies that have shown that the addition of very small quantities (0.001 – 0.5%) of nanoparticles to water (the absorbing medium) results in great improvements of the efficiency of different solar thermal systems (e.g. nanofluid-based direct absorption solar collectors or concentrating parabolic solar collectors (NCPSC). Several different nanomaterials have been investigated, such as aluminium nanoparticles, CNTs, graphite, copper and silver (Abdin et al., 2013; Kasaeian et al., 2015).

Abdin et al. (2013) also mentions several studies which have investigated the performance of nanofluid-based solar collector systems and compared them with conventional systems. One study stated that by substituting water with a graphite/therminol VP-1 nanofluid as the working medium, a 10% improvement in efficiency might be possible. Another study found that injection of 0.05 vol% aluminium nanoparticles suspended in therminol VP1 as base fluid in a NCPSC resulted in 5-10% improvements in efficiencies compared to a conventional parabolic solar collector. Yousefi et al. observed a 28.3% improvement in efficiency by using 0.2% weight fraction nanofluid (Al_2O_3/water) as compared to water (cited in Abdin et al., 2013).

6.1.2 Hydrogen fuel cells

Fuel cells are devices which convert chemical energy with a high efficiency directly to electrical current. Hydrogen is one of the most widely investigated fuels for fuel cells, but natural gas, methanol, benzene or biogas may also be used (Luther, 2008). This section is, however, delimited to hydrogen fuel cells. The possible applications of fuel cells are broad-ranging; stationary fuel cells can, for example, be used for backup power or power for remote locations, and fuel cells have the potential to power almost any portable application typically using batteries. One area in which fuel cells are expected to play an important role is the transportation sector, including personal vehicles, buses, trucks etc. (US Department of Energy, 2006). According to a report by the United Kingdom Department for Environment Food & Rural Affairs (DEFRA), hydrogen powered vehicles could possibly eliminate all noxious emissions from transport, which would lead to an improvement in public health (DEFRA, 2007).

Hydrogen fuel cells are devices in which hydrogen and oxygen are used as fuel to generate electricity and water. This is an area of renewable energy sources, in which nanotechnology is likely to play a large role in its development, as nanotechnology may help to overcome the great technological challenges that are currently prohibiting hydrogen fuel cells from wide scale implementation. The different types of hydrogen fuel cells are classified depending on the electrolyte as Polymer Electrolyte Membrane Fuel Cell (PEMFC), Phosphoric Acid Fuel Cell (PAFC), Alkaline Fuel Cell (AFC), Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC) (Serrano et al., 2009).

According to Luther (2008), the innovation potentials for fuel cells resulting from nanotechnologies would mainly be due to higher electricity yield from the conversion of chemical energy, especially through nanostructured electrodes, catalysts and membranes. However, others also indicate hydrogen storage as an area where nanotechnology may play a leading role in overcoming the current problems and barriers (DEFRA, 2007; Filipponi and Sutherland, 2007). Nanotechnology is thus likely to be a key component in generation, storage and use of hydrogen as a fuel source (DEFRA, 2007).

6.1.2.1 Hydrogen generation

Hydrogen is not freely available; it must be extracted from a source, such as a hydrocarbon (e.g. methane) before it can be utilized. The current industrial method for hydrogen generation involves partial oxidation of methane (stream reformation of methane), and upon this process methane is converted into CO_2 or water. However, using this method, eleven tonnes of CO_2 is created for every tonne of hydrogen (DEFRA, 2007). Generation of hydrogen using a renewable, non-exhaustive energy source is therefore preferred.

Use of nanotechnology include:

- **Hydrogen generation via electrolysis:** hydrogen may be generated via electrolysis, where electrical charges are applied to two plates containing a catalyst, and water is thereby converted to hydrogen and oxygen. The problem with this method is that it requires a significant amount of energy (Serrano et al., 2009). If nanoparticles and nanostructures are used on the surface of these plates, the overall efficiency and speed of the process is increased (DEFRA, 2007), which may lead to lower energy requirements.
- **Hydrogen generation from photolysis:** as certain materials have been shown to split water into hydrogen and oxygen using sunlight as an energy source, solar cells that uses nanostructured materials in the splitting of water have been investigated in the UK (DEFRA, 2007). TiO_2 nanotubes arrays, nanostructured TiO_2 and Ag/TiO_2 nanocomposite films have shown promising properties for use in the generation of hydrogen (Filipponi and Sutherland, 2007; Hussein et al., 2015).

6.1.2.2 Hydrogen storage

Hydrogen storage is mentioned as one of the biggest barriers to wide scale use of hydrogen fuel cells (DEFRA, 2007; Filipponi and Sutherland, 2007). Due to the much lower energy to volume ratio of gaseous hydrogen compared to conventional gasoline (about ten times lower), storage of hydrogen for example for use in vehicles become a big problem. The ideal hydrogen storage system should have a hydrogen gravimetric capacity >6 mass % and low thermodynamic stability, leading to hydrogen desorption near room temperature and under moderate pressures, fast kinetics for both hydrogen release and uptake, and a long cycle life (>1000 cycles). At present, there is no material that fulfils all of these criteria (Christian and Aguey-Zinsou, 2012). Examples of uses of nanotechnology include:

- **Light metal hydrides:** hydrogen is 'loaded' through a chemical reaction with a solid support forming a hydride product, where it can be extracted when needed, returning the solid material ready for a new storage cycle. The main challenge is loading capacity and regeneration kinetics, but nanotechnology can contribute to these fields by developing new hydride structures and materials, which allow high hydrogen loading capacity and acceptable regeneration kinetics for re-extraction of hydrogen from the support (Filipponi and Sutherland, 2007). In order to maximise hydrogen storage, light metal hydrides should most likely be in the form of nanopowders or nanoporous matrices, in order to increase the surface area exposed to the hydrogen gas. Nanocrystalline Mg powder or other nanohydrides, as well as zeolites (three-dimensional porous material), have been suggested as possible nanomaterials for use in hydrogen storage processes (DEFRA, 2007). **Core-shell nanoparticles** such as sodium borohydride ($NaBH_4$) have also been shown as a promising hydrogen storage material because of its high storage capacity (10.8%) (Christian and Aguey-Zinsou, 2012).
- **Carbon storage**: carbon surfaces can store adsorbed hydrogen on e.g. carbon nanotubes; both multi-wall (MWCNT) and single wall (SWCNT) have been suggested as suitable candidates for hydrogen storage (Serrano et al., 2009). However, it is doubtful whether the hydrogen storage capacity of CNT can meet the desired >6% gravimetric capacity, as study results have indicated that the hydrogen storage capacity of CNT is less than 1.7% (Brinker and Ginger, 2011).
- **Carbon-metal composite structures** may be used as matrices for complex metal hydrides for hydrogen storage. Carbon aerogel matrix may, for example, accommodate metal hydrides such that the storage kinetics are strongly enhanced (Lambauer et al.,2012).
- The EUR 2.4 million FP7 ENERGY project NANOHy has investigated the use of novel nanocomposite materials for hydrogen storage. The project was finalized in 2011 and found that "nanocomposite materials based on complex hydride particles held in place by nanocarbon templates or polymer layers could be a viable option for hydrogen storage". Among the nanocomposite materials investigated was $NaAlH_4$/AC (AC=activated carbon) (European Commission, 2013).

6.1.2.3 Hydrogen fuel cell operation

The operation of a hydrogen fuel cell occurs as follows (DEFRA, 2007):

1. A catalyst splits the hydrogen molecule into atoms and then further into two protons and two electrons.
2. A membrane selectively allows the proton to travel through it whilst preventing the electron from doing so, so that the electron travels through a copper wire to generate an electrical current.
3. A second catalyst on the other side of the membrane combines the proton with the electron and oxygen to form water.

Current state of the art hydrogen fuel cells use platinum as a catalyst and a nanoporous polymer Proton Exchange Membrane (PEM) as the membrane. The catalyst activity can be maximised by using nanosized particles at the catalyst, since these are more reactive due to their larger surface area. According to DEFRA (2007), there are well-documented concerns that the quantity and cost of platinum required to produce large numbers of automotive fuel cells will prevent their large-scale adoption. By using a nanosized catalyst, the quantities of Pt, which also is a rare metal, can be decreased, leading to reductions in the cost of the fuel cell as well. For instance, CNT have been found suitable as support for the dispersion of nano-sized Pt, which reduces the weight of Pt needed to produce the same surface area of active Pt catalyst (Filipponi and Sutherland, 2007).

Nano-based alternatives to platinum as hydrogen fuel cell catalysts are furthermore being investigated, for example a graphene sheet covered by cobalt and cobalt-oxide nanoparticles (Understanding nano, n.d. c).

6.1.3 Nanotechnology-based catalysts

This section describes examples of uses of nanotechnology in catalytic devices, and therefore not the use of the nanomaterial itself as a catalyst[3]. Catalysts are used in many different systems, and the chemical process happens more rapidly and uses significantly less energy when it is catalytically enhanced. With a catalytic converter it is thus possible to produce more without using more energy, saving resources. Nanotechnology is used in catalytic devices in order to provide a nanostructure inside the catalyst, effectively increasing the ratio between the surface area and volume, and thereby increasing the amount of so-called reaction centres (Lambauer et al., 2012).

According to industry, examples of uses of catalysts which may result in reduced energy consumption as a consequence of more optimised/effective industrial processes are:

- **Effective exploitation of raw materials,** e.g. in oil refineries. Catalysts are used in the refinement of oil for use in diesel and gasoline in order to remove environmentally hazardous compounds such as sulphur from the oil and to optimise fractionation leading to more clean fractions and less loss as flare gas. Thus, more effective exploitation of the oil raw material is achieved. It is roughly assessed that together with other optimisation processes, the use of catalysts might close to double efficiency. Molybdenum trioxide is a well known catalytic material used for the hydrodesulphurization process.

- **Increase the efficiencies in the production of chemicals**, e.g. in the production of ammonia (for use in fertilizers) or styrene (one of the most important basic chemicals in the chemical industry (Lambauer et al., 2012)). The use of catalysts in the synthesis of ammonia is believed to reduce the energy requirements by approx. 50% as compared to other manufacturing processes, which is significant considering that ammonia production accounts for about 1% of world energy consumption (according to an interview with the industry). Magnesium, aluminium, nickel and iron oxide are known catalytic materials used in the production of ammonia.

Common to the two above-mentioned processes is that the use of catalysts decreases the operating temperature required, which also leads to a reduction in energy consumption.

As also described in section 5.1.3 and as mentioned in section 6.1.8 the effectiveness of catalytic converters in vehicles and automobiles may be increased by applying catalytically active nano-sized metals. See those sections for more information on this issue.

6.1.4 Batteries and supercapacitors

6.1.4.1 Batteries

Most of the active research in this field is currently focused on rechargeable lithium batteries. Compared to aqueous batteries, Li-ion chemistry can lead to an increase of 100-150% in energy

[3] A catalyst is defined as a substance that increases the rate of a chemical reaction without being consumed or chemically altered itself. Due to their large specific surface area, and thus increased reactivity, nanomaterials may be regarded as catalysts in many applications, some of which are covered elsewhere in present report; see chapter **Fejl! Henvisningskilde ikke fundet.** for the application in water purification and chapter **Fejl! Henvisningskilde ikke fundet.** for use in air purification.

storage capability per unit weight and volume. Rechargeable Li-batteries are, for example, used in transportable devices, such as mobile phones, laptops or digital cameras, as well as in cordless power tools and hybrid electric cars. There are, however, some challenges associated with rechargeable lithium batteries which affect the performance of conventional Li-batteries. These challenges are related to low energy efficiency, insufficient power density, a large volume change on reaction, safety and costs. These shortcomings may be – or are already being – reduced with the use of nanotechnology. Use of nanomaterials for both the electrodes and the non-aqueous electrolyte are being investigated (Serrano et al., 2009).

According to the website www.understandingnano.com, a webpage that gathers and disseminates information regarding the use of nanotechnology from manufacturers' webpages, recent research articles and stories from the news, the use of nanotechnology in the manufacture of batteries may offer benefits such as increasing the available power from the battery and decreasing the time required to recharge it (Understandingnano, n.d. a). These benefits are achieved by coating the surface of an electrode with nanoparticles, which increases the surface area of the electrode, thereby increasing the rate of electron transport and the contact between the electrode and the electrolyte. Promising high capacity materials and conductive additives for anode applications include CNTs, several graphene-based nanostructures and possibly silicon nanowires. There has also been emerging interest in metal oxide nanomaterials such as SnO_2, TiO_2 and especially $LiFePO_4$ for anode and cathode applications (as reviewed by Iavicoli et al., 2014). Studies have also found that the conductivity of the electrolyte may be increased up to six times by introducing aluminium oxide, silicon or zirconium nanoparticles to the non-aqueous electrolyte (Serrano et al., 2009).

Nano-based batteries have been commercialized for a couple of years now, as Serrano et al. (2009) mentioned Sony's Nexelion batteries in their review, with a tin-based anode consisting of multiple elements (e.g. tin, cobalt, carbon) mixed on nanometer-level, which was the first time a nanoalloy replaced the traditional graphite electrode (Serrano et al., 2009; Sony, 2005). The webpage for Understandingnano also has a directory of companies using nanotechnology to improve batteries (most likely based on information from the companies' websites), comprising more than 15 companies (Understandingnano, n.d. b).

6.1.4.2 Supercapacitors

Electrochemical capacitors, also known as supercapacitors or ultracapacitors, are used to store electrical energy where higher power densities are needed than batteries can provide, but compared to batteries they do not store as high an energy density. While batteries store the energy chemically, supercapacitors store it physically, by separating the positive and negative charge (Serrano et al., 2009). The main determining factor for power density and maximum power output is the surface area of each of the electrodes in the capacitor. Therefore, in order to increase capacity of the supercapacitors compared to conventional capacitors, the electrode has to provide large surfaces, achievable using nanostructured materials (Serrano et al., 2009; Lambauer et al., 2012). Supercapacitors are being used in the same types of applications as batteries, e.g. mobile phones. They can be used in combination with batteries, providing peak power in devices, such as laptops, and reducing power demands on the battery, thereby extending the lifetime of the battery. They can be used in a similar manner in electrical vehicles, providing power for acceleration and allowing a primary power source, such as a fuel cell, to supply the main/average power. When used in electrical vehicles, supercapacitors also allow for energy to be recuperated during braking, improving the efficiency of the vehicle (Jayalekshmi and Puthirath, 2014).

Depending on the type of supercapacitor (redox-based supercapacitors (pseudocapacitors), electrochemical double layer capacitors (EDLCs) and hybrid capacitors), different nanostructured materials may be applied. Redox-based supercapacitors may utilize mixed metal-oxide nanomaterials as electrode materials, such as RuO_2, MnO_2, Fe_3O_4 or V_2O_5 (Serrano et al., 2009; Iavicoli et al., 2014). The performance of EDCLs may be improved by using carbon-based nanostructures such as CNTs or carbon nanofibers as electrode material (Serrano et al., 2009). Carbon aerogels, which have a large inner surface as well as controllable pore distribution and pore diameters may also been used as electrode materials (Luther, 2008; Lambauer et al., 2012).

6.1.5 LED and OLED lighting

Light-emitting diodes (LEDs) are promoted as a solution to energy-efficient lighting. These are considered to exploit nanotechnology, "*primarily by virtue of the fact that they comprise very precisely deposited layers of nanoscale semiconductors and the light-emitting process itself takes place within a nanoscale volume of material. Since LED chips generate light internally and have smooth layers, much light cannot escape due to total internal reflection unless special surface structures or chip shapes are used. Nanostructured surfaces can be used to enhance light output, including coatings based on plasmonic nanoparticles*" (Cortie et al., 2014). Further optimization of LEDs via utilization of quantum dots may improve efficiency and light yield (Luther, 2008).

Organic light-emitting diodes (OLEDs) are another alternative to light bulbs, which may provide a more energy-efficient lightening solution. An OLED is a thin, flat luminous component with a thickness of usually less than 1 micrometre. It consists of at least one light-emitting layer (emitter layer) made of organic semiconductor material, is generally built with several layers, each with a thickness of up to 100 nanometres, which are positioned between two electrodes. It is therefore not nanomaterials, within the meaning of the EU commissions' definitions that are being applied in OLEDs, but rather nanostructured thin layers of different materials (Umweltsbundesamt, 2013).

According to Chen and Kwon (2014): "*Nanocrystallized organic thin films have emerged as promising light extractors for OLEDs due to their advantages of easy preparation, low cost, scalability, and compatibility. Reported materials, including TPE, BTPE, BCP, bathophenanthroline (Bphen), NET16, and NLE- 17, can all form nanostructures easily due to self-crystallization of organic molecules… With further research efforts, the nanocrystallized organic thin films are expected to serve well as effective light extractors and they may find a wider variety of applications in various optoelectronics devices*".

According to Luther (2008), the further development of OLED will also depend on nanotechnological innovations, e.g. regarding the optimization of the field carrier materials, succession and thickness of layers, application of dopants and the purity of the materials used.

6.1.6 Insulation of buildings

Thermal insulation is a way of reducing energy consumption for example in buildings, as the insulation reduces the heat transfer into and out of the building. Thus, the insulation will prevent the heat from escaping the building and thereby reduce the consumption of energy used for heating, but also prevent hot outside air from entering the buildings, thereby reducing the use of air conditioning in the summer months. In Denmark, about 40 % of the total energy consumption is used for buildings, so proper thermal insulation may play a big role in reducing the energy consumption for heating of buildings. In the following sections, three different examples of nano-based products/technologies which can be used for insulation purposes are given.

6.1.6.1 Silica aerogels

As up to 75% of residential dwellings needed by 2050 already have been built (Revertz, 2008, as cited in Hanus and Harris, 2013), retrofit insulation has been identified as an efficient solution for reducing energy consumption for heating/cooling, and thus also reducing the CO_2 emissions from buildings. Increasing the thickness of traditional insulation may, however, be impractical and the development of new generations of efficient, thin and lightweight insulation materials is therefore desirable (Hanus and Harris, 2013). Sol-gel-derived porous materials, or aerogels, are types of material with high porosity in the nanometre range which may be used in different kinds of applications, depending on their composition and properties. One example is silica aerogels, which consist of a cross-linked internal structure of SiO_2 particle chains with large number of air-filled pores (typically < 100nm), depending of the purity and fabrication method (Hanus and Harris, 2013).

Silica aerogels demonstrate excellent potential as thermal insulators, as they minimize conduction, convection and radiation (the three methods of heat transfer). Conductive heat transfer is reduced due to the ultra-low density and weakly connected fractal silica framework. Convective diffusion is suppressed because of the pore size of the aerogel, which is less than the mean free path of the gas molecules at ambient temperature. The mean free path for the gas molecule at ambient temperature and pressure is about 70 nm (Lambauer et al., 2012). Radiation is minimized as the aerogel strongly absorbs infrared radiation (Brinker and Ginger, 2011). Silica aerogels are furthermore non-flammable and translucent (or even transparent), which add to their qualities as thermal insulators.

Combining the abovementioned properties of silica aerogel results in extremely low thermal conductivity: from 0.03 W/m·K down to 0.004 W/m·K upon moderate evacuation. This corresponds to thermal R-values[4] of 14–105 for 8.9 cm thickness, greater than for typical wall insulation, where the R-value is 13 for 8.9 cm thickness (Brinker and Ginger, 2011).

Applications of silica aerogel for building insulation include:

- Insulating windows. Nanogel windows are highly energy efficient windows with silica aerogel in the interspace. According to literature reviewed by Hanus and Harris (2013), a 55% reduction in heat loss (and 25% reduction in light transmittance) occurred when monolithic aerogel was placed in the interspace compared to a conventional double glazed window with a low-emittance layer. Granular aerogel resulted in a 25% reduction in heat loss and 66% reduction in light transmission, relative to the same conventional window.
- Other daylighting systems e.g. polycarbonate systems, structural panels for continuous facades with translucent granular aerogel (Buratti and Moretti, 2013).

Aside from use as building insulation, silica aerogel may also be used as insulation material for oil and gas pipelines (Buratti and Moretti, 2013).

According to Buratti and Moretti (2013) there are several manufacturers of nanogel window products, mainly from the USA, Germany, UK, Canada and China, and many products are already on the market.

6.1.6.2 Window glass coatings

Advanced glazing material, with thin film coatings and selective surfaces, has the ability to modulate the properties of window glass, which may influence the climate in the buildings in which they are used. The glazing may be used for (cited from Mohelníková, 2011):

- limiting heat losses and maximizing solar gains and natural lighting in buildings to reduce energy consumption for heating and artificial lighting;
- reducing glare (causing difficulty to see due to bright light) and lowering the energy demands for cooling and air conditioning, and
- reducing the amount of cleaning water and solvents due to reduction in maintenance requirements in glazed windows.

[4] The R-value is a measure of the materials thermal resistance, which is used in the building and construction industry (Den Store Danske; http://www.denstoredanske.dk/It,_teknik_og_naturvidenskab/Teknik/Bygningsisolering/varmeisolering)

Nanotechnology have several applications for window glass coatings:

- Thermotropic glazing for windows. The glazings change their translucence with changes in temperature, from clear states to light-scattering, non-transparent states. The thermotropic devices contain a special gel embedded between two glass panes. The gels consists of thermotropic material of two components with different refractive indices. At low temperatures the gels are homogenous and the glazing is transparent. When the temperature rises above the limit value (20-50 °C), the components phase-separate and form very small nanoparticles. The nanoparticles cause scattering of solar radiation and the glazing turns white-coloured and non-transparent (Mohelníková, 2011). Thus, in this case the use of nanotechnology is not due to application of a nanomaterial, but rather to the scattering effect of nanoparticles created from the phase separation of the gels.
- Thermochromic glazings for windows. The glass alters its optical properties with response to temperature changes. Thermochromic laminates with VO_2 nanoparticles are used, for example (Mohelníková, 2011).
- Photoelectochromic glazings with nanoporous TiO_2. Photoelectrochromic glazings combine the principles of photochromic and electrochromic technologies. In photochromic glazings, the colour of the glazing changes due to absorption of light, and in electrochromic glazings, the optical properties are altered under the application of voltage. A thin nanoporous TiO_2 film covered with a dye may be used in these glazings. Under illumination the dye is excited and donates electrons to TiO_2, which conduct them to a WO_3 layer in the glazing. This process reduces the tungsten and changes its colour from transparent to blue (Mohelníková (2011). The change in colour of the glazing on hot days with high illumination results in energy savings as less energy is needed for air conditioning and other cooling of the building.

According to DEFRA, ultra-thin films on windows to reduce heat loss already exist on the market and there are claims that nano-enabled windows are up to twice as efficient as the level required by current building standards (DEFRA, 2007).

6.1.7 Self-cleaning coatings

The photocatalytic properties of nanomaterials, such as TiO_2, resulting in the decomposition of organic materials are utilized in many different applications and products and for many different purposes. In this section, the use of nanotechnology in self-cleaning coatings is described from an energy saving point of view, i.e. how the use of self-cleaning coatings may result in reduced energy consumptions in different ways. TiO_2 is by far the most commonly used nanomaterial for self-cleaning coatings for building exteriors and glass. Other nanomaterials may provide self-cleaning or anti-bacterial surfaces as well; however, these are mostly utilized for purposes other than those covered in this section. For more information on the photocatalytic/anti-bacterial effects of nanomaterials such as TiO_2, please refer to chapter 3 (water treatment), 5 (air purification) and 6 (hygiene-improving applications).

Coatings can create self-cleaning or easy-to-clean surfaces by providing (cited from (Mohelníková, 2011):

- A photocatalytic function (decomposition of organic materials on the glass surface),
- A hydrophilic function (strongly wettable surface, which allows water sheeting, which cleans the surface), and
- A hydrophobic function (weakly wettable surface, which makes attachment of dust and dirt more difficult), sometimes referred to as the lotus effect.

For instance, a porous TiO_2 thin film coating can provide both the photocatalytic and hydrophilic functions, which can be used e.g. on glass. Organic material on the surface is decomposed due to the photocatalytic effect of the material, and decomposed organic material is removed because of the hydrophilic effect, as water droplets wet the surface and washes away the material. Another self-cleaning system is a hydrophobic surface coating. It consists of a water polymer matrix which creates a surface with nanoscale pores. The self-cleaning effect is achieved due to water surface tension. Water drops form almost spherical droplets on the hydrophobic surface, which, because of gravity, fall off the surface together with dust and small dirt particles from the surface (Mohelníková, 2011, Cortie et al., 2014). Therefore in this case it is not necessarily TiO_2 nanoparticles which provide the self-cleaning effect, but rather that the TiO_2 is applied as a thin-film with a thickness of a few nanometers. These products have been commercialised for a decade now (Cortie et al., 2014). Self-cleaning coatings with TiO_2 nanoparticles are, however, also commercialised (see section 7.2). Nanomaterials, such as SiO_2 or CNT, may also be used to create super-hydrophobic surfaces (Hanus and Harris, 2013).

Self-cleaning surfaces may reduce energy consumption by:

- Providing an easy-to-clean surface, so that the amount of water and energy needed for cleaning is reduced, or by providing surfaces that do not need to be cleaned so often (Greßler and Nentwich, 2012),
- Keeping windows clean and clear, thereby increasing the amount of sunlight entering a room, which reduces the need for heating and artificial light, and
- Allowing more light to enter e.g. solar cells; dirt decreases the amount of light to penetrate the solar cell, thus decreasing the energy yield from the cell. If the cells are coated with a self-cleaning surface, the problem is reduced.

6.1.8 Fuel additives

As also described in section 5.1.3, nanoporous catalysts or nanoparticles can enhance efficiencies of combustion processes and reduce emissions (Lambauer et al., 2012). Cerium oxide is the most commonly used nanomaterial for use as a fuel additive in order to optimize combustion efficiencies, and it has been commercialized since 1999. CeO_2 nanoparticles as diesel fuel additives are designed to increase mileage by performing as a combustion catalyst, thus increasing fuel combustion efficiency (Cassee et al., 2011). According to Luther (2008), fuel savings of 5-10% may be achieved by using cerium oxide based nanoparticular diesel additives.

Nanotribological wear protection products used as fuel or motor oil additives could also reduce fuel consumption of vehicles and extend the engine life (DEFRA, 2007; Greßler and Nentwich, 2012). For instance, micro-and nanosized silicate particles aggregate under pressure and temperature with metal atoms of components of the engine, and thereby build up a wear-resistance metal-silicate coating. Oil and fuel consumption of the combustion engines can thereby be reduced. According to literature reviewed by Lambauer et al. (2012), 15% of fuel consumption by car engines is caused by engine friction, and the abovementioned coating technology may result in a reduction of the fuel consumption by around 11% (Thesenvitz et al., 2007, as reviewed by Lambauer et al., 2012). According to a review by Senthilraja et al. (2010), dispersion of CuO and TiO_2 nanoparticles in mineral oil created nanofluids with tribological properties for use in automobiles in order to increase vehicle life and performance.

6.1.9 Overview of nanotechnologies in products/technologies reducing energy consumption

The table below presents an overview of the nano-technologies identified in products/technologies reducing energy consumption including nanomaterial involved, functionality, application areas and stage of development.

TABLE 5
OVERVIEW OF NANOTECHNOLOGY APPLICATION IN PRODUCTS/TECHNOLOGIES WHICH REDUCES ENERGY CONSUMPTION

Application/product		Involved "nano" (material and/or surface and/or...)	Why is "nano" applied?	Development stage
Photovoltaic devices	Solar cells	Au, Ag, Pt, Cu, Al, TiO_2 NPs,	Increase performance of the existing technologies.	Still in the research phase
	Antireflective coatings	SiO_2 NPs, ITO nanowhiskers		
	Solar collectors	Cu, Ag and Al NPs, CNT, graphite	Increase performance of the existing technologies.	
Hydrogen fuel cells	Hydrogen generation	TiO_2 nanotubes	Replace existing technologies with a greener technology	Still in the research phase
	Hydrogen storage	Metal hydrides (e.g. Mg), zeolites, CNT, carbon aerogels, $NaBH_4$ nanoparticles	Improving existing technology	
	Cell operation	Pt NPs	Reduce the material quantity, alternative materials to rare metals	
Nanotechnology-based catalysts		Molybdenum trioxide, magnesium, aluminium, nickel and iron oxide	Reduce energy demands in production by optimising processes	On the market
Batteries		CNT, graphene-based nanostructures, silicon nanowire, SnO_2, TiO_2, $LiFePO_4$, aluminium oxide, silicon or zirconium NPs	Increase and optimize performance of the existing technologies.	Batteries exploiting nanotechnology is on the market Optimisation research is on-going
Supercapacitors		RuO_2, MnO_2, Fe_3O_4 or V_2O_5 nanomaterials, CNTs or carbon nanofibers, carbon aerogels	Increase and optimize performance of the existing technologies.	Nano-based supercapacitors not commercialized yet, however, prototype exists.

Application/product		Involved "nano" (material and/or surface and/or...)	Why is "nano" applied?	Development stage
LED and OLED lighting		QDs, Nanostructured surfaces based on plasmonic nanoparticles, nanocrystallized thin films of e.g. TPE, BTPE, BCP, bathophenanthroline (Bphen), NET16, and NLE- 17	Improve efficiency and light yield	LEDs are on the market, but the role of nanotechnology in these products is uncertain. OLEDs are already on the market, but are not yet being utilized in many products.
Insulation	Aerogel	Porous SiO_2 (nanofoam)	Novel material with optimized properties and applications	Commercialised products are available
	Window glass coating	Nano-porous TiO_2 films, VO_2 nanoparticles	Added functionalities and optimized efficiencies	Only prototypes or commercials products delivered to select customers or markets have been presented so far
Self-cleaning coatings		Nanostructured TiO_2 films, CNT, SiO_2 nanoparticles	Increased reactivity and thus optimized properties	Windows with self-cleaning coatings in the nanometre-range have been commercialised for the last decade.
Fuel additives		CeO2, silicate, CuO and TiO_2 NPs	Enhance efficiencies	On the market

6.2 Market considerations – today and in the future

The market considerations for the different products and technologies are based on expert knowledge and feedback from interviewed persons within this field of research. In case of a lack of information or knowledge, information from the reviewed literature has been used and related to the Danish market to the extent possible.

Photovoltaic devices

Solar cells

The abovementioned uses of nanotechnology in photovoltaic devices essentially remain in the research phase. Thin-film solar cells surfaced coated with nanomaterials for greater efficiencies showed great promises and it was expected that this type of solar cells would dominate the market. However, as China introduced first generation thick silicon solar cells to the market, which were very low in cost compared to the thin-film cells, the European production of thin-film solar cells decreased and many manufacturers went bankrupt. It is therefore not expected that these types of solar cells will dominate the market any time soon and the growth potential is therefore limited, unless a breakthrough is made resulting in efficiencies above ~15% (Nylandsted Larsen pers. comm. (2015)). The Danish Innovation Foundation has recently granted 23 million DKK to the research project SunTune, which *inter alia* will investigate how the efficiency of first- and second-generation solar cells may increase via up-conversion using nanoparticles.

There are many other ongoing research initiatives within the field of nanotechnology and photovoltaic devices and Danish companies are working together with academia in relation to commercialisation. Therefore, there may be a market potential for Danish companies, although challenges with products from China and solar cell efficiency should be recognised.

Solar collectors
The use of nanotechnology (i.e. nanofluids) in solar collectors is to the authors' knowledge still in the research phase.

Based on the information collected during this project, it is not possible to estimate whether Danish companies are currently or considering exploiting market potentials within this area.

Hydrogen fuel cells
The use of nanotechnology in hydrogen fuel cells is to the authors' knowledge still mainly in the research phase.

However, the Danish Partnership for hydrogen and fuel cells estimates that 10.000 to 15.000 Danish jobs may be created within this sector over the next 10 years (Hydrogennet, 2015).

Batteries and supercapacitors
As noted in section 6.1.4, batteries exploiting nano-technology are already on the market and research is ongoing in relation to further developed/optimised batteries based on nano-technology. The state of the art is in relation to supercapacitors is unclear.

Based on the information collected during this project, it is not possible to estimate whether Danish companies are currently or considering exploiting market potentials within this area.

LED and OLED lighting
According to an analysis from IDTechEx, a research company conducting market examinations of emerging technologies, the market for LED and OLEDs is primarily driven by the use in displays. They state that the OLED lighting market is still in its infancy and that no mass production takes place as yet. It is however forecasted that the market for LEDs and OLEDs will grow in the near future, reaching a market of 1.9 billion USD in 2025 in an optimistic scenario (IDTechEX, 2012; 2014).

A great deal of research is ongoing within the field of nanotechnology application in LED and especially OLED, but it has not been possible for the authors to determine how big a role nanotechnologies will play in the commercialisation of the products.

Based on the information collected during this project, it is not possible to estimate whether Danish companies are currently or considering exploiting market potentials within this area.

Insulation
Aerogel
Hanus and Harris (2013) note that: "*Despite the obvious potential for aerogel products in glazing applications, commercially available products are limited. In terms of the aerogel market in general (not just glazing products), the market is quickly developing*". Insulation panels incorporating aerogels are now commercialised in Germany, but to the authors' knowledge not yet available on the Danish market.

A great deal of Danish research on aerogel as glazing and insulation material is ongoing and based on the knowledge collected in the current study, it is estimated that there may be good opportunities for Danish companies to exploit this market in the future.

Window glass coating
No large-scale implementation of nanotechnology-based glazing material has yet taken place. Due to a worldwide awareness and a need for eco-efficient and 'green' technologies, especially within the construction industry, the market for eco-efficient and energy-saving windows is likely to expand in the near future (Granqvist, 2013).

Based on the information collected during this project, it is not possible to estimate whether Danish companies are currently or considering exploiting market potentials within this area.

Self-cleaning coatings
Nano-based self-cleaning coatings are on the market today. These products also normally have the potential to clean air and to disinfect. The market situation for these products are addressed in Chapter 5 on air cleaning and Chapter 7 on hygiene improving products.

Fuel additives
Nano-based fuel additives are on the market today, but to the knowledge of the authors there are no Danish companies involved in exploitation of this technology.

6.3 Health and environmental pros and cons during use

Photovoltaic devices and hydrogen fuel cells
Based on expert judgement, it is not expected that these devices would cause any significant health and environmental problems in the use phase as it is not expected that nanomaterials would be released.

Batteries and supercapacitors
Based on expert judgement, normal use of batteries and supercapacitors are not expected to cause health and environmental problems in the use phase unless they are mistreated. Furthermore, Nanokommission (2008) states the following: "*Lithium batteries can be regarded as environmentally friendly as long as they replace lead or cadmium compounds and do not contain cobalt. There is also a functioning recycling system for lithium batteries which ensures that when they are handled appropriately, no (nano) materials can leak into the environment*".

LED and OLED lighting
Based on expert judgement, it is not believed that LED or OLED lighting would cause any significant health and environmental problems during use.

Insulation
In the current project, the authors have not identified literature on possible problems with this type of technology in the use phase. However, it cannot be excluded that surfaces treated with nano-enabled solutions might in some cases release nanomaterials during the use phase.

Self-cleaning coatings
Application of nanomaterial based coatings on walls and other surfaces might be associated with human exposure (e.g. if applied during spraying). Fischer et al. (2015), Sørensen et al. (2015), Larsen et al. (2015) and Christensen et al. (2015) have looked into the literature in relation to nano-TiO_2 in paints and coatings (including spraying applications), and assessed whether such applications could be associated with a human risk.

Once on the surfaces, nanomaterials may be released to the surrounding air and environment via wear and tear. Current knowledge on this issue has been reviewed in Christensen et al. (2015, in press).

Fuel additives
According to a review by Cassee et al. (2014) on the health and ecological effects of nanoscale Ce and CeO_2 it has been shown, in controlled combustion studies, that cerium diesel fuel additive decreases particulate and NOx emissions while dramatically increasing the ultrafine particles (particles <100nm), CO, hydrocarbon content and volatile organic compound emissions. Engine test have furthermore shown that a small amount of cerium is emitted in the exhaust in the particulate phase. Cerium detected in diesel exhaust emissions employing nanoscale cerium based fuel additive was found to be in the nanoscale or ultrafine size mode, composed of agglomerates of carbonaceous spherules as well as metallic aggregates composed mainly of CeO_2 nanoparticles. The effect of CeO_2 nanoparticles on human health has not been well investigated, and the available data is mainly derived from *in vitro* toxicological studies. CeO_2 nanoparticles may persist in the environment and biological systems due to structural properties; if they are used at a larger scale for a longer period of time, this may lead to potentially higher concentrations and/or accumulation of CeO_2 nanoparticles, resulting in a potential public health risk (as reviewed by Cassee et al., 2014).

7. Hygiene improving products/technologies (disinfectants)

This chapter addresses applications of nanomaterials, nanoproducts and nano-technologies applied for hygiene improving purposes, where the involved nanomaterials provide the disinfecting/biocidal effect.

7.1 Overview of nanoproducts and technologies

Several types of nanomaterials have biocidal properties: i.e. the ability to kill bacteria, viruses, fungi, etc. These properties are being utilized in a range of applications for disinfection/improving hygiene, providing benefits for human health and the environment. Table 6**Fejl! Henvisningskilde ikke fundet.** gives an overview of nanomaterials and technologies providing anti-microbial properties.

Antimicrobial nanomaterials may, for example, also be used as cosmetic ingredients, for food preservation, as drug carriers, for water disinfection, in wound dressing and as dental fillers and adhesives (Moritx and Geszke-Moritz, 2013).

TABLE 6
OVERVIEW OF NANOMATERIALS AND TECHNOLOGIES PROVIDING ANTI-MICROBIAL PROPERTIES

Primary function	Type	Biocidal effect	Nano Material	Application	Types of products/applications
Photocatalytic	Inorganic	Oxidation	TiO_2, NiO, ZnO - particles	Additives in aqueous solutions	Paints, Coatings, Rubber, Films
Hydrophilicity	Organic	Anti-adhesive, non-stick	Silane - mono/multi-layer	Polymer coatings and liquid glass	Wax, Varnish, Floor coatings
			PDFE (teflon) - mono/multi-layer	Polymer coating	Paper, Iron, plastics
	Inorganic	Anti-adhesive, non-stick	SiO_2 - mono/multi-layer	Metallic deposition, Sol-Gels and functional groups	Medical instruments, Coatings
Electro static /mechanical	Organic	Electro deformation	MEP - furan, Polyhexa-methylene biguanide	Additives in aqueous solutions/binder	Surface coating
Mechanical	Organic	Mechanical deformation	Sharklet plastic sheeting/film	Structure host surface or as laminates	Laminate, structured materials
			Nanopillar surfaces (Chitosan films)		

Primary function	Type	Biocidal effect	Nano Material	Application	Types of products/applications
Ions	Inorganic		Silver - salts (e.g. AgCl, $AgNO_3$)	Additives - needs liquid to release ions	Nylon, Coatings, Paints, Fibres, Films
Metallic /oxide	Inorganic		Ag, Mg, Zn, Ca, Cu	Additives in aqueous solutions	Nylon, Coatings, Paints, Fibres, Films
Hybrids (two or more functions)	Inorganic/ Organic	Mechanical deformation, non-stick	Block-Co-polymers	Polymer coating	Surface coating
			Polydopamine /Silver nanocomposites	Additives in aqueous solutions	Nylon, Coatings, Paints, Fibres, Films
			Si-Derivatives (Ormocomp)	Polymer coating	Solar-Cells, Windows, Screens
		Oxidation, non-stick, mechanical & electro deformation	Gold/polythio-phene composites	Additives in aqueous solutions	Nylon, Coatings, Paints, Fibres, Films
	Inorganic	Non-stick, electro deformation, oxidation	Multi-Metal coating (e.g. Fe, Ti, Ag, Au)	Sol-Gel coating	Medical instruments, high-end industrial equipment
		Oxidation, non-stick, electro deformation	Doped TiO_2 (any transitional metal)	Additives in aqueous solutions /binder	Paints, Coatings, Rubber, Films
	Organic		Chitosan/ethylene -vinyl copolymers	Polymer coating	Coatings, Fibres, Films

As can be seen from Table 6, nanomaterials with biocidal properties are used in a very wide range of applications.

It has been decided to focus the remaining parts of this chapter on existing/upcoming materials/technologies intended to be applied in the healthcare sector, a sector known to be challenged in terms of hygiene e.g. due to the presence of resistant bacteria and contagious viruses. This sector is also of interest as it is known that a number of Danish companies are active in this market.

Biocidal nanoproducts relevant for the healthcare sector may be divided into the following sub-categories, depending on their applications:

1. General surface coatings applied on-site, i.e. all-purpose coatings and antibacterial paints used on general surfaces e.g. wall, floors and furniture;
2. Biocidal purging or fuming, applied at locations of high risk by damage control units that disperse the nanomaterial in a room by a purging protocol;
3. Articles pre-treated with biocidal products with the purpose of avoiding spread of microbes, and
4. Articles used to disinfect other articles such as cleaning cloths or nano-functionalized washing machines.

It can be noted that the all-purpose biocidal coatings and paints have potential applications in a broad range of sectors, including hospitals, childcare centres, nursing homes etc. because of their ability to minimise the spread of disease and reduce the prevalence of illness and discomfort as a result of their antimicrobial effect (Hanus and Harris, 2013).

Antimicrobial (and self-cleaning) surfaces may also have other benefits, such as reducing the need for cleaning and harsh cleaning agents.

The authors have not been able to identify reliable data as to how disinfectants based on nanomaterials perform as compared to conventional biocides, but have been informed by some suppliers that some of the solutions presented in more detail in the following may have the potential to dramatically improve hygiene in the health care sector.

7.1.1 All-purpose-coatings and antibacterial paints (applied on-site)

A range of anti-microbial paints and coating products on the European market are based on the photocatalytic anatase form of nano-TiO_2. Upon radiation with light and in the presence of water, the nano-TiO_2 releases free oxygen radicals, which react with and kill microbes by burning their cell membranes. The anti-microbial properties of free oxygen radicals are also known from hydrogen peroxide.

An added benefit of these products is that they may also improve the indoor environment by oxidising organic matter to water and CO_2, thereby reducing odour and removing organic contaminants in indoor air.

Poly(ethylene imine)s or PEIs are a nano network of charged polymers that attracts and captures microorganisms. This attraction occurs given the negative charge of common cell walls. In some cases this charge difference is so great that the cell will deform to the point of rupture and result in the anti-microbial effect.

Polyhexanide, polyhexamethylene biguanide (PHMB) is a polymer that has a well-known anti-microbial effect. This anti-microbial effect is obtained via electrostatic destruction breaking down cell walls and thus killing the microorganisms.

7.1.2 Biocidal purging or fuming

Products based on a combination of nanosilver and hydrogen peroxide are used for disinfecting contaminated rooms by purging/fuming. In this situation, the nanomaterial itself is the product made airborne in the room requiring disinfection.

Silver ions are well-known disinfectants and applying silver in the nano-form increases the surface area from which silver ions may be released, thus increasing efficiency as compared to larger sized silver particles.

7.1.3 Coatings for instruments, tools and other articles (pre-treatment)

Instruments, tools and furniture might be treated with a biocidally active coating prior to entering the healthcare premise in question in order to protect it from being contaminated and also to assist in avoiding spread of microbes. Examples of products which are or could be treated (if the proper permission was given) include:

- Hospital room-specific inventory (chairs, beds, tables, wheel chairs, bed-side lighting, cupboards);
- Contact surfaces (light switches, alarm buttons, hand rails, taps, toilet flush buttons), and
- Mobile patient monitors & machines (e.g. respirators, various devices for measuring blood pressure/ECG/heart rate, respirators, as well as various ECG, BP & HR monitors etc.).

This coating could be of the same type of nano-TiO_2 based coatings discussed in section 7.1.1 or the process could involve silver-doped hospital beds or anti-microbial carpets.

Two other main types of coatings are known to be applied, one based on composites with e.g. silver, gold or palladium nanoparticles and the other based on "liquid glass Si", which when hardened becomes glass-like. These coatings apply one or both of two disinfecting mechanisms: i) Anti adhesive, where a surface becomes undesirable for microorganisms to settle on, ensuring reduced overall microbial growth resulting in a disinfecting effect, and/or ii) Electron donation or electrostatic destruction, through injecting an electron into the cell wall, the functionality of the cell is changed leading to its death, thus reducing microbial activity.

7.1.4 Articles used to disinfect other articles

Nanosilver functionalized cleaning tools, e.g. cloths, mops and brooms, might be used to clean and disinfect other articles such as furniture and floors. Use of the same active compound can also be found in more complex systems such as washing machines and dishwashers that provides an added disinfecting effect from the nanosilver during washing.

More short-term solutions contain one or both PEI and PHMB in one time use products e.g. wet wipes and band aids. These disinfecting properties are described in section 7.1.1.

7.1.5 Overview of nanotechnologies in hygiene improving products/technologies (disinfectants)

The table below presents an overview of the nano-technologies identified in hygiene improving products/technologies (disinfectants) including nanomaterial involved, functionality, application areas and stage of development.

TABLE 7
OVERVIEW OF NANOTECHNOLOGY APPLICATION IN HYGIENE IMPROVING PRODUCTS/TECHNOLOGIES (DISINFECTANTS)

Application/product	Involved "nano" (material and/or surface and/or...)	Why is "nano" applied?	Development stage
All-purpose-coatings and antibacterial paints (applied on-site)	Nano-TiO_2	Release free oxygen radicals which kill microbes, Radicals are released when exposed to light in the presence of water/humidity	On the market

Application/product	Involved "nano" (material and/or surface and/or...)	Why is "nano" applied?	Development stage
	PEI (polymer)	Charged polymer which attract and capture microorganisms leading to rupture and death of microbes	On the market
	PHMB (polymer)	Electrostatic destruction breaking down cell walls and thus killing the micro-organisms	On the market
Biocidal purging or fuming (where the nanomaterial itself is the product made airborne in the room requiring disinfection)	Nanosilver	Efficient release of the anti-microbial silver ion due to large surface area of nanoparticles	On the market
Coatings for instruments, tools and other articles (pre-treatment) (E.g., hospital beds, light switches, toilet flush buttons, devices for measuring blood pressure/ECG/heart rate, etc.)	Nano-TiO_2	Release free oxygen radicals which kill microbes. Radicals are released when exposed to light in the presence of water/humidity	On the market
	Nanosilver	Efficient release of the anti-microbial silver ion due to large surface area of nanoparticles	On the market
	Liquid glass Si	Anti-adhesive surfaces and/or electron donation leading to electrostatic destruction of microbes	On the market
	Silver, gold or palladium nanoparticles	As above	On the market
Articles used to disinfect other articles (cleaning cloths and washing machines)	Mainly nanosilver	Efficient release of the anti-microbial silver ion due to large surface area of nanoparticles	On the market

7.2 Market considerations – today and in the future

The types of products described in section 7.1.1 to 7.1.4 are all on the Danish and European market today. The extent to which they have already entered the health care sector varies, as especially application in hospitals is associated with various mandatory and hospital specific assessment and approval procedures.

A challenge for the nano-based biocides is also that they have to be authorised according to the Biocidal Products Regulation, which requires specific assessments and approvals of nano-forms of the active substances. The overall costs for such authorisations are significant.

Some Danish companies are in the forefront in relation to exploitation of several of these technologies, including all-purpose nano-TiO_2 based coatings, fuming/purging systems, nanosilver-based textiles/cloths, and instrument coatings based on liquid glass Si. These companies expect highly significant European and global market shares. The European healthcare market is perceived as conservative and cautious in the adoption process for new hygiene technologies, while at the same time, successfully adopted technologies are dissipated throughout the system. This situation means that any one Danish company that can secure a significant market share will also be exposed to large growth potential by multiple parallel markets within the EU.

7.3 Health and environmental pros and cons during use

7.3.1 Resistance and toxicity

Hanus and Harris (2013) discuss some benefits and drawbacks associated with applications of nanomaterial based antimicrobials: "*Nanoparticle-based antimicrobials can offer significant benefits over conventional chemical, photochemical or physical disinfection methods. Unlike some conventional antimicrobial agents, many antimicrobial nanomaterials (e.g. Ag nanoparticles and Cu nanoparticles) exhibit strong toxicity towards a broad range of microorganisms found in industrial processes and the human body, but a remarkably low toxicity to humans. In contrast, many conventional disinfectants are toxic to humans; for example, most antifungal chemicals are non-specific to the organism affected and can be detrimental to the environment (toxic to plants and animals). It has also been suggested that disinfection with some nanomaterial compounds (e.g.* TiO_2*) can be more effective than conventional disinfection (e.g. with chlorine) [87] and, particularly when supported in a substrate, some nanoparticles have demonstrated good stability and long-term activity. Opinions are divided regarding the development of resistance by microbes to nanoparticle-based antimicrobial agents. Some studies report that there has been no evidence of microorganisms developing resistance to nanoparticles and that the development of resistance is unlikely due to the different antimicrobial mechanisms of nanoparticles when compared to that of many conventional antimicrobial agents. Others have suggested that silver resistance already occurs extensively, but it is not recognised due to a lack of testing for silver resistance*."

From the experts interviewed as part of this project, it is evident that there is some concern regarding using silver in the health care sector because of the possibility of microorganisms developing resistance.

On the other hand, it can be argued that if hygiene could be improved (and the number of infections decreased), the need for antibiotics would also decrease. Antibiotics are well-known to cause resistance. Therefore, there is a trade-off to consider. Furthermore, it can be noted that to the knowledge of the authors, no concerns have been raised about possible development of resistance to nano-TiO_2 based antibiotics acting via release of free oxygen radicals.

Linked to the applications themselves, purging/fuming especially has the potential to lead to significant exposure if not properly controlled.

As already discussed in section 6.3, potential exposure may also occur during application of coatings on walls (e.g. via spraying) and/or due to subsequent wear and tear. See section 6.3 for further details.

7.3.2 Indirect benefits and drawbacks

As already discussed in section 5.3, photocatalytic TiO_2 based paints and coatings might not only react with antimicrobials and NOx, but also with VOCs, possibly leading to toxic intermediates if not completely oxidised to CO_2 and water. On the other hand, if the reaction with VOC is more complete, it might significantly improve the indoor environment by reducing odour and organic matter in the indoor air.

Furthermore, the use of e.g. coatings and paints which not only disinfect, but also prevent dirt from sticking to surfaces, may lead to significantly reduced need for cleaning, including less use of harsh cleaning agents. This usage could thus save water, energy and the use of toxic chemicals.

Overall, it appears that proper life cycle assessments (LCAs) of these types of applications would be welcome in terms of assessing the overall environmental benefits of these applications.

List of abbreviations

AFC	Alkaline fuel cell
BNP	Bimetallic nanoparticle
BTEX	Benzene, toluene, ethylbenzene and xylenes
CMC	Carboxy-methyl-cellulose
CNT	Carbon nanotube
COC	Chlorinated organic compound
DANVA	Dansk vand- og spildevandsforening (Danish water and wastewater association)
DEFRA	Department for Environment, Food & Rural Affairs (UK)
DNAPL	Dens non-aqueous phase liquid
DSSC	Dye-sensitised solar cell
DTU	Danish Technical University
EDLC	Electrochemical double layer capacitors
EPA	Environmental Protection Agency
EZVI	Emulsified zero-valent iron
FC	Fuel cells
HVAC	Heating, ventilation and air condition
ITO	Indium-tin-oxide
LCA	Life cycle assessment
LED	Light-emitting diode
MCFC	Molten carbonate fuel cell
MWCNT	Multi-walled carbon nanotube
NAC	Nitroaromatic compound
NCPSC	Nanofluid-based concentrating parabolic solar collector
NM	Nanomaterial
NO_X	Nitrogen oxides
NP	Nanoparticle
nZVI	Nanoscale zero-valent iron
OECD	Organisation for Economic Co-operation and Development
OLED	Organic light-emitting diode
PAFC	Phosphoric acid fuel cell
PAHs	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyl
PCE	Perchloroethylene
PCO	Photocatalytic oxidation
PEI	Poly(ethylene imine)
PEM	Proton exchange membrane
PEMFC	Proton exchange membrane fuel cell
PFC	Perfluorinated compound
PGM	Platinum group metals
PHMB	Polyhexamethylene biguanide
PRB	Permeable reactive barrier
PV	Photovoltaic
QD	Quantum dot
ROS	Reactive oxygen species
SAMMS	Self-assembled monolayers on mesoporous supports

SCR	Selective catalytic reaction
SME	Small and medium-sized enterprise
SOFC	Solid oxide fuel cell
SWCNT	Single-walled carbon nanotube
TCE	Trichloroethylene
UV	Ultra violet
VOC	Volatile organic compound
WPN	Working party on nanomaterials
ZVI	Zero-valent iron

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Appendix 1 Summary of available life cycle assessments of nano-enabled environmental technologies

Considering that health and environmental benefits obtained in the use phase of nano-enabled technologies might be reduced or balanced out by drawbacks in other life cycle stages, several authors have pointed out that Life Cycle Assessment (LCA) is a very appropriate decision-support tool in an overall environmental assessment of nano-enabled technologies and solutions (e.g. Grieger et al., 2012; Gavankar et al., 2012).

However, considering the wide application area of nanomaterials, surprisingly few LCA studies have been published (see e.g. reviews by Miseljic and Olsen, 2014; Gavankar et al., 2012; Hischier and Walser, 2012). This lack might be associated with the fact that relatively limited inventory data are available for processes in the life cycle (Miseljic and Olsen, 2014; Hischier and Walser, 2012). Challenges associated with assessing the impact of nanomaterials in a life cycle perspective are also pointed out (e.g. Upadhyayula et al., 2012; Gavankar et al., 2012).

In 2009, the OECD Working Party on Nanotechnology (WPN) organised an "OECD Conference on Potential Environmental Benefits of Nanotechnology: Fostering Safe Innovation-Led Growth"[5]. This conference confirmed that life cycle considerations are appropriate in relation to judging the overall environmental impact of nano-enabled technologies. In association with this conference, an NGO position paper was published (IPEN/EEB, 2009) and Christensen (2010) published some reflections from the workshop. Both papers point out that key issues to address in such assessments are energy consumption during manufacturing of the nanomaterials, use of scarce metal resources, and the inherent toxicity of nanomaterials, as well as their possible emissions throughout the life cycle. DEFRA (2007) also discusses the issue of use of scarce metals and that production might be associated with significant environmental burdens in a life cycle perspective.

These issues are also to some extent addressed in the limited number of published LCAs addressing nano-enabled environmental technologies that are the focus of the current project. Most attention appears to be paid to the apparent high energy consumption associated with the manufacturing of some carbon-based nanomaterials (including CNT) (Kim and Fthenakis, 2013; Upadhyayula et al., 2012) and carbon nanofiber polymer composites (Khanna and Bakshi, 2009).

Kim and Fthenakis (2013) reviewed 22 LCA-based case studies and concluded that that isolated cradle-to-gate considerations might disfavour nanomaterials due to the intense energy use required for production, whereas most of the reviewed studies showed lower energy demand when considering the full life cycle (cradle-to-grave). The lower energy demand in the full life cycle was due to the fact that nanomaterials are typically used in lower amounts than materials in conventional products and upgraded functionality offers more energy-efficient operation of the nano-enabled technologies (Kim and Fthenakis, 2013).

Şengül and Theis (2011) look into the use of quantum dot photovoltaics and point out that this technology has the potential to overcome current barriers with solar technology. On the other hand, the authors flag the use of scarce and toxic materials such as cadmium selenide, cadmium telluride and lead sulphide in the quantum dots.

Babaizadeh and Hassan (2012) present a life cycle assessment of nanosized TiO_2 coating on residential windows. They conclude that TiO_2 nano-coated glass is the most cost-efficient and environmentally friendly window-glass for use in buildings.

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[5] Program, background paper, abstracts and presentations can be downloaded here: http://www.oecd.org/innovation/oecdconferenceonpotentialenvironmentalbenefitsofnanotechnologyfosteringsafeinnovation-ledgrowth.htm

As can be seen, the relatively few current life cycle assessments indicate that some nano-enabled environmental nanotechnologies seem to perform better than conventional alternatives in a life-cycle perspective. Nonetheless, it should be realised that knowledge gaps may exist that could affect the conclusion of such assessments.

In any case, generalisations from these limited studies should not be generalised to nano-enabled environmental technologies in general. Given the spread and diversity, a case-by-case approach is warranted.

Based on theoretical considerations and empirical knowledge generated so far, LCAs of nano-enabled environmental technologies should, between others, address:

- the entire life cycle (partial LCAs might lead to opposite conclusions);
- energy consumption associated with extractions of raw materials and manufacturing of the nanomaterials;
- amount of scarce metals/resources used, and
- possible release and impacts of nanomaterials throughout the life cycle.

Appendix 2 Information search and sources

This section describes the details of the information search and sources for each technology.

Chapter 3: Water treatment
Work and research for this chapter was done using various academic and scientific journals and textbooks in relevant fields for nano-enabled technologies. More specifically, certain keywords were searched for using the scientific search engines of "Web of Science" and "Google Scholar." Some of the primary keywords searched for were nano, water, wastewater, treatment, review, Denmark, nanoparticle, nanomaterials, among others. The journals include, but are not limited to: *Nature, Journal of Nanoparticle Research, Science of the Total Environment, Energy & Environmental Science*. The textbooks employed include: *Nanotechnology for Water and Wastewater Treatment* - IWA Publishing, *Wastewater Engineering: Treatment and Reuse* – Metcalf & Eddy –McGraw-Hill, and *Water Chemistry* – Mark M. Benjamin. A complete list of references can be found at the end of this report.

Furthermore, the general expertise and experience at DTU Environment within water treatment technologies was utilised in the preparation of this chapter.

Chapter 4: Soil and groundwater remediation
Work and research for this chapter was based on literature identified from searches on primarily ISI Web of Science. The information gathering was conducted with following search terms: "nano*" combined with "soil" or "groundwater" or "sediment" and with "remed*" or "remov*" or "clean-up" or "decontam*" or "treatment" or "reduc*". In the first search round, the search was particularly aimed at identifying review and overview articles and reports on the subject. Google searches on nanotechnology and soil/groundwater were also conducted. The literature list has subsequently been supplemented with key articles and reports identified via the literature reviewed in the first round.

In addition to the literature review, an American expert on nanotechnology applied in soil and groundwater remediation, Dr Neil Durant from Geosyntec Consultants, MD was interviewed on the matter. Furthermore, one of the authors of the report (Mr Torben Højbjerg Jørgensen) has been closely involved in nano- and micro-ZVI trials in Denmark.

Chapter 5: Air pollution reduction/air purification
Work and research for this chapter was based on literature identified from searches on primarily ISI Web of Science. The information gathering was conducted with the following search terms: "nano*" combined with "air" or "emission" or "exhaust" and with "remed*" or "remov*" or "clean-up" or "decontam*" or "reduc*". In the first search round, the search was particularly aimed at identifying review and overview articles and reports on the subject. Google searches on nanotechnology and air were also conducted. The literature list was subsequently supplemented with key articles and reports identified via the literature reviewed in the first round.

In addition to the literature review, information on the application of nanotechnologies for air purification/air pollution reduction was gathered through interviews with a few companies identified as active in different parts of the market for such technologies/products.
The companies interviewed were a major developer and vendor of industrial catalyst systems and a smaller company specialised in various nano-solutions, including passive air purification technology for outdoor as well as indoor purposes.

Finally, one of the co-authors of the report (Mrs Nana Schumacher) is an expert in and has hands-on experience with air cleaning technologies in industry.

Chapter 6: Products/technologies reducing energy consumption
Work and research for this chapter was based on literature identified from searches on primarily ISI Web of Science. The information gathering was conducted with the following search terms: nano* combined with energy and consumption, saving, efficien*, storage or conversion. Searches on nano* combined with fuel additives, hydrogen storage, catalysts, insulation, construction, solar cells and batteries have also been conducted, where only reviews and key studies have been selected. Searches were supplemented with searches in Google Scholar using the abovementioned search terms when relevant. Google searches on nanotechnology and energy and construction have also been conducted, as well as ad hoc searches for more information regarding specific products/technologies. The literature list was subsequently supplemented with relevant citations identified in the reviewed literature.

It should be noted that most of the identified literature on applications of nanotechnology in the area of production, storage and use of energy is relatively old, taking into consideration that nanotechnology is an emerging and fast growing technology. Therefore, in addition to the above and when possible, this information were supplemented with other knowledge from experts within the field, as detailed below.

An interview has been conducted with Arne Nylandsted Larsen, professor in the Department of Physics and Astronomy/iNANO at Aarhus University, who provided information and input regarding the use of nanotechnology in solar cells and the market potential for nanotechnology in solar cells in Denmark. Arne Nylandsted Larsen works on projects in close collaboration with Danish companies developing and providing solar cells; these companies referred to Arne Nylandsted Larsen.

Furthermore, Kristian Mølhave, associate professor at DTU Nanotech, Department of micro- and nanotechnology commented on and provided input to the chapter.

In addition, an interview with a major developer and manufacturer of industrial catalyst systems was conducted. Finally, several companies within the glass industry were approached, but it was not possible to plan interviews with these within the time frame of the project.

Chapter 7: Hygiene improving products/technologies (disinfectants)
This chapter is to a large extent based on input and information from a Danish expert who has worked with nanotechnology in academia, as well commercial exploitation of biocidal properties of nanomaterials for disinfectant purposes. Where relevant, this information was supplemented with information from the literature.

Nano-enabled environmental products and technologies – opportunities and drawbacks

Projektet om nano-baserede miljøteknologier og -produkter har til formål at undersøge de miljø- og sundhedsmæssige fordele, som anvendelsen af nanomaterialer i produkter og teknologier kan give. Mere specifikt sigter projektet på at give et overblik over de mest relevante nano-baserede miljøteknologier og –produkter, hvilke typer af produkter og teknologier på markedet (herunder det danske), samt produkter og teknologier, som stadig er under forskning og udvikling samt de Miljø- og sundhedsmæssige fordele og ulemper ved disse teknologier.

Projektet har set på teknologier, der anvendes til: 1) rensning af vand og spildevand, 2) rensning af jord og grundvand, 3) rensning af luft, 4) reduktion af energiforbruget og 5) at forbedre hygiejnen i sundhedssektoren ved at udnytte de antibakterielle egenskaber af visse nanomaterialer.

The current project on nano-enabled environmental products and technologies aims to investigate the benefits for health and environment that the use of nanomaterials in products and technologies may have. More specifically, the project provides an overview of the most relevant nano-enabled environmental technologies, different types of products and technologies on the (Danish) market, as well as products and technologies, which are still in R&D and it will provide a qualitative overview of health and environmental pros and cons of these technologies.

The project has focused on technologies applied in: 1) purification of water and wastewater, 2) remediation of soil and groundwater, 3) cleaning of air, 4) reduction of energy consumption and 5) for improving hygiene in the health care sector by utilizing the antibacterial properties of certain nanomaterials.

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