

Benefits and risks of nanozerovalent iron, titanium dioxide nanoparticles and carbon nanotubes for water treatment technologies

David G. Rickerby*

European Commission Joint Research Centre, Directorate F, Via Fermi 2749, 21027 Ispra VA, Italy

*Corresponding author: Tel: (+39) 0332785972; E-mail: david.rickerby@jrc.ec.europa.eu

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Abstract

An overview is presented of potential improvements in performance that can be achieved by using three different types of nanomaterials in water treatment applications: (i) zerovalent iron for reducing concentrations of chlorinated hydrocarbons and heavy metals in groundwater; (ii) titanium dioxide for photocatalytic drinking water purification, enabling reduced consumption of chemicals for disinfection; (iii) carbon nanotube membrane filters that transport water molecules at elevated fluxes, while rejecting other molecules and ions. The distinctive characteristics of the nanomaterials, such as high specific surface area, enhanced reactivity and adsorption capacity, have already led to significant increases in efficiency. Future developments are expected based on surface modification of zerovalent iron to improve its reactivity and transport characteristics, advanced chemical synthesis methods to increase the area of photoreactive facets and doping to inhibit electron-hole recombination or to allow visible light photocatalysis in titanium dioxide, and functionalization of carbon nanotubes to increase ion rejection rates. Implementation of these innovative methods for removal of contaminants from water will be contingent on reduction of the present high cost of the nanomaterials and assessment of the possible risks associated with their, as yet only partly understood, toxic and ecotoxic properties. Copyright © 2017 VBRI Press.

Keywords: Water treatment, remediation, desalination, nano zerovalent iron, titanium dioxide, carbon nanotubes.

Introduction

Water is an indispensable resource that has been considered, in the past, to be of comparatively little value because it was so readily accessible. However, the effects of industrialization, urbanization and intensive agriculture have created greater demand, while the accompanying increase in pollution has reduced the availability of safe drinking water, with negative effects on human health [1]. Together with water scarcity caused by climate change [2] and population growth [3], this presents a challenge to the quality and security of the water supply in many countries, as well as a threat to delicate ecological systems [4]. These issues have created the need to exploit alternative water sources, such as wastewater recycling and desalination of seawater [5]. Present day water treatment technologies require significant energy consumption, which has stimulated research to develop more efficient and economical methods for the remediation of contaminated groundwater, recycling of wastewater and purification of drinking water, while reducing the environmental impacts of water treatment [6, 7].

Approximately 97% of the water on Earth is saline and can only be made potable by means of expensive desalination technology. The rest is freshwater but two

thirds of this is frozen in glaciers and the polar ice caps, so that only 1% is accessible for human use. Approximately 0.7% of this available water is in the form of groundwater, while the remaining 0.3% is surface water. Groundwater is an important source of drinking water and its quality is therefore a major public health concern [8]. Interaction between surface water and groundwater can affect the quality of both, as well as exerting an influence on the interrelated aquatic and terrestrial environments [9, 10]. Aquifer systems are able to dilute diffuse pollution, while attenuation of point source pollution may occur due to mixing with surface water [11].

The hazardous volatile organic compounds (VOCs) commonly found in groundwater include chlorinated hydrocarbons, such as trichloroethylene (TCE) and tetrachloroethylene (PCE) [12]. Their application as industrial degreasing solvents and in dry cleaning, has led to the widespread presence of these two toxic contaminants in the environment. They are known to cause liver damage and foetal abnormalities, as well as being carcinogenic. Natural degradation of TCE may furthermore lead to the production of hazardous intermediates such as vinyl chloride.

Arsenic is considered to be a priority pollutant due to its high toxicity. Environmental contamination due to arsenic

may originate from either natural or anthropogenic sources. It is generally found at higher levels in groundwater than in surface water and, because in many regions of the world groundwater contaminated with arsenic is used for drinking water and irrigation, represents a serious hazard. Long term exposure to arsenic can damage human health and is a significant environmental cause of cancer [13, 14]. Exposure to arsenic may also cause a range of other diseases including respiratory, digestive, circulatory, renal, reproductive, developmental, immunological and neurological disorders [15, 16]. Current methods for arsenic removal from drinking water suffer from disadvantages in terms of either cost or efficiency. There is consequently a demand for development of inexpensive and more effective techniques.

Water quality can be significantly influenced by the presence of natural organic matter (NOM), which is a complex mixture of organic compounds originating from decayed plant and animal material. NOM can adversely affect drinking water quality by interfering with water treatment processes, owing to its ability to adsorb hydrophobic organic compounds and mobilize heavy metals [17, 18]. It can also create problems by reacting with disinfectants to form potentially toxic disinfection by-products [19-21]. Interaction between NOM and chlorine or bromine based disinfectants is a major concern because the compounds generated by reactions with heavy metals and other chemicals can prove extremely difficult to remove.

Conventional water treatment technologies employ physical, chemical and biological techniques. The methods currently in use function inefficiently and well below the full capacity to degrade or remove chemical substances and eliminate pathogens in water [22]. Innovative techniques that exploit the specific properties of nanomaterials could accomplish a great deal to mitigate the environmental impact of water treatment methods and improve water quality [23]. It can therefore be expected that nanomaterials will enable remarkable progress in water treatment technologies [24-27]. For responsible technological development it is essential that any environmental and health risks presented by nanomaterials are properly addressed [28, 29]. The cost-effectiveness of employing nanomaterials in water purification and remediation applications will be furthermore decisive in determining their widespread acceptance [30].

The present review provides a concise introduction to this field with an update on recent advances in three of the most important application areas: nano zerovalent iron (nZVI) for groundwater remediation, photocatalytic drinking water purification with nano titanium dioxide (TiO₂), and carbon nanotube (CNT) membrane filters for seawater desalination. The main advantage of using nanomaterials is that their unique properties, due to small size, increase the efficiency of contaminant removal, while engineering at the nanoscale can bring about further improvements in performance. Faster reaction rates are obtained, in the case of nZVI and nano-TiO₂, and higher fluxes with greater selectivity, in the case of CNT filters.

Cost savings can be realized due to the resultant reduction in the use of chemical disinfectants and decreased energy requirements. The health and safety concerns related to the possible toxicity of the nanomaterials are considered, with the aim of providing a balanced overview of the potential benefits and risks of their use in water treatment applications.

Zerovalent iron for groundwater remediation

Nano zerovalent iron (nZVI) is a powerful reducing agent that undergoes corrosion reactions with water and dissolved oxygen and can be employed for the treatment of hazardous chemicals in groundwater [31]. It is capable of degrading organic contaminants, such as chlorinated hydrocarbons, and immobilizing heavy metals, like hexavalent chromium and arsenic. Two aspects influence the effectiveness of nZVI for remediation: the increased reactivity due to the very high specific surface area, and transport and the fate of the nanoparticles in the aquifer.

Both top-down and bottom-up processes may be used to synthesize nZVI. Methods that have been utilized for this purpose are vacuum sputtering from a pure iron target, decomposition of iron pentacarbonyl in organic solvents, reduction of goethite or hematite at high temperature in a hydrogen atmosphere, and reduction of ferric chloride with sodium borohydride [32]. Studies by high resolution electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) indicated that the nanoparticles prepared by this latter method have a core-shell type structure, consisting of a zerovalent iron interior surrounded by an outer layer of iron (hydr)oxide a few nanometres in thickness [33, 34].

Reactions with iron play an essential part in various remediation technologies for soil and groundwater [35]. These include its use as a sorbent in assisted natural remediation and the removal of arsenic by adsorption from contaminated groundwater serving as a source of drinking water. Iron also functions as an electron donor in Fenton type reactions producing hydroxyl radicals, which are potent oxidizing agents that are able to oxidize organic compounds. Reactive barriers containing iron have been in operation for decades but the use of nZVI is of more recent origin. The advantage of using nanoparticles in remediation applications is the greatly increased reactivity, due to a higher surface area to volume ratio, which permits rapid and cost-effective bonification of contaminated sites.

There are many reports describing the effectiveness nZVI for remediation of groundwater and treatment of wastewater containing chlorinated hydrocarbons, nitroaromatic compounds, arsenic, heavy metals, nitrates, dyes, and phenols [36]. In particular, it has proved to be suitable for dechlorination of highly toxic, persistent chemicals such as trichloroethylene (TCE), tetrachloroethylene (PCE), polychlorinated biphenyls and organochlorine pesticides, which are contaminants typically present in aquifers. Arsenic occurs in groundwater mainly as arsenite, As(III), and arsenate, As(V), and the effectiveness of its removal by nZVI depends on a number of factors, such as pH, dissolved

oxygen, water hardness and the presence of humic acid. Toxic heavy metals, such as chromium, copper, cobalt, nickel, mercury, cadmium and lead, which are water pollutants of particular concern because they accumulate in living organisms, can also be successfully removed.

Owing to its many industrial applications Cr(VI) is a common groundwater contaminant. A large amount of work has consequently been carried out on the use of zerovalent iron for reduction of chromium from its hexavalent to trivalent form, both at laboratory scale and in field trials [37]. The presence of additional inorganic and organic substances may act to inhibit the reaction to an extent, though there is controversy regarding this. The reaction chemistry of Cr(III) and Cr(VI) with nZVI has been investigated by XPS and X-ray absorption spectroscopy (XAS) [38]. Results indicated that Cr(VI) could be completely reduced to Cr(III) by treatment with nZVI and that the reaction product consisted mainly of hydroxylated Cr(OH)₃, possibly containing also some Cr_xFe_{1-x}(OH)₃. Carbon supported nZVI has been found to be highly effective for reduction of Cr(VI) and has excellent transport properties in porous media [39].

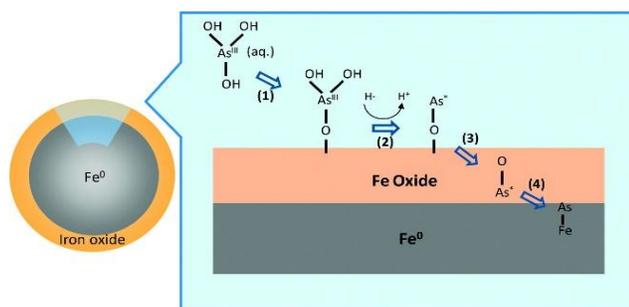


Fig. 1. Reaction mechanism of nZVI with As(III): (1) adsorption of As(III) at the surface; (2) reduction of As(III); (3) translocation through the oxide shell with breaking of As-O bonds; (4) diffusion into the Fe⁰ core. As* is an intermediate state between As(III) and the Fe-As intermetallic (Reprinted with permission from Yan, W.; Vasic, R.; Frenkel, A.I.; Koel, B.E.; *Environ. Sci. Technol.*, **2012**, *46*, 7018. Copyright © 2012, American Chemical Society.)

Because it is a known carcinogen, chronic exposure to arsenic in drinking water represents a major health problem in areas where high levels of groundwater contamination exist. Investigations of the adsorption kinetics of nZVI supported on activated carbon have confirmed the rapid removal of As(III) and As(V) from water [40]. The presence of metal cations, such as Mg²⁺ and Ca²⁺, increased the efficiency of arsenic removal, whereas the presence of humic acid tended to decrease it. High resolution XPS evidenced As(0) species on the surface of nZVI after reaction with solutions of As(III) and As(V) [41]. The adsorption, oxidation and reduction processes that occur can be interpreted on the basis of the core-shell structure. In situ time-resolved XAS studies of aqueous As(III) adsorbed on nZVI [42] revealed that reduction takes place initially at the surface, followed by diffusion through the external oxide shell into the zerovalent iron core, resulting in breaking of As-O bonds and the formation of an Fe-As intermetallic, as illustrated schematically in Fig. 1.

Intraparticle diffusion, in combination with surface diffusion, is also believed to play a decisive part in determining the adsorption kinetics for removal of Cd²⁺ ions from water by nZVI [43]. The structure of the nanoparticles evolves with time due to reactions with the metal ions, thereby influencing adsorption. Examination by HRTEM has indicated the existence of coprecipitation and cavity corrosion structures in nZVI exposed to Co²⁺ solutions [44]. The presence of these cavities facilitates translocation of the adsorbed metal from the surface into the zerovalent iron core.

The effectiveness of nZVI in degrading chlorinated hydrocarbons, such as polychlorinated biphenyls and TCE, can be improved by decreasing the size of the iron nanoparticles to increase the reaction rate [45]. Equally beneficial is the use of a polymer stabilizer for the purpose of reducing aggregation to maintain the high specific surface area and sorption capacity of the nZVI. Bimetallic Fe-Pd nanoparticles stabilized with carboxymethyl cellulose have been employed to increase the degradation efficiency against TCE [46]. Hydrogen produced by corrosion of nZVI acts as an electron donor for the dechlorination reaction, while the presence of the Pd catalyst serves to increase the reaction rate with respect to pure Fe nanoparticles. Spherical silica particles can be used as carriers for nZVI to increase mobility and prevent aggregation, while at the same time enhancing the adsorption of TCE molecules due to the presence of surface silanol groups [47].

The operation of a large-scale permeable reactive barrier, for remediation of groundwater contaminated with TCE, was monitored over a ten year period [48]. Water samples were extracted from wells that were drilled at various locations in and around the barrier. The concentrations of TCE determined by gas chromatography-mass spectrometry (GC-MS) were consistently below the detection limit, compared to initial upstream values of several hundred mgL⁻¹. Mineral precipitates, mainly consisting of calcium and iron carbonate together with iron sulphides and iron (hydr)oxides, were detected inside the reaction zone. Microbial analysis, carried out by means of polymerase chain reaction denaturing gradient gel electrophoresis (PCR-DGGE), indicated the presence of sulphate and iron reducing bacteria. These may have improved the effectiveness of the reactive barrier by producing sulphite, which subsequently reacted with iron to form FeS, and by reducing iron (oxyhydr)oxides to green rust, since both of these can significantly increase reactivity towards TCE. The assistance provided by microbial dechlorination in increasing remediation efficiency has been confirmed in field tests [49].

The potential benefits and risks of nZVI have been assessed in full-scale tests at contaminated sites in the U.S. [50] and several European countries [51]. Some significant differences in practice can be noted, as indicated in Fig. 2. An example is the reluctance to employ bimetallic nanoparticles in Europe, owing to concerns regarding the toxicity of the catalyst metals, even though they are more efficient for degradation of organic compounds [52].

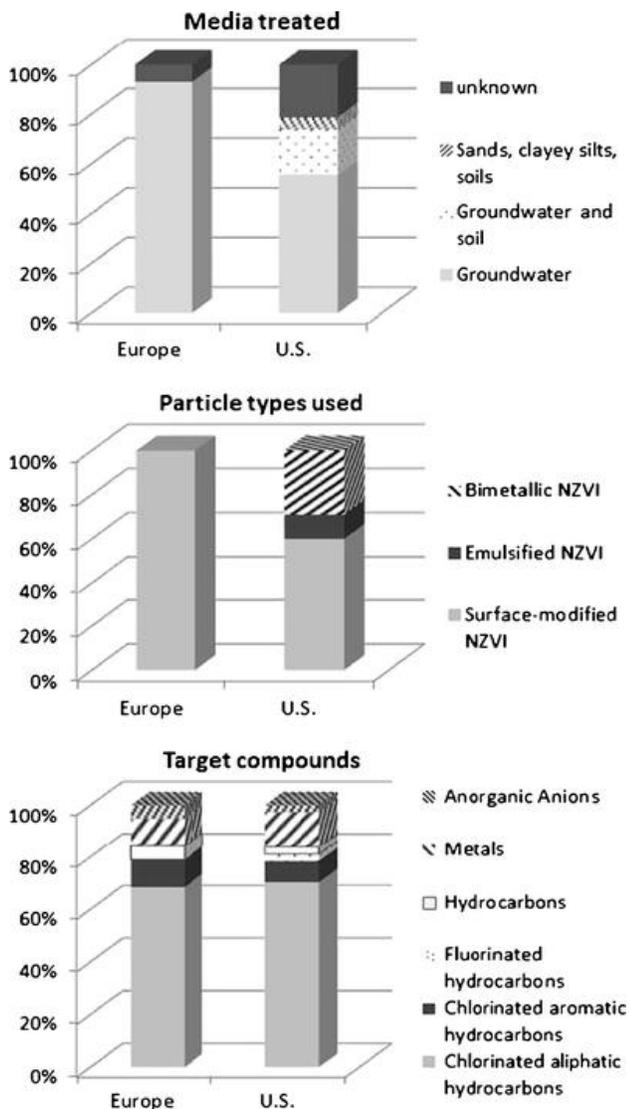


Fig. 2. Comparison of the treated media, nZVI types and target compounds for applications in Europe and the USA. (Reprinted with permission from Mueller, N.C.; Braun, J.; Bruns, J.; Černík, M.; Rissing, P.; Rickerby, D.; Nowack, B.; *Environ. Sci. Pollut. Res.*, **2012**, *19*, 550. Copyright © 2012, Springer.)

Some outstanding issues remain concerning aggregation, mobility, persistence and fate [53]. Surface modifications with polymers and surfactants have been studied as a method of promoting colloidal stability to inhibit aggregation and increase mobility. Stabilized iron nanoparticles have enhanced mobility in porous media, as a result of the more efficient, longer range transport of single particles compared to aggregates. Other approaches include the use of emulsified suspensions containing biodegradable oils, or immobilization of nZVI on larger particles of carbon or other materials.

While laboratory scale experiments and field tests have demonstrated the efficacy of nZVI in removing a variety of water pollutants, the eventual fate of these nanoparticles in the environment remains an open question. It can be expected that, as a result of aggregation, the majority will be deposited as iron oxide in the sediment, causing potential effects on both groundwater chemistry and aqueous organisms, together

with reduction in the permeability of the aquifer [54]. The parameters that can be employed to monitor the fate and to characterize the effects of nZVI in groundwater include pH, total Fe, colour, absorptivity, dissolved oxygen, water chemistry, and oxidation/reduction potential [55].

An investigation of the colloidal behaviour of iron oxyhydroxide nanoparticles by dynamic light scattering (DLS) and small angle X-ray scattering (SAXS) [56] has shown that they form stable clusters that remain in suspension for several weeks. These stable clusters are potentially extremely mobile and could therefore provide a route for long-range transport of adsorbed contaminants. The aggregation and sedimentation of concentrated nZVI dispersions in water occur rapidly, however, which will tend to prevent transport over large distances [57]. Both aggregation and sorption properties of iron nanoparticles are influenced by the presence of natural organic matter [58]. The mobility of nZVI is enhanced by sorption of NOM on the surface of the iron nanoparticles [59], which reduces the sticking coefficient, but transport is ultimately limited by the rapid falloff in velocity with distance from the injection point.

Two dimensional transport experiments indicated that non-stabilized nZVI were not transported away from the injection point in porous media, whereas particles stabilized with poly(acrylic acid) were [60]. This finding has important implications regarding the choice of the appropriate type of nZVI, either for creation of a static treatment zone or to be injected upstream and transported with the groundwater flow toward the contaminated region [61]. Embedding the nZVI in silica particles greatly improved transport properties in laboratory column and capillary tests, while functionalizing the silica surface with alkyl groups increased the adsorption efficiency for TCE [62]. Full-scale field trials, employing a fluorescein tracer to determine the mobility of carboxymethyl cellulose stabilized nZVI injected into an aquifer, indicated that less than 2% of the nanoparticles were transported as far as a metre [63].

The ecotoxicity and environmental safety issues surrounding the use of nZVI in remediation have been carefully considered [64, 65], with emphasis on the known effects of oxidative stress on cytotoxicity in microbial populations. The potential toxicity of nZVI originates from its high reactivity, which leads to the production of reactive oxygen species (ROS). It is important to understand clearly the effects of nZVI on the geochemistry and bacterial populations in aquifers. These bacteria are essential in promoting natural remediation processes and increasing the iron concentration in the water affects bacterial diversity [66]. On the other hand, the bactericidal properties of nZVI, which rival those of nanosilver, may be useful for inactivating harmful bacteria, such as *Escherichia coli* [67]. There is also experimental evidence that zerovalent iron exhibits selective toxicity against cyanobacteria [68], which despite an important role in conserving aquatic ecosystems can give rise to serious environment and health problems due to the production of toxins.

The toxicity of nZVI to freshwater and marine organisms is strongly dependent on whether the

nanoparticles are coated or uncoated, since this affects the reactivity and aggregation properties [69]. Rapid aggregation of uncoated nZVI reduces the likelihood of transport in the environment and thus the potential for causing toxic effects at locations distant from the remediated site. Partial oxidation by aging and surface modification with polyaspartate decrease toxicity by reducing redox activity, while promoting agglomeration and sedimentation [70]. Stabilization with carboxymethyl cellulose increases the toxicity as a result of the inhibitory effect on aggregation, while oxidation increases the capacity for bioaccumulation [71]. Interaction with NOM may significantly reduce the toxicity to bacteria, though the precise details of the cause of this remain still to be identified [72].

Nano titanium dioxide for water purification

Disinfection with chlorine has customarily been the preferred technique for drinking water purification. However, concerns regarding the production of toxic disinfection by-products (DBPs) and the development of chlorine resistance by certain microorganisms have stimulated research to find suitable alternatives. There exist numerous reports of the successful use of photocatalytic water treatment methods for bacterial disinfection [73] and degradation of toxic chemical substances [74]. Photocatalytic disinfection has been demonstrated to be effective against Gram-negative and Gram-positive bacteria as well as viruses, fungi, protozoa, algae and microbial toxins [75]. Anatase TiO₂ is the photocatalytic material most commonly employed in practical applications because it has the highest photoreactivity.

The mechanism of semiconductor photocatalysis can be explained the following way. Photoexcitation of electrons from the valence band to the conduction band, due to irradiation by photons of energy greater than the bandgap, results in creation of electron-hole pairs. Most of these electrons and holes will rapidly recombine but some migrate until they arrive at the surface of the photocatalyst. Here they can react with water and dissolved oxygen to form oxygen anions and hydroxyl radicals, which are able to inactivate bacteria by destruction of cell membranes and react with toxic organic chemicals to transform them into water, carbon dioxide and inorganic ions. There is evidence that other types of ROS, such as superoxide radical anions, hydroxide radicals and hydrogen peroxide, may also play an active part in destruction of microorganisms [76]. The disinfection process is not yet fully understood and the existing models for chemical disinfection processes cannot satisfactorily describe the complex reactions that take place during heterogeneous photocatalysis [77].

There are several factors that limit the performance of TiO₂ as a photocatalytic material. Firstly, because it is a wide bandgap semiconductor, with $E_g = 3.2$ eV, it is only able to absorb light in the ultraviolet (UV) range with wavelengths shorter than 388 nm. The UV component represents around 5% of the spectrum of solar radiation, while visible wavelengths constitute

approximately 46%. Secondly, recombination of the photogenerated electrons and holes decreases the quantum efficiency and hence the photocatalytic reaction rate [78]. Thirdly, only a relatively minor fraction of the total surface area of anatase crystals is typically composed of {001} facets, which are highly photoreactive because they contain unsaturated five-fold coordinated Ti atoms and two-fold coordinated O atoms [79]. Current research is therefore directed towards methods to red shift the light absorption into the visible region of the spectrum, ways of inhibiting recombination of electrons and holes, and synthesis of chemically engineered anatase TiO₂ nanocrystals that have a higher percentage of photoreactive {001} facets [80].

A substantial research effort has been dedicated in recent years to the development of visible light photocatalysts. The width of the absorption spectrum can be expanded by doping with anions or cations to modify the bandgap, thereby increasing the range of usable light wavelengths for photocatalysis. Anions occupy either substitutional O or interstitial lattice sites, while cations occupy substitutional Ti sites. The types of dopant that have been studied include rare earth elements, noble metals, transition metals and various non-metals [81]. Depending on the element used, doping may be carried out by ion implantation, sputtering, gas phase reactions, or chemical synthesis techniques. The non-metals commonly employed are B, C, N, F, P and S; the transition metals include V, Cr, Mn Fe, Co, Ni, Cu, Nb, Mo and Ru; while the noble metals comprise Pd, Ag, Pt and Au [82]. It appears that the influence of transition metal dopants on photoreactivity is determined to a large extent by their ionic radius [83]. In fact, the absence of a red shift after doping with Rb, Y and La is attributable to their incompatible ionic radii, which thus precludes occupation of substitutional Ti lattice sites [84].

Tests with N-doped anatase TiO₂ nanopowders indicated increased visible light absorption and photocatalytic activity against 2,4-dichlorophenol [85] and methylene blue or methyl orange dyes [86]. Similarly improved performance was achieved by doping with N and B individually, or co-doping with both, for degradation of methyl orange [87] and methyl tertiary butyl ether [88]. The photoreactivity of N-doped and N-F co-doped TiO₂, in experiments on methylene blue under solar radiation, increased with dopant concentration and was higher for the co-doped material [89]. A narrowed bandgap of 2.92 eV was measured in N-F co-doped TiO₂, which showed visible light photoreactivity to 4-chlorophenol [90]. C-doped TiO₂ exhibited enhanced absorption in the visible range and a higher photocatalytic degradation rate for the cyanobacteria toxin Microcystin-LR [91], while co-doping with N and C improved visible light absorption and photoreactivity towards phenol [92]. Multiple doping with C, N, B and F increased visible light photocatalytic activity for the degradation of methylene blue and procion blue dyes [93].

Reduction of the crystal size decreases the distance that the electrons and holes need to migrate to reach the surface, thereby diminishing the probability of recombination, while appropriate doping can further

decrease recombination. On the basis of experimental evidence obtained by means of surface photovoltage spectroscopy (SPS) and electrochemical impedance spectroscopy (EIS) on Fe-doped TiO₂ nanoparticles, it appears that doping with low concentrations of transition metals inhibits recombination and increases the charge carrier density by providing traps for holes and electrons [94]. Zn-doped TiO₂ showed a higher photocatalytic activity towards methylene blue than in the undoped state, owing to the effects of bandgap modification and a lower rate of recombination [95]. Higher photoreactivity towards methylene blue was also achieved by doping TiO₂ with Sm, which acted to suppress recombination, increase the adsorption capacity and promote the formation of hydroxyl free radicals at the surface [96]. Photocatalytic activity in W-doped nanocrystalline TiO₂ thin films was found similarly to be increased in comparison to undoped films [97].

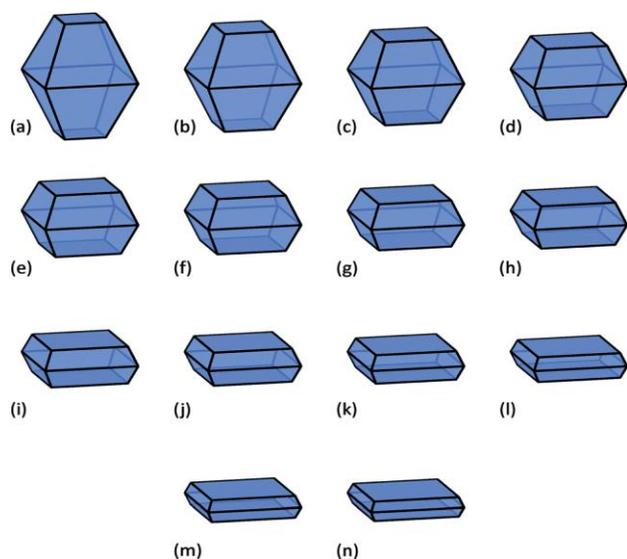


Fig. 3. Anatase TiO₂ nanoparticles with different percentage areas of {001} surfaces: (a) 10%, (b) 15%, (c) 20%, (d) 25%, (e) 30%, (f) 35%, (g) 40%, (h) 45%, (i) 50%, (j) 55%, (k) 60%, (l) 65%, (m) 70%, (n) 75%. (Reprinted with permission from Barnard, A.S.; *J. Mater. Chem. A*, 2015, 3, 60. Copyright © 2015, American Chemical Society.)

Co-doping with a combination of both metals and non-metals may be advantageous for increasing the photocatalytic activity by narrowing the bandgap to enable visible light photocatalysis and/or inhibiting recombination. Transition metal-nitrogen pairs have been extensively investigated for this purpose [98]. Cr-N co-doping of TiO₂ has been shown to increase visible light absorption by modifying the bandgap [99]. This enabled more efficient photodegradation of methyl orange than with N-doping alone. Co-doping with V-N was effective in reducing the bandgap of nanocrystalline TiO₂, resulting in increased visible light photoreactivity towards methylene blue [100] and petachlorophenol [101]. Theoretical studies have indicated that Fe-N co-doping modifies the electronic band structure of TiO₂, leading to narrowing of the bandgap causing visible light photoreactivity [102]. Visible light photocatalytic activity due to the same mechanism has also been observed in Fe-

C and Fe-S doped TiO₂. Other pairs of co-dopants investigated include V-B [103] and Ag-B [104], which increase photoreactivity by trapping photoexcited electrons to reduce charge carrier recombination.

The facility to manipulate the size, shape and surface chemistry of crystals is fundamental to the development of improved photocatalytic properties. Numerical calculations of the nanocrystal shape by application of density functional theory (DFT) have indicated that there is an increasing contribution to the Gibbs free energy due to the surface component [105], together with additional effects from edges and corners [106], as the particle size decreases. This has important ramifications for the way in which crystal size, through minimization of the total free energy, influences the shape. Simulations based on the DFT model correspond closely with the shape of anatase nanocrystals synthesized under quasi-equilibrium conditions [107]. Preferential growth of low energy {101} surfaces causes the bipyramid shape predicted by the standard Wulff construction to elongate as the crystal size is decreased, leading to a consequent reduction in the area of the {001} truncation facets. Reduction of the crystal size alone is therefore not sufficient to optimize performance but it is necessary also to increase the percentage area of photoreactive {001} surfaces, as shown in Fig. 3.

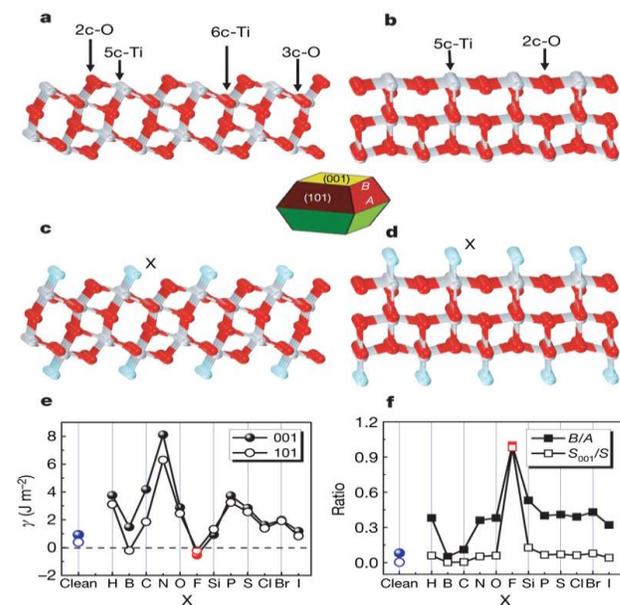


Fig. 4. (a, b) Clean (001) and (101) surfaces. (c, d) (001) and (101) surfaces with adsorbed atoms X. (e) Calculated energies of the (001) and (101) surfaces with various adsorbed atoms. (f) Ratio of lengths of the sides of the {001} facets and the bipyramid, B/A, and the percentage {001} surface area, S₀₀₁/S, for anatase crystals with various adsorbed atoms. (Reprinted with permission from Yang, H.G.; Sun, C.H.; Qiao, S.Z.; Zou, J.; Liu, G.; Smith, S.C.; Cheng, H.M.; Lu, G.Q.; *Nature*, 2008, 453, 638. (Copyright © 2008, Nature Publishing Group.)

Recognition of the influence that surface chemistry can exert on crystal morphology has led to research to discover techniques for shape controlled synthesis of TiO₂ crystals. This requires modification of the surface chemistry to promote preferential growth of the highly photoreactive facets [108]. Motivated by theoretical

calculations for different adsorbed atoms, the results of which are summarized in **Fig. 4**, that suggested that the surface energy of the fluorine terminated {001} surface is lower than that of {101}, the first successful attempt was made by employing a hydrothermal synthesis technique with an aqueous solution of titanium tetrafluoride as a precursor and hydrofluoric acid as the crystal growth controlling agent [109]. This method yielded large (~1 μm) flat single crystals with 47% of the surface consisting of {001} facets. Further refinement of the technique, with 2-propanal as an additional capping agent [110], allowed preparation of crystals of a few hundred nanometres thickness with 64% {001} facets. These showed an enhanced rate of hydroxyl formation per unit area compared to commercial TiO_2 .

For practical applications a much smaller particle size would be required. This was accomplished by employing a hydrothermal synthesis method with a titanium sulphate precursor in hydrofluoric acid [111] to produce octahedral anatase nanocrystals with diameters less than 100 nm, which displayed higher photoreactivity than their micron-sized counterparts. Other techniques for shape controlled synthesis of TiO_2 nanocrystals were subsequently developed. Gas phase reaction of titanium tetrachloride with oxygen was used to produce decahedral nanocrystals with {001} and {101} facets [112]. The photoreactivity of these was higher than that of octahedral anatase nanocrystals with only {101} facets, synthesized by the hydrothermal reaction of titanium dioxide in a potassium hydroxide solution [113].

A wide variety of different TiO_2 nanocrystal shapes have been produced by the solvothermal technique, with water vapour as a hydrolysis agent and adjusting the ratios of two capping agents, oleic acid and oleylamine, to regulate crystal growth [114]. Another method, using titanium tetraisopropoxide (TTIP), the ionic liquid [bmin][BF₄] and acetic acid in aqueous solution, enabled the growth of tetragonal cuboidal anatase nanocrystals with exposed {001} and {100} surfaces, the aspect ratios of which were dependent on the molar ratios of the starting chemicals [115]. The technological possibilities of tailoring crystal shape to increase the photocatalytic efficiency by preferential growth of the photoreactive facets, have led to intensive research in this area [116]. Further improvements in photocatalytic efficiency would be realizable by combining controlled crystal growth techniques with appropriate doping to activate visible light photocatalysis [117, 118].

Titanium dioxide is generally regarded to be of low toxicity and is a frequent additive in food products, pharmaceuticals, cosmetics and toothpastes [119]. Nevertheless, the nanoscale form of anatase TiO_2 has been reported to be 100 times more cytotoxic than rutile [120] and is also suspected of being a potential carcinogen [121]. The results obtained from in vivo ecotoxicity studies are highly variable and, because the nanoparticles that have been tested have different physicochemical properties and in many cases are insufficiently characterized, it is not possible to draw any definite conclusions regarding the properties that are responsible for biological effects [122]. However, it has

been suggested on the basis of in vitro studies in human epidermal cells that generation of ROS due to TiO_2 nanoparticles causes oxidative stress leading to cytotoxic and genotoxic effects [123]. Application of transcriptional profiling has allowed elucidation of those characteristics, such as particle size and surface functionalization, which influence gene and protein expression in pulmonary cells [124].

The toxic properties derived from in vitro studies on mammalian cells are in general determined at unrealistically high dose levels and are therefore difficult to extrapolate to realistic exposure scenarios [125]. The majority of toxicological studies on TiO_2 nanoparticles have tended to focus on the inhalation and dermal routes because these would represent the primary sources of occupational exposure [126]. Oral and gastrointestinal exposure, which would be more relevant to risk assessment for photocatalytic water treatment, have been rather less studied. However, the results of recent work on oral exposure in relation to applications in the food industry have indicated that any toxicological effects are negligible [127]. Provided that the nanoparticles are immobilized, as would generally be the case in photocatalytic water treatment applications, the probability of release and therefore of exposure can be considered to be relatively low, so that the greatest risk is probably presented by the formation of toxic intermediates.

Carbon nanotubes for desalination

Membrane technologies have diverse applications in liquid filtration and gas separation. The performance of existing polymer membranes for water purification is limited by the competing demands of selectivity versus permeability. However, isoporous membranes containing carbon nanotubes (CNTs) are emerging as a potential means to achieve elevated fluxes with high solute rejection [128]. For this reason they are considered to be promising materials for increasing the efficiency of seawater desalination systems and for removal of biological contaminants and toxins from drinking water [129]. CNT membranes have the potential to replace reverse osmosis membranes, with advantages in terms of lower energy consumption and reduction of membrane fouling [130].

There has been much recent progress in techniques for fabrication of self-assembled parallel arrays of CNTs, measuring their water transport properties and gaining a theoretical understanding of nanofluidics by means of molecular dynamics (MD) simulations [131]. By growing vertical aligned CNT arrays on a substrate by chemical vapour deposition (CVD), then infiltrating the interstitial spaces with a polymer, free standing permeable membranes can be constructed [132]. Theoretical studies indicate that the surfaces of the internal walls of CNTs offer very low frictional resistance to fluid flow, permitting much faster transport of water molecules through the nanotubes than predicted by classical hydrodynamics [133]. At the nanometre length scale, the Navier-Stokes equation is no longer applicable and the

behaviour is dominated by the motion of the individual molecules, influenced by modification of hydrogen bonding due to confinement [134]. Depending on the diameter of the nanotubes, the pressure-driven flow rate through such membranes may be several orders of magnitude greater than that expected from the Hagen-Poiseuille equation for continuum laminar flow, which needs to be modified to take into account the effect of liquid slip at the water-carbon boundary [135]. Simulation studies have been used to investigate the divergence from continuum flow conditions as the diameter of the nanotube decreases [136]. In the extreme case of CNTs of diameter less than 1 nm, single file motion of the water molecules can occur, as shown in Fig. 5, while for nanotubes with diameters larger than 1 nm there is a gradual transition to conventional type fluid behaviour.

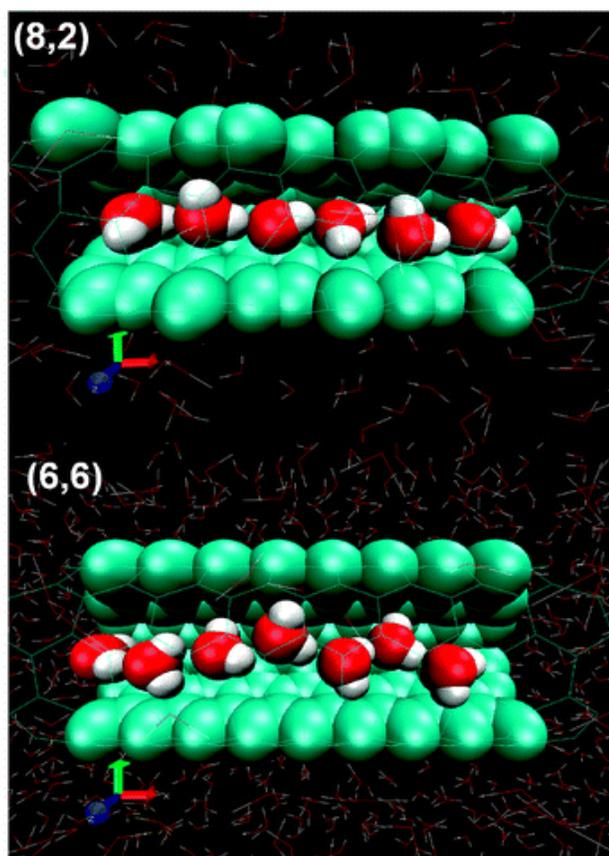


Fig. 5. MD simulation of single file transport of water molecules in single walled (8,2) and (6,6) carbon nanotubes (Reprinted with permission from Alexiadis, A.; Kassinos, S.; *Chem. Rev.*, **2008**, *108*, 5014. Copyright © 2008, American Chemical Society.)

Flow rates predicted by MD simulation were found to be in reasonable agreement with those measured experimentally in CNT membranes, after taking into account that the theoretical model assumes idealized flawless nanotubes, whereas the real ones inevitably will contain defects [137]. Both the orientation of the water molecules and the surface roughness of the nanotube walls can significantly affect the flow rate [138]. Diffusion of confined water molecules would be expected to follow Fickian type behaviour, if it is assumed that they are able to pass one another in the flow stream [139].

When this is not possible because the fluid flow is restricted within a narrow nanotube, single file motion will take place. Ballistic diffusion may occur under certain conditions, when the water molecules move in a coordinated manner as a result of the formation of stable hydrogen bonds. In wider nanotubes, because of Fickian diffusion of the water molecules along the central axis and ballistic type behaviour closer to the wall, the effective diffusion coefficient is dependent on the diameter [140].

Determining the water transport rate through CNTs embedded in membranes is complicated due to the need to know the effective pore density [141]. This problem was overcome by making measurements in an isolated long nanotube with a field effect transistor array to detect water flow by the variation induced in the electrical current [142]. The measured flow rates were lower than those found for CNT membranes but agreed well with results of MD simulations. These experiments confirmed the occurrence of a transition from continuum to sub-continuum flow conditions at a nanotube diameter of ~1 nm. Fluid transport is dependent on the strength of the interaction between oxygen atoms in the water molecules and the carbon atoms in the nanotube wall [143]. The curvature of the graphitic surface in CNTs might also exert an influence by reducing liquid/solid friction in small diameter nanotubes [144].

The properties of the confined liquid are dependent on the nanotube diameter relative to the size of the water molecule. Confinement produces alterations in the structure of the water, which forms a vapour-like phase in small (0.8-1 nm) diameter nanotubes, an ice-like phase for intermediate diameters of 1.1-1.2 nm, and a liquid-like phase for diameters larger than 1.4 nm [145]. Calculation of the forces required for ion and water transport through CNTs has shown that the energy barrier is much larger for ions than for water molecules [146]. Ions cannot be transported through nanotubes of diameters less than 1 nm but they are able to pass through wider ones. Rejection of ionic species in aqueous solution can theoretically be up to 98% under optimum conditions, using electrostatic charges produced by ionization of carboxylic groups at the nanotube ends to increase ion exclusion [147].

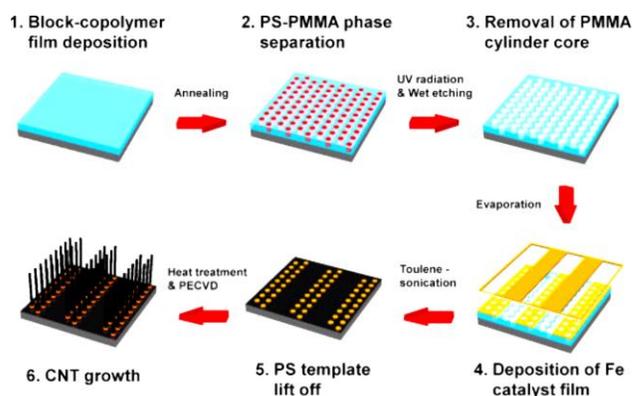


Fig. 6. Diagrammatic representation of the processing steps needed for fabrication of vertically aligned CNT arrays. (Reprinted with permission from Lee, D.H.; Shin, D.O.; Lee, W.J.; Kim, S.O.; *Adv. Mater.*, **2008**, *20*, 2480. Copyright © 2008, John Wiley and Sons.)

The insights provided by MD modelling into the physical mechanisms governing selective transport of water in nanotubes can be applied to the design of innovative membrane separation technologies [148]. Fabrication of the CNT membranes is a technically complex process based on growth by CVD of dense, parallel nanotube arrays on a substrate with metal catalyst particles deposited on its surface [149], as outlined in Fig. 6, followed by infiltration with a polymer matrix. The size of these catalyst particles determines the inner diameter of the nanotubes, while the water flux is proportional to their areal density and inversely proportional to the thickness of the membrane [150]. Theoretical calculations to evaluate the performance of CNT membranes in desalination applications have shown that ion rejection depends on the applied hydrostatic pressure and membrane permeability is affected by salt concentration [151]. Improvements in water permeability can be achieved by using mechanically densified vertically aligned nanotube membranes without a supporting polymer matrix [152].

Modification of the CNTs by adding differently charged functional groups can improve ion rejection at the expense of a decreased flux caused by the increased electrostatic interaction between the water molecules and carbon [153, 154]. Negatively charged or polar groups are effective for rejection of Cl^- ions, while negative carboxylate anion (COO^-) or positive amine cation (NH_3^+) groups aid rejection of Cl^- and Na^+ ions. MD simulations indicated that termination of the nanotubes with hydroxyl, carboxylic acid and carboxylate functional groups retards the water flow by decreasing the diffusion coefficient [155]. The increased concentration of sodium ions in the vicinity of the membrane-water interface forms an osmotic barrier that reduces the flow rate. Functionalization of CNTs with zwitterion groups, which have been shown theoretically and experimentally to increase water transport and ion rejection more than single charge functional groups, allows a compromise to be achieved between permeability and selectivity [156].

The fibrous nature of CNTs has led to concern that they might have toxic effects similar to those of asbestos. However, toxicity is related to length and whether they are in the form of straight, high aspect ratio fibres or tangled bundles [157]. Long, straight nanotubes can induce oxidative stress, inflammation and toxic or genotoxic effects like asbestos, whereas short or tangled CNT may not produce inflammatory response at all [158]. The potential risks of the use of CNTs for water purification and desalination will depend to a large extent on whether they remain tightly bonded within the polymer matrix or can be released into the water [159]. Although no data are available on release of nanotubes from membranes, tests on abraded CNT-epoxy composite dusts both in vitro [160] and in vivo [161] have shown negligible increased pulmonary toxicity compared to dusts from unmodified epoxy because a relatively small amount of free nanotubes were generated.

Extensive investigation has been carried out of the environmental and human health effects of CNTs in relation to their pulmonary toxicity, dermal toxicity,

neurotoxicity, cytotoxicity, translocation in the body, environmental fate and bioavailability [162, 163]. The human health risks of CNTs have been mainly considered in relation to inhalation exposure and dermal exposure, with comparatively little attention being given to oral exposure [164]. Ingestion by this route would evidently be of most concern for water filtration applications. Various factors are known to influence the toxicity of CNTs; these include size (length and diameter), shape (aspect ratio), impurities (from the metal catalysts), and functionalization (by surface coatings or with functional groups) [165]. Interestingly, functionalization with carboxylic acid was found to reduce cytotoxicity in comparison to untreated single-walled or multi-walled nanotubes.

Oxidative stress caused by CNTs is one of the main processes responsible for cellular damage leading to inflammation and apoptosis but non-oxidative stress mediated effects may also result in genotoxic and cytotoxic effects [166]. Physicochemical properties are crucial in determining the toxicity of different types of nanotubes. Short curved and longer straight multi-walled CNTs induced similar inflammatory responses, while longer nanotubes caused an earlier onset of damage to DNA together with increased evidence of pulmonary fibrosis [167]. Trace metal contaminants may lead to biological effects, such as generation of reactive oxygen species, even in the absence of acute toxicity [168]. Other characteristics that can have a significant influence on toxicity are the tendency for agglomeration or aggregation and surface chemistry [169].

Information on ecotoxicology of CNTs to aquatic organisms is relatively scarce, though evidence exists of toxicity in fish and other freshwater species [170]. Aquatic organisms in general appear to be more susceptible than terrestrial ones to exposure, while vertebrates tend to be more strongly affected than invertebrates [171]. Differences in surface properties of the nanotubes or the presence of other substances in the water, such as NOM and chemical pollutants, may influence agglomeration and sedimentation and thus uptake and bioaccumulation in aquatic plants and animals. Interaction with organic contaminants may increase the ecotoxic potential of CNTs, which because of their excellent sorption properties could act as carriers for toxic substances [172].

Conclusion and future perspectives

Exploitation of the properties of nanomaterials can make it possible to reduce treatment times and costs for groundwater remediation and drinking water purification. Remediation of aquifers with nZVI is less expensive than using conventional pump and treat methods, with complete reduction to non-toxic end products feasible in many cases. Photocatalytic treatment of drinking water with nano- TiO_2 enables chlorine-free disinfection and effective destruction of toxic contaminants. Rapid progress has been made in development of CNT membranes for application as selective water filters for desalination of seawater. These advances can be expected to

lead to improved water quality, alleviation of water scarcity and the reduction of waterborne disease.

The main risks associated with these applications are the potential toxicity of the nanomaterials and the possible formation of toxic intermediate by-products due to reactions with nZVI and nano-TiO₂. There are also concerns regarding unpredictable effects arising from release of nanomaterials into the environment, Immobilization of the nanomaterials on a substrate or in a membrane will reduce the risk of environmental release. Agglomeration and sedimentation may also prevent long range dispersion. Future progress in this area will be largely dependent on improvements in the reactivity and transport properties of nZVI by surface modification, increasing the percentage area photoreactive surfaces and inhibiting electron-hole recombination or attaining visible light photocatalysis in TiO₂, and functionalization of CNT to increase ion rejection. Potential barriers to development are that performance may be less effective than anticipated on scale up from laboratory testing and the high cost of nanomaterials production.

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