

Basic science of water: Challenges and current status towards a molecular picture*

Sheng Meng¹ (✉), Lauren F. Greenlee² (✉), Yuen Ron Shen³, and Enge Wang⁴

¹ Beijing National Lab for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

² Applied Chemicals and Materials Division, National Institute of Standards and Technology, 325 Broadway, MS 647, Boulder, CO 80305, USA

³ Department of Physics, University of California, Berkeley, CA 94720, USA

⁴ International Center for Quantum Materials, School of Physics, Peking University, Beijing 100871, China

Received: 1 March 2015

Revised: 23 May 2015

Accepted: 25 May 2015

© Tsinghua University Press
and Springer-Verlag Berlin
Heidelberg 2015

KEYWORDS

water,
molecular structure,
surface water,
water treatment,
nanotechnology,
water properties

ABSTRACT

Rapid developments in both fundamental science and modern technology that target water-related problems, including the physical nature of our planet and environment, the origin of life, energy production via water splitting, and water purification, all call for a molecular-level understanding of water. This invokes relentless efforts to further our understanding of the basic science of water. Current challenges to achieve a molecular picture of the peculiar properties and behavior of water are discussed herein, with a particular focus on the structure and dynamics of bulk and surface water, the molecular mechanisms of water wetting and splitting, application-oriented research on water decontamination and desalination, and the development of complementary techniques for probing water at the nanoscale.

1 Introduction

Water is extremely abundant in nature, covering approximately 70% of the Earth's surface in the form of seas, lakes, rivers, and morasses. In addition, water composes 58%–67% of the weight of the human body. Water exists in various forms and plays important roles in many diverse phenomena and processes (Fig. 1),

including rock efflorescing, soil freezing, regulation of the Earth's temperature, acid-base balance, ion transport, protein folding, catalysis, corrosion, cloud formation, lightning, and rainfalls. Water has also been found in outer space, in comet nuclei, and in cosmos dust.

Water is not only plentiful and important, but it is also peculiar in terms of its physical properties.

Address correspondence to Sheng Meng, smeng@iphy.ac.cn; Lauren F. Greenlee, lauren.greenlee@nist.gov

* Contribution of NIST, an agency of the US government; not subject to copyright in the United States.

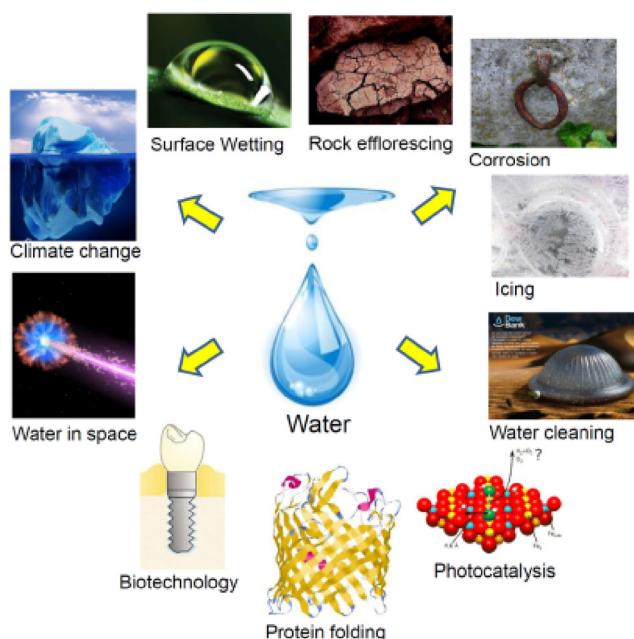


Figure 1 Water is intrinsically linked to a variety of natural processes and the development of new technologies.

Water has numerous oddities, many of which remain unknown. For instance, the melting and boiling points of water are much higher than expected for molecules of similar size. Water has a maximum density at 4 °C, which is unexpected based on the general laws of thermal expansion. A pressure increase can lead to both the freezing of liquid water and the melting of ice. The viscosity of confined water films, only a few molecular layers thick, shows a two- to threefold increase, rather than the diverging increase observed for other liquids [1]. In addition, water has an extremely large heat capacity, which is responsible

for the thermal stability of living organisms and of the earth's environment.

In recent years, an increasing interest towards understanding water and its properties (water anomalies) from the molecular point of view has taken place. Researchers have realized that water remains a key problem in modern science and technology, and an increasing number of studies have been devoted to deepening our understanding of the basic science of water (Fig. 2). An outstanding example is Nobel Prize laureate and nanoscience spokesman Dr. Richard E. Smalley. In his final years, Smalley listed his top ten grand challenges facing humanity for the next 50 years. Water is listed in second place, between energy (1st) and food (3rd) and the environment (4th). However, water is in fact intricately linked with challenges in sustaining our energy needs, food quality and consumption, and the health of the environment. Considering that the most usable energy in the natural world is generated from photosynthesis through water splitting, and that the “water/semiconductor” approach is promising in terms of producing renewable hydrogen fuel from artificial photosynthesis, water research is essential, and plays an important role in allowing researchers to solve energy challenges. Water will continue to be intimately connected to man-made energy production, whether through renewable energy sources (e.g., hydroelectric power), alternative energy technologies (e.g., novel battery and fuel cell technologies), or fossil fuel energy generation (e.g., oil and natural gas extraction). In addition, the manipulation and optimization of water-related

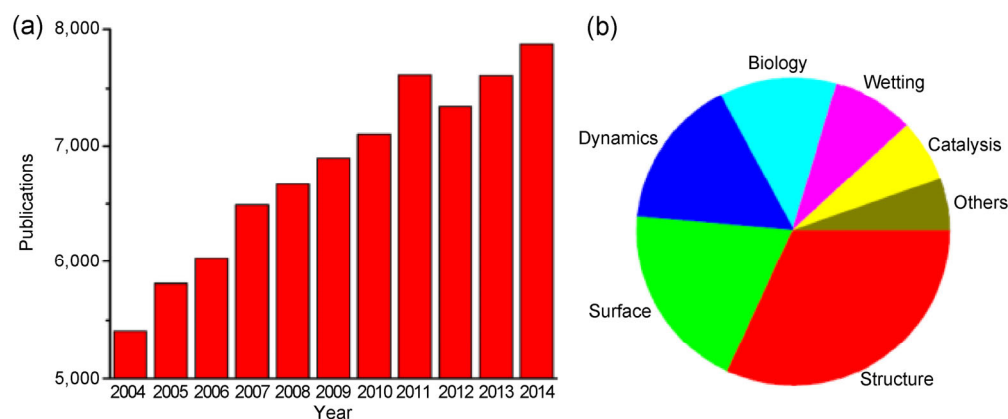


Figure 2 (a) Steady growth in the number of publications indexed in the Web of Science database with the term “water molecule.” (b) A fraction of publications in different areas of basic water research.

industrial processes plays a vital role in food and environmental sciences. As a result, water research (including water splitting and purification) is a significant challenge that humankind will face for many years to come.

However, even the basic structure of water both in bulk and in other forms (e.g., thin films) is unclear and still under heavy debate. Questions such as whether water molecules organize in a tetrahedral or chain-like ordering or whether liquid water contains free non-hydrogen-bonded OH groups await convincing experimental and theoretical evidence [2–4]. Well-controlled surface science studies have made significant progress in unraveling the structure of very thin, ice-like, surface-bound water clusters, and monolayers at very low temperatures (a few Kelvin) and under ultrahigh vacuum (UHV) [5–11]. However, how the knowledge obtained from UHV experiments translates to an understanding of the phenomena of water molecules under ambient conditions, or how it assists real world applications such as water catalysis and water decontamination remains to be seen. In addition, the quantum nature and ultrafast dynamics of water molecules and hydrogen bonds (HBs) under ambient conditions add further difficulties to developing a complete understanding of basic water science.

This perspective discusses the challenges and current progress on the development of basic water science at the molecular level. We focus on key problems in the science and technology of water that are representative and challenging, and that lie at the forefront of current water research activities. The discussion focuses on our current understanding of water structure, dynamics, and properties at the nanoscale, as well as current challenges and requirements in the field of water purification. We believe that the basic science of water, which forms the roots of physics, chemistry, and biology, remains an unresolved challenge and an excellent topic for interdisciplinary research.

2 Discussion

2.1 Major challenges for understanding bulk water

2.1.1 Molecular structure of liquid water

The molecular structure of liquid water has not yet

been fully determined and remains under heavy debate. Firstly, it is arguable what parameters should be used for characterizing the molecular structure of liquid water; the chosen parameters should be well defined in theory, and easily detectable by experimental means. Parameters proposed include the average number of hydrogen bonds (N_{HB}) of each water molecule, the number of free OH groups, the lifetime of a HB, and the space-time correlation of neighboring HBs. These parameters are readily accessible in theoretical models (albeit with unknown precision), but are challenging to probe experimentally. They are also sensitive to the exact conditions at which they are probed, and the experimental probe itself. Based on X-ray absorption and X-ray Raman scattering spectra, Wernet et al. proposed that the average N_{HB} is 2.2 for liquid water at 298 K in a sub-femtosecond snapshot [2]. This means that 80% of water molecules at room temperature are bound by only two hydrogen bonds serving as an HB acceptor and an HB donor. As a result, in liquid water, the majority of water molecules form a one-dimensional (1D) chain- or ring-like local structure with neighboring water molecules. This picture contrasts with conventional “static” views from averaged neutron and X-ray diffraction data over longer timeframes, where water has ~3–4 HBs in its first coordination shell, resulting in a tetrahedral network [3]. Recent results by Wernet et al. [2] also differ from molecular dynamics simulation results based on popular empirical force fields such as SPC and *ab initio* density functional theory (CPMD), where 80% of water molecules take part in 4 HBs. Subsequent X-ray absorption experiments performed by Smith et al. gave a different result, with an average of $N_{\text{HB}} = 3.3$ for liquid water [3]. Using Raman spectroscopy, Lin et al. presented evidence for the existence of the non-hydrogen-bonded OH, but this fraction was only 3% [12]. As a result, the question of the molecular structure of liquid water remains a matter of debate, with current consensus centering on $N_{\text{HB}} = 2.8$. Thus, in the near future, the structure of the hydrogen bond network and its ultrafast dynamics await accurate measurements with novel probes, along with a consistent theoretical explanation.

2.1.2 Phase transitions at low and high temperature

The phase diagram of water (ice) is complex and exhibits more than 15 crystal phases and a number of amorphous phases at various pressures and temperatures (Fig. 3). In addition, the phase diagram exhibits numerous new phases when confined at the nanoscale. Amorphous ice, formed by the rapid cooling of liquid water or by compressing ice crystals at low temperatures, is of particular importance, as it may serve as a useful, general model for understanding the local structure of liquid water and glassy materials. Low density ($\sim 0.96 \text{ g/cm}^3$), high density ($\sim 1.17 \text{ g/cm}^3$), and very high density (1.26 g/cm^3) amorphous ice can be identified as three distinct phases that can exist at 77 K under ambient pressure. The structures and transitions between these amorphous phases are currently under debate [13, 14]. The phase space between amorphous ice and supercooled liquid water between 160 and 230 K is not reachable because of the high tendency of crystallization. It is thus called “no man’s land” [15] and remains highly challenging in terms of experimental determination of the properties of supercooled water and phase behavior. There is also evidence for the existence of liquid-to-liquid phase transitions [16]. The details of these various phase transitions are likely important in

macroscale applications where temperature and pressure changes occur during water usage (e.g., hydraulic fracturing), or where confined water is critical to material performance (e.g., polymeric membrane water filtration).

Water exhibits a supercritical point at 647 K and 22 MPa, where the difference between the liquid and gaseous phases disappears. However, as HBs are still present under such extreme conditions [17], it is of interest to determine under what conditions the HB will completely disappear. At 673 K and 40 MPa, there is still approximately one HB per water molecule, with the number of HBs per molecule decreasing to 0.6 at 873 K and 134 MPa [18]. The presence of water monomers, dimers, clusters, and small droplets/particles in the atmosphere plays a central role in determining the physical “fitness” of our planet’s environment. For example, despite the diminishing concentration of water dimers in the atmosphere, it was reported that 4.6% of the sunlight is absorbed by water dimers at 298 K [19]. It is therefore vital to investigate the optical absorption of water at a range of wavelengths, and to study the thermal, chemical, and electrical properties of molecular water complexes and nanoparticles.

2.1.3 Are water anomalies unique?

Water and ice differ from ordinary liquids and solids, and their unique properties are known as water anomalies. Indeed, water exhibits more than 69 anomalies, some of which are well known, including its density maximum at 4 °C [20–23], which maintains both the temperature of water bodies in the winter, and water’s unusually high surface tension. Other anomalies are less well known, such as the specific heat capacity minimum and maximum at 36 °C and –45 °C, respectively [24–30]. Whether these anomalies are relevant to the body temperature of homothermal animals, developing over billions of years of evolution, remains an open question. Some water anomalies are controversial, and require more accurate scientific phrasing and explanation. For example, the Mpemba effect [31] states that hot water freezes faster than cold water. It has been argued that only water containing significant dissolved gasses or other contaminations exhibits this effect, while others believe that it also applies to pure water. The reasons behind this effect

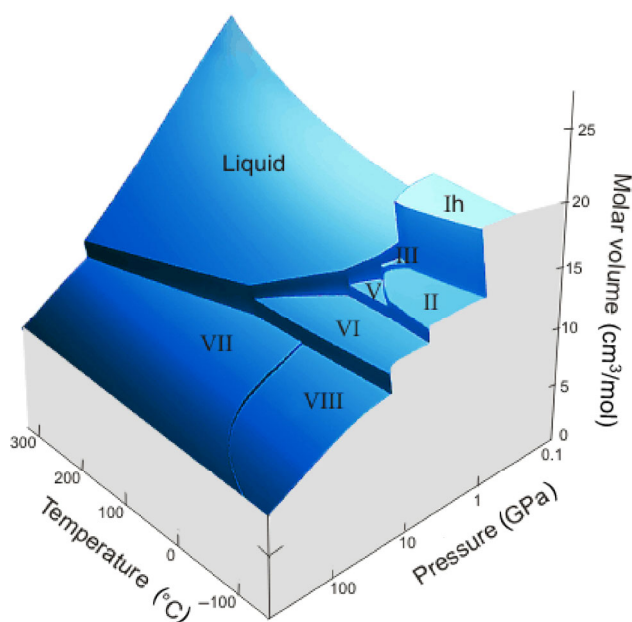


Figure 3 The phase diagram and associated molar volume of water under different conditions.



are complex, with one or more factors, including supercooling, heat gradient induced convection, and evaporation, being dominant [19–24]. Intensive research efforts to rationalize and develop a full understanding of the Mpemba effect and other water anomalies are ongoing, and often remain a matter of debate. In contrast, it remains to be seen whether these anomalies are unique to water. Some anomalies currently attributed solely to water may be generalized to other solids and liquids; for example, the density of frame-structured solids including Si, Ge, and SiO₂ also increases with temperature [32–34]. Accurate data obtained from studies devoted to water may therefore be applicable as models for other condensed matter systems.

2.1.4 Quantum effect and the half-naked proton

Hydrogen plays a critical but mysterious function in determining the peculiar properties of water. It is often assumed to be a “half-naked proton” (i.e., missing a part of its one full electron) rather than an “atom” when chemically bonded to other elements. HBs, formed between hydrogen and another electronegative element, are the source of many water anomalies. Due to the low mass of hydrogen, it is widely suspected that the quantum effects of hydrogen play an indispensable role in the molecular structure of water and its resulting HBs [35–38]. It is therefore insufficient to treat hydrogen classically as a point particle in conventional water models, which are typically based on either empirical force fields or *ab initio* electronic structure calculations [39, 40].

Recent progress suggests that the quantum effect of hydrogen plays a key role in determining the fundamental properties of water. Due to the quantum nuclear effect, which delocalizes hydrogen distribution and modulates HB strength, liquid water (H₂O) behaves like deuterated water (D₂O) at elevated (5–30 °C) temperatures [41]. The quantum effect of the hydrogen nucleus was found to reduce the barrier of proton transfer from 55 to 15 meV during OH[−] transport in liquid water, therefore promoting the proton transfer/tunneling probability [37]. However, for H₃O₂[−] clusters in the gas phase and hydrated H₃O⁺ in liquid water [35], this barrier is cancelled by nuclear quantum effects. The rearrangement of HBs through quantum

tunneling is essential to the rapid diffusion of water dimers on Pd(111), observed in scanning tunneling microscopy (STM) experiments [36]. Generally, the quantum effect of hydrogen may explain why plants irrigated with D₂O grow more slowly (c.f., H₂O), and why D₂O is toxic to many animals. Determination of how the static and dynamic properties of water change in the quantum-mechanical treatment of hydrogen is a major challenge for uncovering water abnormalities, and requires significant advances in both theoretical and experimental tools.

2.2 Molecular behavior of surface water and confined water

To understand the behavior of water, it is important to understand how water interacts with materials such as solid surfaces and biomolecules. Many important processes involve or require surface water, such as water photolysis and purification, performed through surface adsorption and interactions. As a result, surface water is the natural environment of a material surface, which must be embraced when moving from an UHV environment to near-ambient conditions. Surface water also exhibits different physical properties to bulk water [42–45], although the magnitude and impact of these differences on the surface behavior of water molecules is often unclear. Investigation of the interactions between water and material surfaces is useful for uncovering and controlling the structure and properties of water.

Solid surfaces, which can serve as ideal model systems for the study of water-material interactions, have received much attention in the literature [42–44]. With rapid advances in surface science probes, information on water structure and electronic interactions are now available with unprecedented molecular details (Fig. 4). Planar water layers with an atomic thickness of ≤ 0.1 Å were found on Ru(0001) [6], and were later assigned to half-dissociated water films (H₂O + OH) [7]. Wetting layers on Pt(111) exhibit a complex ($\sqrt{39} \times \sqrt{39}$)-R16.1° pattern with respect to the (1 × 1) surface lattice of Pt(111), which contains pentagonal and heptagonal defective rings in its HB network [10]. At low coverage, water forms a 1D chain on Cu(110), consisting of five-membered rings alone [9]. Such findings have led researchers to

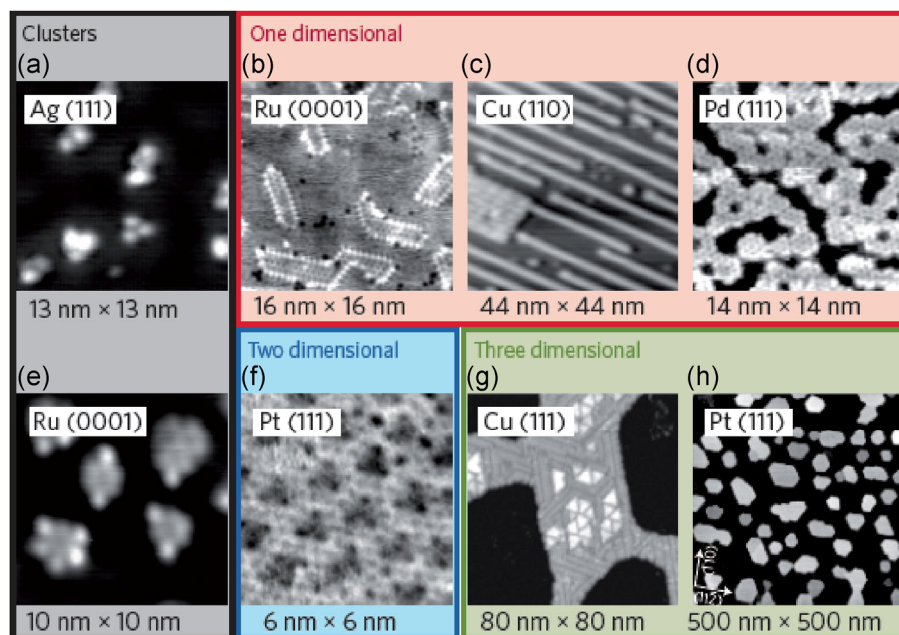


Figure 4 Different forms of water on metal surfaces observed by STM experiments: (a) water clusters on Ag(111); (b) water ribbon structures on Ru(0001); (c) water chains with a width of about one water hexagon; (d) water laces on Pd(111); (e) water clusters on Ru(0001) with bright and flat spots indicating water molecules in upright and flat orientations, respectively; (f) 2D water overlayers on Pt(111); (g) 3D ice pyramids on Cu(111); and (h) 3D ice islands on Pt(111). Reproduced with permission from Ref. [11], © Nature Publishing Group 2012.

discard the traditional “bilayer” model [5] for water on surfaces that was speculated in early 1980s. The basic tenet of the traditional “bilayer” model states that the first layers of water resemble layers in bulk ice, which comprise buckled hexagonal rings [11]. Despite these recent advances, which have greatly enriched our knowledge regarding the structure and behavior of water, a number of problems have yet to be solved for water at surfaces.

2.2.1 The controversial structure of surface water

Besides a few exceptions (e.g., single crystal metallic surfaces such as Ru and Pt), the precise molecular structure of water on material surfaces is unknown. The majority of materials have a complex surface structure, which may not be well defined or homogeneous. The molecular structure of water on these complex surfaces is therefore extremely difficult to measure or predict. In addition, surface water is denser than bulk water even at a hydrophobic surface, due to water’s high surface tension, thus resulting in differences in molecular structure on the heterogeneous material surface. It is also arguable that surface water

at ambient conditions appears ice-like in terms of its structure, diffusion behavior, and thermal properties [46–48]. However, whether water molecules are in a liquid or solid/solid-like state at a surface, the molecules and the HB network remain dynamic, thus creating additional difficulties in its characterization.

Even at clean, single-crystal model surfaces under a UHV environment, water structures are controversial. With the assistance of high-resolution real space images obtained by STM, Cerda et al. observed the rosette structure of water stripes (the microscopic morphology of “snow”) when water adsorbed on a Pd(111) surface (Fig. 4(d)) [8]. In contrast, state-of-the-art density functional theory calculations showed that a water monolayer at full coverage is more stable by 30–50 meV per molecule of water than the rosette structure. However, a full coverage water monolayer was never observed experimentally [49]. It therefore remains to be seen whether the rosette and full coverage structures of water layers are correct, or whether the present exchange-correlation functionals to describe the quantum electronic interactions in density functional theory are accurate. To remove such



ambiguities, further improvement in the accuracy of theoretical methods and the resolution of experimental probes is necessary.

2.2.2 The molecular picture of surface wetting

Surface properties, such as mechanical properties (i.e., lubrication), chemical reactivity, and hydrophilicity, among others, are extremely sensitive to water wetting. For water structures at the nanometer scale that are not in the liquid state, the macroscopic concept of water contact angle does not apply. A new measure of surface wetting at the molecular level must therefore be developed.

Rather than averaged surface tension measurements, Meng et al. proposed that surface wettability could be rationalized by the energetics of chemical bonds formed between a water molecule and a surface, and with its water molecule neighbors [50]. A new microscopic parameter, the hydrogen bond energy to water adsorption energy ratio (for water monomers), $\omega = E_{\text{HB}}/E_{\text{ads}}$, was therefore defined as surface wettability [50]. In general, $\omega = 1$ is the border between hydrophilic and hydrophobic interactions (where $\omega < 1$ for hydrophilic interactions and $\omega > 1$ for hydrophobic interactions), and a simple correspondence between ω and contact angle, θ , where $\theta = 180^\circ - 108^\circ/\omega$, exists for certain surfaces. Calculated wettability data shows an order of $\omega_{\text{Ru}} \leq \omega_{\text{Rh}} < \omega_{\text{Pd}} \leq \omega_{\text{Pt}} < \omega_{\text{Au}}$, giving a wetting order of $\text{Ru} > \text{Rh} > \text{Pd} > \text{Pt} > \text{Au}$, in agreement with experimental results [51]. This wetting order essentially results from variation in water–metal interactions, due to only small changes in HB energy.

Besides the microscopic characterization of wettability, a better understanding of the molecular nature of surface wetting is required. One example is the unusual observation that water does not wet on a surface water layer [52]. In addition, Zhu et al. found that wetting angles have a nontrivial dependence on the surface lattice constant; a hydrophilicity maximum is observed for surfaces with a lattice constant matching the lattice constant of ice, even if the surface energy decreases [53].

2.2.3 How does water split on photocatalysts?

The production of hydrogen gas (H_2) from water via photosplitting, for use as a fuel, is a promising

alternative to the production and use of fossil fuels. The production of H_2 therefore represents an important step towards solving current and future global energy needs through alternative and renewable energy sources. However, the sunlight-to- H_2 energy efficiency remains very low (1%–2%), and materials used in the process are costly. To make photosplitting a viable alternative, new materials with higher photocatalytic activity and efficiency must be developed. Recent years have witnessed rapid progress towards efficient novel materials for water photosplitting, including MoS_2 and WS_2 nanoflakes and nanotubes for electrocatalysis [54–56], ZnO nanorod photoanodes activated in visible light by Cu ion implantation [57], Bi_2WO_6 quantum dot-intercalated ultrathin montmorillonite nanostructures [58], and alumina-coated Ag nanocrystal monolayers as surface-enhanced Raman spectroscopy platforms for the direct spectroscopic detection of water splitting reaction intermediates [59]. Despite great research efforts [60–63], the primary obstacle remains the lack of fundamental understanding of the physicochemical processes involved in water splitting at surfaces. Oxygen atoms at the original surface lattice participate in O exchange and O_2 generation. However, it is unclear whether the theory of electron-hole separation in heterogeneous semiconductor surfaces is relevant, or whether water photosplitting is simply the product of thermodynamic ground-state reactions after electron-hole recombination and local heating [64]. The atomic site for H_2O oxidation and reduction is also a source of current debate [64].

2.2.4 How special is confined water?

Water in a confined space exhibits unusual behavior that differs from the bulk. Phenomenologically, water can be confined in three ways, namely 1D pores, confined 2D layers or thin films, and 3D cavities of different shapes (Fig. 5). Examples include water in porous Vycor glass, water between biomembranes, and water in the grooves of protein and DNA molecules. Recently, laser irradiation has been employed to control the encapsulation of water inside individual single-walled carbon nanotubes [65]. Generally, confinement may lead to two different effects. Firstly, a reduction in water space, resulting in the shortening of hydrogen

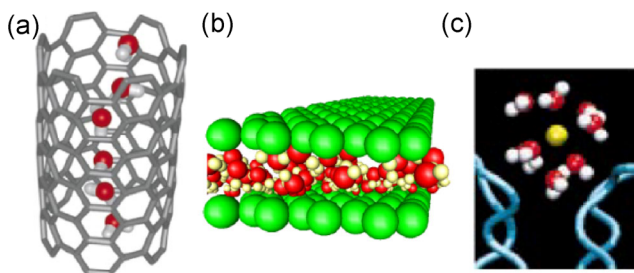


Figure 5 Different geometric confinements on water: (a) cylindrical restriction; (b) confinement between two parallel surfaces; (c) cave or spherical restrictions.

bonds and reorientation of water molecules. At its limit, the reduction in water space may lead to the penetration of water molecules into regions where the molecules are not allowed to exist, i.e., the so-called “excluded volume” effect [66]. Secondly, HB disruption and the formation of new water–surface bonds at the confining interfaces, phenomena proven critical to maintain biomolecule stability [67], may also occur.

Confinement modifies both the structure and the dynamics of water. In addition, it leads to a variety of novel phenomena, many of which remain poorly understood. For example, peaks in the oxygen–oxygen radial distribution function measured by neutron scattering are softened upon confinement [66]. Water molecules confined in carbon nanotubes form a variety of new phases that are not observed in bulk water [68]. Furthermore, ice nanotubes with square, pentagonal, hexagonal, and heptagonal rings can form in carbon nanotubes, with diameters varying from 1.1–1.4 nm [68]. These new phases are not only scientifically interesting, but also offer new opportunities for water transport and purification [69].

Confined water also determines the structure and functions of its confining environment in various ways, including polar ordering, intermolecular coupling, viscosity, dissipation, and conformational transformations [70, 71]. Furthermore, ions in confined aqueous solutions add a further layer of complexity, since the ionic coordination number, the structure of the hydration shell, and the ion–ion interactions are different in a confined environment [72, 73]. Proton transport through water nanotubes in an Eigen-like hydration state in molecular porous crystals has been studied experimentally [74]. Large anions prefer to bind at the surface of aqueous solutions, while small

anions and cations remain in the bulk [75]. Understanding these behaviors is important, and will attract intensified attention in coming years.

2.2.5 Biological water

Water is the medium for life on Earth. All biomolecules survive in water, while biological processes take place in aqueous solution. The role of water in biology can be substantiated by numerous examples at different levels of complexity [76, 77]. Water is a natural component at fixed positions in many proteins (so-called “biological water”) [78, 79]. The HBs of water can tie different biomolecules or different parts of biomolecules together (e.g., the ribonuclease water bridge). Water acts as a buffer to maintain DNA and proteins in their native states, while also acting as a messenger, mediating DNA–protein interactions. Water splitting into hydrogen and oxygen by the hydrogenase enzyme, to produce electrons, is the key process for driving photosynthesis in plants. Water can be transported 100 m to the top of trees after death of the tree, which is 10× higher than atmospheric pressure can sustain.

Although the importance of water is widely known, knowledge of how water is involved in given biological processes is unclear. The complexity of biological water lies in that the structure and function of water are closely coupled to the surrounding environment, which is composed of biological molecules, ions, and other water molecules, thus offering a large and complex system for any experimental or theoretical study. The liquid state of water, and in particular, its fluidity and dynamics, is another fundamental challenge for quantitative *in situ* measurements and theoretical modeling. Furthermore, the long-range polarization of water causes difficulties in distinguishing interfacial water (i.e., active water molecules in close contact with biological molecules) from the bulk medium. Developments in optical spectroscopy to differentiate the shell structure of water molecules around ions, molecules, and surfaces from bulk water represent progress in this direction [80].

2.3 Water purification

2.3.1 Water in the environment: Pollution and contamination

Access to clean water for residential and commercial

use is the cornerstone of all industrialized nations, with water needs continuing to increase as the global economy continues to advance and grow. Water pollution can occur from a variety of sources, and can be extremely difficult to control and treat once pollutants have entered the water system. Both groundwater and surface waters (e.g., lakes and rivers) can be affected by pollution, with some pollutants being naturally-occurring components of water sources that prevent the water from being used as drinking water or process water (e.g., salts and natural organic matter).

Worldwide, each nation has specific water contamination issues that must be dealt with to provide people and industry with clean and ample water supplies. Some contamination issues are specific to the geology and environment of the geographic region (e.g., locations with naturally occurring high arsenic content in the ground water [81–90]), while other issues stem from anthropogenic sources and industrial activity [91–93], as well as water treatment strategies and policies. For example, the explosion of population and economic growth in northern China, which has minimal water resources, has caused a severe water-shortage issue, and prompted the introduction of water conservation and water supply projects [94–96]. In the USA, the southwest states of the country (i.e., California, Arizona, Nevada, and New Mexico) suffer from water scarcity, with projects such as the Colorado River Aqueduct and salt-water desalination projects [97–99] being used to relieve water demand. Both China and the USA suffer from pollution from a wide range of industrial and farming activities. The challenge for such nations is to balance industrial and economic success with environmentally sustainable practices

that allow continued access to and the protection of natural resources, such as clean water.

In a number of countries, the primary water contamination issue is microbial contamination. Many lack basic access to clean water, with their water sources being contaminated with bacteria and other organisms that can cause illness, disease, and death. For these nations and their inhabitants, a lack of financial resources, water treatment methods, access to nearby water resources, and training on simple water decontamination methods prevent significant improvements in the availability of clean water. In such countries, even daily access to water for cooking and drinking is a challenge. In addition to water being a basic requirement for survival, limited access to water causes a myriad of associated challenges, including increased risk of disease and infection, and reduced education and professional opportunities, particularly for women and children [100, 101]. Such problems stem from the time required to obtain fresh water on a daily basis, an activity that largely rests on women and young girls, which significantly reduces the time available for activities such as attending school or running a business.

In addition to microbial contamination, several other types of water contaminants exist, including particles and colloids, salts, heavy metals, algae, compounds promoting algal growth, industrial/pharmaceutical organic compounds, pesticides/herbicides, and natural organic matter. For organic contaminants, it is important to know the size, molecular conformation, functional groups (e.g., halogen, phosphate, nitrate, benzene, carbonyl, or carboxyl), polarity, charge, and hydrophilicity/hydrophobicity (Fig. 6). For heavy metals, it is useful to know the speciation of the

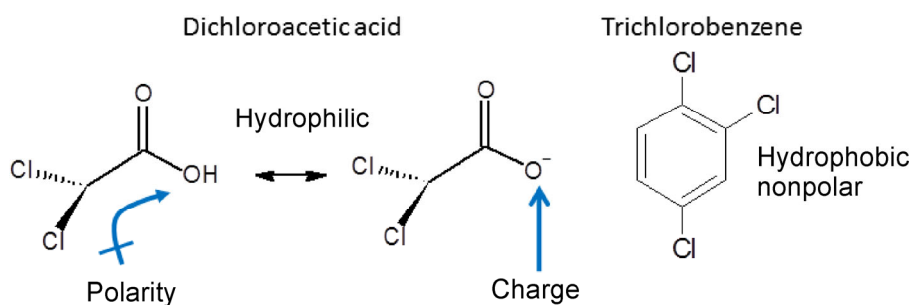


Figure 6 Two common drinking water contaminants, dichloroacetic acid and 1,2,4-trichlorobenzene, and their polarity, hydrophilicity, and charge properties.

metal in a water matrix and the solubility of the metal as a function of pH (Fig. 7) and as a function of the concentrations of key anions in solution (e.g., carbonate, hydroxyl, nitrate, and phosphate anions). These properties are intrinsically linked to molecular level interactions between the compound of interest and surrounding water molecules. For salts (except heavy metal cations), the overall salt concentration must be known, and the concentrations of sparingly soluble salts (e.g., calcium, barium, and strontium) must be measured. During treatment, knowledge of such details is crucial to be able to remove each type of contaminant, whilst enabling the treatment processes to work efficiently for long periods without significant issues. The majority of water treatment processes involve the contact of water with a solid or gas at an interface, contact between water and beneficial microbes, or contact between water and specific chemicals to achieve removal of specific water contaminants. Thus, the study and understanding of surface water, confined water, and biological water are critical to the improvement of water treatment materials and technologies.

Many reports have concluded that the number and types of water contaminants have increased in recent years [102–105]. Several factors that have contributed to our increased knowledge of water contaminants include the improved ability to measure a wide variety of contaminants at lower concentrations, the increase in number and types of industries using water in industrial processing steps, and the increase in direct reuse of treated or untreated wastewater as a drinking water resource. The development of analytical instruments and techniques for the measurement of specific water contaminants at low concentrations (parts per billion, ppb, or lower) has allowed the recent detection of water contaminants that have likely been present in drinking water sources for many years. Such techniques include gas chromatography (gas phase separation of analytes based on size and the interaction of functional groups through a packed column), liquid chromatography (liquid phase separation of analytes based on size, solvent-analyte interactions, and analyte-column interactions), inductively coupled plasma mass spectrometry (to measure cationic metals in solution), flame ionization (for accurate measurement

of low concentrations of single cationic metals), ion chromatography (for measurement of anions in solution), and total organic carbon analysis (to measure the organic carbon concentration of a solution), among others. Development of these techniques have allowed the identification of industrial chemicals, pharmaceuticals, pesticides, and heavy metals in drinking water sources, as well as toxic compounds resulting from disinfection strategies (i.e., byproducts from reactions between naturally occurring organic matter and chlorine, chloramines, or ozone) [106–109]. The advent and growth of the industrial age has resulted in a large number of processes that produce wastewater and water contaminants, from paper and textile production, to the electronics and personal care products industries. Furthermore, the worldwide population explosion, with associated growth of major cities within the same watershed, has resulted in both direct (i.e., treated wastewater is taken directly from a wastewater treatment plant and sent directly to a drinking water treatment plant) and indirect (i.e., treated wastewater is released into a receiving water body such as a river and is taken into a drinking water treatment plant downstream) water reuse. As industrial development and diversification, along with water requirements for both residential and industrial activities, continue to grow, the continued development of analytical techniques will undoubtedly allow the identification and measurement of additional water contaminants.

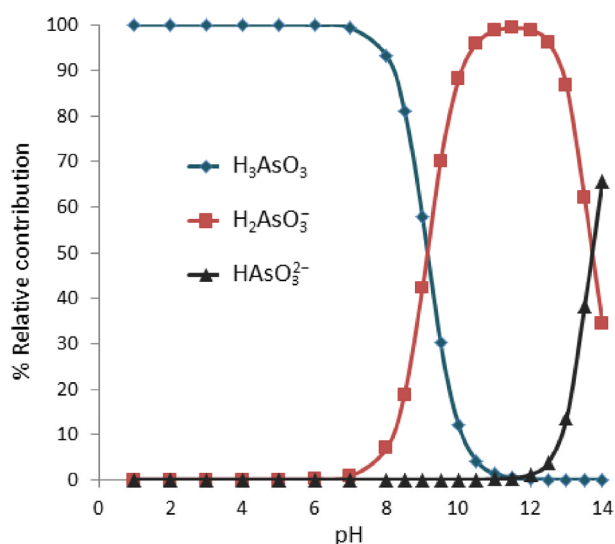


Figure 7 Arsenic(III) speciation as a function of pH in a typical groundwater composition.

We must therefore continue to work towards understanding the basic science of water, including the behavior and properties of water contaminants, to enable improvements in water treatment and water quality.

2.3.2 Water purification: Current status and challenges

A number of traditional treatment processes continue to be effective for the treatment of a range of contaminants in water treatment plants. However, as the demand for limited water resources increases, and communities move towards water recycling and reuse strategies, the number and complexity of water contaminants continues to increase. In addition, as industrial and consumer products continue to advance and increase in number, we will likely see a continued increase in the number and types of contaminants in our water sources. Furthermore, as detection strategies for specific types of water contaminants continue to improve, contaminants that have previously gone undetected will be identified, increasing the general awareness of the types and concentration levels of contaminants in different water sources. In addition, with a worldwide increase in water demand, an increasing number of impaired water sources must be used to supplement traditional fresh water lakes, rivers, and groundwater. Thus, there is a requirement for treatment materials and technologies that can provide improved water quality, both in terms of process efficiency and contaminant removal effectiveness. Furthermore, novel and improved technologies must be cost-effective to compete with incumbent, traditional technologies.

Several traditional treatment processes include sand filtration, dissolved air flotation, precipitation and flocculation, sedimentation, chlorination (i.e., disinfection), and use of granular activated carbon [110–113]. More recently, membranes have become an important water treatment technology that continues to grow in both usage and importance. Membranes are generally used as a physical barrier to a specific size of contaminants, acting as a filter or size-based sieve, removing contaminants larger than the membrane pore size while allowing smaller contaminants and water molecules to pass through the membrane. Membranes are typically made of either a polymer or

a ceramic material and can be designed to have a specific pore size or pore size range. They have been developed to the point where a variety of membranes is available for different contaminant types and sizes. Furthermore, different membrane configurations and technologies designed for specific industries (e.g., milk production, beer production, salt-water desalination, and solvent separation) have also been developed [114–119]. Today, several commercial membrane technologies are available for the removal of contaminants as large as particulate matter and colloids ($\sim 5\text{--}10\text{ }\mu\text{m}$), to contaminants as small as a monovalent salt ions (e.g., sodium or chloride ($0.1\text{--}1\text{ nm}$)) (Fig. 8).

Membranes have also been combined with other processes to address specific needs in water treatment and water production. For example, membrane bioreactors combine the use of a polymeric membrane with a controlled biological environment to treat wastewater. The membrane acts as a filter to small contaminants, while the microbes actively degrade organic contaminants. Another example is membranes for engineered osmosis, a process that includes reverse osmosis desalination, forward osmosis, and pressure retarded osmosis. Membranes were first

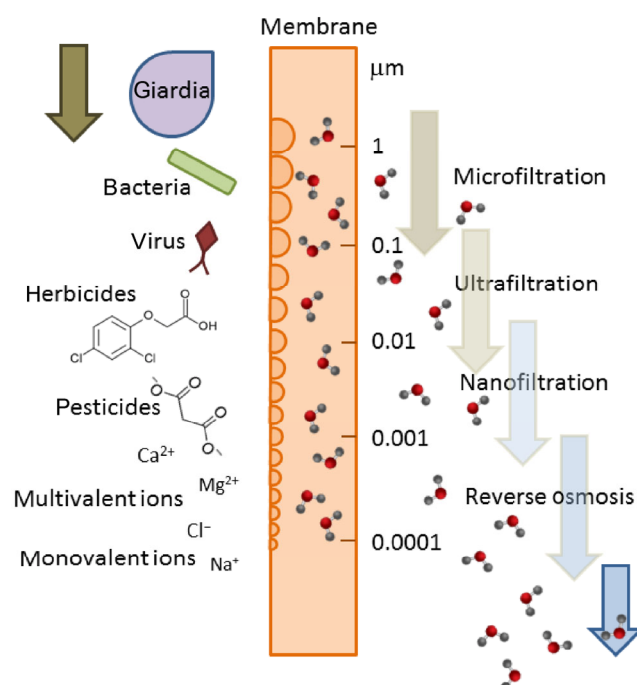


Figure 8 Polymeric membrane illustration displaying different types of polymeric membranes, pore size ranges, and example water contaminants removed for each pore size range.

developed for reverse osmosis desalination, which uses hydrostatic pressure to drive the separation of salt from water molecules. Water molecules then pass through the reverse osmosis (RO) membrane, while the majority of salt ions are retained by the membrane [120–124]. More recently, the RO membrane has been modified and novel membranes have been developed for forward osmosis and pressure retarded osmosis applications, where the driving force for separation is the osmotic gradient rather than hydrostatic pressure [125–129]. The change in driving force and differences in the water separation process resulted in the development of a range of membranes based on the need of each process.

The use of nanoparticles and nanostructured materials for water treatment is a relatively new area, but one that has received much attention and research focus. Several key materials are currently in use for water treatment, with many more under development. Generally, nanoparticles possess enhanced or unique properties due to their small size and variable morphology. Metallic, metal oxides, carbon-based nanoparticles, and nanocomposite materials are often reactive or catalytic in water systems, and are promising materials for the removal and degradation of a wide variety of water contaminants [130–156]. In addition, some types of metal nanoparticles (e.g., silver and copper) exhibit antibacterial properties [157–160], which could be of great use to control biological growth in water treatment and distribution systems, as well as within current treatment technologies. In particular, iron nanoparticles (Fig. 9(a)) have been used to treat contaminated groundwater through *in situ* injection strategies, and although challenges remain,

the results have largely been successful. Furthermore, silver nanoparticles have been used in ceramic pot filters [161], and show promise for simple, point-of-use applications [162–165] to disinfect water for drinking or bathing. The widespread use of nanoparticles and other nanomaterials for water treatment applications has not yet been achieved, partly due to the infancy of the field in terms of research and development, and partly due to the hurdles associated with verifying the safety of a nanomaterial-based water treatment technology.

With the use of nanoparticles and nanomaterials in many commercial products, and the potential of nanoparticles for treating contaminated water, the threat of water contamination also exists. Several key aspects of understanding nanoparticles as a potential water contaminant have been researched, including the development of a definition of toxicity for nanomaterials [166–168], understanding how nanomaterials change in natural environments [169, 170], understanding the toxicity of individual nanomaterials on specific cell types [171–178], and understanding the fate and transport of nanomaterials [179–185]. A number of treatment options have been proposed for the removal of nanoparticles from water [186–192]. However, research has focused on the use of nanoparticles for water treatment, or in commercial applications such as textiles. In addition, research on the fate of engineered nanoparticles has demonstrated that it is extremely difficult to identify and quantify the presence of anthropogenic and potentially toxic nanomaterials in water sources because of the presence of naturally occurring nano-sized materials [193–195].

Today, significant challenges remain in the field

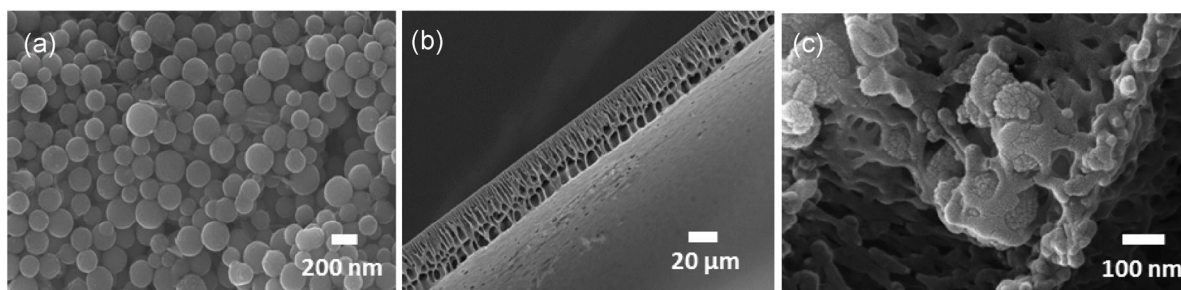


Figure 9 (a) Iron nanoparticles are currently under development for water treatment applications [245, 246]. (b) To immobilize nanoparticles for water treatment, a polymeric water filtration membrane, such as a polyethersulfone microfiltration membrane, can be used as a support structure to embed nanoparticles. (c) Iron nanoparticles embedded in the pore wall of a polyethersulfone microfiltration membrane.

of water treatment, with many revolving around effectiveness, efficiency, and reliability. It is clear from the growing number of identified water contaminants and increase in water demand that next-generation water treatment materials and technologies must show an improvement in their ability to remove water contaminants. However, these materials and technologies must also be robust and cost-effective; otherwise, novel and improved technologies will be unable to replace current technologies as viable commercial alternatives. This is both a materials challenge and an engineering challenge. Novel or improved materials that can operate reliably in an aqueous environment, and that are cost-competitive with other commercial technologies must therefore be developed. Advances in engineering design are also required to improve process efficiency and create novel approaches to water treatment using commercially available materials in novel and improved ways (e.g., the combination of solar energy with desalination for rural, off-grid, and natural disaster applications). Such challenges require innovation in many areas of research and development, from bench-scale science, to industrial engineering. Researchers and engineers must therefore work hand-in-hand to succeed in creating novel water treatment solutions.

Key challenges for the development of water treatment materials include the following: 1) control, reduction, or elimination of biological, organic, and inorganic fouling; 2) increasing the lifetime of materials in aqueous environments (i.e., reducing mechanical and chemical degradation of the material); 3) improving the trade-off between selectivity (i.e., types and number of contaminants removed) and clean water production; and 4) balancing functionality and design with cost. Key engineering challenges include the reduction of energy required (including energy recovery and renewable energy strategies), design of treatment systems for remote locations and challenging, highly polluted water sources, and management of waste streams (e.g., solid waste from wastewater treatment plants or salt waste from desalination).

2.3.3 *Nanoscience and water*

Advances in nanoscience will play a critical role in novel and improved technologies for water treatment,

from high-tech desalination and removal of industrial organic contaminants at a large municipal treatment plant, to ceramic pot filters embedded with nanoparticles that can disinfect drinking water for a rural village. Currently research efforts focus on the development of novel nanomaterials, including nanoparticles and nanostructured materials, for water treatment applications, where the overall objective is the discovery of next-generation materials for treating a larger number of water contaminants, enabling cleaner water for both human use and environmental sustainability. The next significant advances in materials for water treatment are expected to result from the design and development of nanomaterials, as novel methods for enhancing material properties by controlling material morphology and design at the nanoscale are constantly being developed. This control and enhancement of material properties is not possible in bulk materials and is therefore a hallmark of nanomaterial development. In this section, several examples of ongoing research areas and specific types of nanomaterials will be outlined, but it should be noted that these are just a small sample of the materials currently under development.

In terms of polymeric membrane-mediated water filtration, significant efforts have been made to improve the durability of the polymer membrane, reduce the fouling tendency of the membrane surface, and improve the selectivity of the membrane while also increasing/maintaining water flux. Several key studies show tremendous promise for the next generation of water filtration membranes. Many studies have been carried out into the surface modification of polymeric membranes to reduce or control fouling during water filtration. In particular, one successful development has been the application of nano-scale dopamine films to the surface of microfiltration, nanofiltration, and reverse osmosis membranes [196–200]. Polydopamine molecules self-assemble into a film on the membrane surface at room temperature, and do not require any further annealing or polymerization treatments to remain on the membrane surface. For membranes modified with polydopamine film, the reduction in water flux over time through membrane fouling is less severe, and the fouling is reversible, with organic foulants being removed by removal and reapplication

of the polydopamine film to the membrane surface.

Current material challenges for polymeric membranes can be addressed through entirely novel approaches for nano-structured membranes. Two key examples are electrospun nanofiber membranes for salt-water desalination and engineered osmosis technologies [126, 128, 201–203], and improved control of membrane pore size through block copolymer membranes [204–212]. Block copolymers can also be used to direct and assemble nanoparticles within a film or membrane material [213–215]. One great challenge for engineered osmosis technologies is the requirement for increased flux with reduced energy input and improved salt rejection. Nanofiber-supported polymeric membranes have both higher water flux and lower salt passage through the membrane compared to commercially available membranes. In addition, the nanofiber-supported membranes appear mechanically robust, and nanofiber morphology can be controlled through modification of the electrospinning process parameters. Furthermore, block copolymers have been used in other fields to produce polymer films with desirable properties based on the length and type of polymer blocks and the resulting film morphology. This general concept is now being applied to water filtration membranes, where block copolymers allow tight control of pore size and pore size distribution based on the polymer blocks used and the membrane casting conditions applied.

While there has been limited use thus far of nanoparticles in water treatment applications, the development of nanoparticles, nanomaterials, and nano-structured composite materials holds great potential for the adsorption and degradation of water contaminants if the challenges of cost, lifetime, and nanomaterial immobilization can be addressed. Many metallic and metal oxide nanoparticles are reactive or catalytic in aqueous systems, producing oxidative or reductive species that can react with water contaminants to break them down into less harmful components. Metallic nanoparticles based on iron, palladium, and nickel, among others, are naturally reactive or catalytic in water and can participate in both reductive (e.g., dehalogenation reactions) [216–220] and oxidative (e.g., production of hydroxyl radicals for pesticide oxidation) [221–223] contaminant degradation

reactions. Metallic nanoparticles are also excellent adsorbents, and can remove contaminants such as heavy metals through adsorption, precipitation, and electron transfer reactions [224–226]. Iron-based nanoparticles (Fig. 9) have received interest in the water treatment community, and continue to be studied for both groundwater remediation and water treatment applications, due to the low cost of iron and the wide variety of contaminants removed. Metal oxide semiconductor nanoparticles, such as TiO_2 nanoparticles, can also be used in combination with visible or solar radiation to produce reactive species that degrade water contaminants [227–230]. When combined with nanomaterials such as graphene or graphene oxide, or when doped with metallic nanoparticles or non-metallic elements (e.g., nitrogen or fluoride), TiO_2 nanoparticles are activated in the visible light spectrum and demonstrate excellent catalytic efficiency [231–235]. In addition, such nanomaterials are themselves potentially useful in the adsorption of heavy metals and organic compounds from water, and as novel filtration membranes [236–244].

One challenge of using nanoparticles in water treatment is the control of nanoparticle location within the treatment system. To address this challenge, current research efforts are focusing on the incorporation of nanoparticles and nanomaterials into a membrane matrix [247–250]. Nanomaterial-embedded membranes (Fig. 9(c)) provide several benefits, such as immobilization of the nanomaterial in a solid matrix; improved treatment efficiency of the nanomaterial (compared to a bulk solution reactor) due to access to the nanomaterial and interactions of the membrane, contaminants, and nanomaterial; and the development of membranes that act as a physical barrier to larger contaminants but a reactive/adsorptive barrier to smaller contaminants. Progress has also been made in the incorporation of nanoparticles into different types of polymeric membranes (from microfiltration to reverse osmosis membranes), and strategies to control where the nanoparticles are located. These strategies include *in situ* versus *ex situ* nanoparticle synthesis, functionalization of the nanoparticle surface, and nanoparticle coating of membrane surfaces and/or pores [251–262]. Membrane casting parameters, including polymer concentration, solvent, and



nonsolvent types, and the inclusion of additives in the casting solution, can also affect nanoparticle location. Key challenges remain, including successful dispersion of nanoparticles throughout the membrane or in a specific location, matching nanoparticle lifetime to membrane lifetime, degradation of the polymer because of nanoparticle reactivity, and maintaining membrane performance. Opportunities therefore exist for the improved control of nanoparticle dispersion and nanoparticle location in the membrane. Furthermore, enhanced nanoparticle-polymer interactions and the use of nanoparticles as a tool to impart additional functionality to a membrane and to control membrane morphology are also desirable.

As water treatment heads towards the purification of more challenging water sources and next-generation technologies based partly on nano-structured materials, an understanding of how water interacts with the surfaces of these materials and with the contaminants must be developed. Often, materials and technologies are developed without a true understanding of the details of the treatment process at the molecular level in terms of water-material interfaces, water-contaminant interactions, and contaminant separation from the surrounding water medium. It is likely that improved material design for water treatment could be achieved if designs were based on a fundamental understanding of how water interacts with such materials. For instance, Zhu et al. recently developed a novel single-atomic-layer carbon membrane made of graphyne, which showed ultrafast water flux (1,000-fold that of a commercial RO membrane and 10-fold that of a porous graphene membrane) and nearly perfect salt ion rejection rates, under realistic pressures [263]. Development and scaling to a commercial level of this novel membrane and the mechanisms involving water flow on the discrete molecular scale could benefit the development of next generation water desalination technologies. Herein lies a tremendous opportunity for interdisciplinary collaboration and discussion to better understand systems from the molecular- to the macro-scale, to provide insight into the fundamental mechanisms that drive a bulk process at the macroscale, and to allow technology engineering based on a mechanistic understanding of how individual water treatment processes work.

3 Summary and future prospects

In summary, developing an understanding of the basic science of water on a molecular scale is a natural consequence of developments in modern science and technology. At present, research on the basic science of water is problematic because the microstructure of water has not yet been clarified, i.e., we are still unaware exactly how water molecules organize themselves in the liquid form, at surfaces, and around biomolecules. As a fragile structure with delicate hydrogen bonding interactions, water is certainly dynamic in nature, with typical HB lives of only a few hundred femtoseconds. Furthermore, real water is a complex mixture of many types of molecular species and substances, such as H^+ , OH^- , D_2O , ions, organic molecules, and biological organisms. Even at $pH = 7$, for pure water, the concentration of H^+ and OH^- ions is 2 parts per billion (2 ppb, 10^{-7} mol/L).

In this respect, it is useful to consider how progress can be made towards establishing a molecular basis to understand water and its interactions. Although current experimental tools do not yield direct specific information about the molecular environment of water, this information is readily available in theoretical simulations. However, it is not yet clear to what level theoretical simulations are accurate and representative.

Theoretical simulations based on molecular dynamics and quantum mechanical calculations are indispensable. Molecular dynamics simulations employing empirical force fields yield unprecedentedly rich information about structural and dynamic properties at a single-molecule level. However, empirical models usually fail to reproduce key thermodynamic properties of water. For instance, the predicted melting temperature of ice varies from 190 to 300 K, depending on which model is adopted [264]. Water models are either too complex, non-transferable, or too inaccurate to reproduce the water properties in question. In addition, the majority of models do not adapt to the nano-confinement environment. It is therefore necessary to build and develop novel water models suitable for examining water-material interactions, water clusters, and confined water.

First principles calculations based on density functional theory and Quantum Monte Carlo, yield

higher accuracy and better transferability, and have been routinely adopted to investigate water structures and surface-water interactions. However, they are limited to small system sizes with hundreds of water molecules, and short simulation times of ~ 10 ps, thus preventing the investigation of water droplets, amorphous phases, surface water, and biological water. The development of quantum mechanical tools to deal with large scale water systems, tackle the quantum effects of the hydrogen core, and develop better exchange-correlation functionals to describe water (many functionals give the melting temperature of ice as 420 K [265]) remains a challenge. One promising approach to increase system size is the development of order- N quantum methods (where N is the number of electrons in the system).

Modern experimental tools such as scanning probe microscopy, advanced electron microscopy, nonlinear optical spectroscopy, femtosecond laser analysis, and synchrotron facilities have been developed rapidly in the past 30 years. They are complementary to more traditional analytical techniques such as neutron scattering, low energy electron diffraction, and ultraviolet photoelectron spectroscopy. A number of inherent difficulties in developing these experimental techniques include: i) experimental tools (ion beam, electron beam, current flow, etc.) being possibly destructive to water structures; ii) detection techniques sensitive only to interfaces are lacking; and iii) adequate resolution in time and space being unavailable. Given the “vulnerability” of the molecular water system (where the strength of the hydrogen bond is approx. $1/10$ – $1/5$ that of a chemical bond) and its complexity (15 bulk phases and many “nanoscale phases”), progress in fundamental water research relies on the design and construction of improved experimental probes with higher resolution. Ultimately, the development of complementary techniques for basic water science is necessary. For example, it is desirable to increase the spatial resolution of scanning probes to sub-Angstrom levels, and increase temporal resolution from picoseconds to sub-femtoseconds in optical spectroscopy. Enhanced surface/tip methods for detecting a single water molecule at work in chemical reactions such as photosplitting are also required.

Acknowledgements

We thank discussion and help from Chongqin Zhu and Dr. Hui Li, Dr. Z. X. Cao, and Dr. Y. Luo during manuscript preparation. Financial support from NIST, the National Basic Research Program of China (No. 2012CB921403) and the National Natural Science Foundation of China (Nos. 11474328, 11290164, and 11222431) and CAS are gratefully acknowledged.

References

- [1] Raviv, U.; Laurat, P.; Klein, J. Fluidity of water confined to subnanometer films. *Nature* **2001**, *413*, 51–54.
- [2] Wernet, P.; Nordlund, D.; Bergmann, U.; Cavalleri, M.; Odelius, M.; Ogasawara, H.; Näslund, L. Å.; Hirsch, T. K.; Ojamäe, L.; Glatzel, P. et al. The structure of the first coordination shell in liquid water. *Science* **2004**, *304*, 995–999.
- [3] Smith, J. D.; Cappa, C. D.; Wilson, K. R.; Messer, B. M.; Cohen, R. C.; Saykally, R. J. Energetics of hydrogen bond network rearrangements in liquid water. *Science* **2004**, *306*, 851–853.
- [4] Head-Gordon, T.; Johnson, M. E. Tetrahedral structure or chains for liquid water. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 7973–7977.
- [5] Doering, D. L.; Madey, T. E. The adsorption of water on clean and oxygen-dosed Ru(011). *Surf. Sci.* **1982**, *123*, 305–337.
- [6] Held, G.; Menzel, D. The structure of the $p(\sqrt{3} \times \sqrt{3})R30^\circ$ bilayer of D_2O on Ru(001). *Surf. Sci.* **1994**, *316*, 92–102.
- [7] Feibelman, P. J. Partial dissociation of water on Ru(0001). *Science* **2002**, *295*, 99–102.
- [8] Cerdá, J.; Michaelides, A.; Bocquet, M.-L.; Feibelman, P. J.; Mitsui, T.; Rose, M.; Fomin, E.; Salmeron, M. Novel water overlayer growth on Pd(111) characterized with scanning tunneling microscopy and density functional theory. *Phys. Rev. Lett.* **2004**, *93*, 116101.
- [9] Carrasco, J.; Michaelides, A.; Forster, M.; Haq, S.; Raval, R.; Hodgson, A. A one-dimensional ice structure built from pentagons. *Nat. Mater.* **2009**, *8*, 427–431.
- [10] Nie, S.; Feibelman, P. J.; Bartelt, N. C.; Thürmer, K. Pentagons and heptagons in the first water layer on Pt(111). *Phys. Rev. Lett.* **2010**, *105*, 026102.
- [11] Carrasco, J.; Hodgson, A.; Michaelides, A. A molecular perspective of water at metal interfaces. *Nat. Mater.* **2012**, *11*, 667–674.
- [12] Lin, K.; Zhou, X.-G.; Liu, S. L.; Luo, Y. Identification of

- free OH and its implication on structural changes of liquid water. *Chin. J. Chem. Phys.* **2013**, *26*, 121.
- [13] Mishima, O. Relationship between melting and amorphization of ice. *Nature* **1996**, *384*, 546–549.
- [14] Loerting, T.; Salzmann, C.; Kohl, I.; Mayer, E.; Hallbrucker, A. A second distinct structural “state” of high-density amorphous ice at 77 K and 1 bar. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5355–5357.
- [15] Denbenedetti, P. G.; Stanley, H. E. Supercooled and glassy water. *Phys. Today* **2003**, *56*, 40–46.
- [16] Xu, L. M.; Kumar, P.; Buldyrev, S. V.; Chen, S. H.; Poole, P. H.; Sciortino, F.; Stanley, H. E. Relation between the Widom line and the dynamic crossover in systems with a liquid-liquid phase transition. *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 16558–16562.
- [17] Hoffmann, M. M.; Conradi, M. S. Are there hydrogen bonds in supercritical water? *J. Am. Chem. Soc.* **1997**, *119*, 3811–3817.
- [18] Sahle, C. J.; Sternemann, C.; Schmidt, C.; Lehtola, S.; Jahn, S.; Simonelli, L.; Huotari, S.; Hakala, M.; Pylkkänen, T.; Nyrow, A. et al. Microscopic structure of water at elevated pressures and temperatures. *Proc. Natl. Acad. Sci. USA* **2013**, *110*, 6301–6306.
- [19] Tretyakov, M. Y.; Serov, E. A.; Koshelev, M. A.; Parshin, V. V.; Krupnov, A. F. Water dimer rotationally resolved millimeter-wave spectrum observation at room temperature. *Phys. Rev. Lett.* **2013**, *110*, 093001.
- [20] Cho, C. H.; Singh, S.; Robinson, G. W. Understanding all of water’s anomalies with a nonlocal potential. *J. Chem. Phys.* **1997**, *107*, 7979–7988.
- [21] Tanaka, H. Simple physical explanation of the unusual thermodynamic behavior of liquid water. *Phys. Rev. Lett.* **1998**, *80*, 5750–5753.
- [22] Vadamuthu, M.; Singh, S.; Robinson, G. W. Properties of liquid water: Origin of the density anomalies. *J. Phys. Chem.* **1994**, *98*, 2222–2230.
- [23] Vadamuthu, M.; Singh, S.; Robinson, G. W. Accurate mixture- model densities for D₂O. *J. Phys. Chem.* **1994**, *98*, 8591–8593.
- [24] Dougherty, R. C.; Howard, L. N. Equilibrium structural model of liquid water: Evidence from heat capacity, spectra, density, and other properties. *J. Chem. Phys.* **1998**, *109*, 7379–7393.
- [25] Alphonse, N. K.; Dillon, S. R.; Dougherty, R. C.; Galligan, D. K.; Howard, L. N. Direct Raman evidence for a weak continuous phase transition in liquid water. *J. Phys. Chem. A* **2006**, *110*, 7577–7580.
- [26] Franzese, G.; Stanley, H. E. The Widom line of supercooled water. *J. Phys.-Condens. Matter* **2007**, *19*, 205126.
- [27] Kumar, P.; Franzese, G.; Stanley, H. E. Dynamics and thermodynamics of water. *J. Phys.-Condens. Matter* **2008**, *20*, 244114.
- [28] Angell, C. A.; Bressel, R. D.; Hemmati, M.; Sare, E. J.; Tucker, J. C. Water and its anomalies in perspective: Tetrahedral liquids with and without liquid-liquid phase transitions. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1559–1566.
- [29] Kumar, P.; Stanley, H. E. Thermal conductivity minimum: A new water anomaly. *J. Phys. Chem. B* **2011**, *115*, 14269–14273.
- [30] Murphy, D. M.; Koop, T. Review of the vapour pressures of ice and supercooled water for atmospheric applications. *Q. J. R. Meteorol. Soc.* **2005**, *131*, 1539–1565.
- [31] Mpemba, E. B.; Osborne, D. G. Cool? *Phys. Educ.* **1969**, *4*, 172–175.
- [32] Shell, M. S.; Debenedetti, P. G.; Panagiotopoulos, A. Z. Molecular structural order and anomalies in liquid silica. *Phys. Rev. E* **2002**, *66*, 011202.
- [33] Hujo, W.; Jabes, B. S.; Rana, V. K.; Chakravarty, C.; Molinero, V. The rise and fall of anomalies in tetrahedral liquids. *J. Stat. Phys.* **2011**, *145*, 293–312.
- [34] Jabes, B. S.; Nayar, D.; Dhabal, D.; Molinero, V.; Chakrabarty, C. Water and other tetrahedral liquids: Order, anomalies and solvation. *J. Phys.-Condens. Matter* **2012**, *24*, 284116.
- [35] Marx, D.; Tuckerman, M. E.; Hutter, J.; Parrinello, M. The nature of hydrated excess proton in water. *Nature* **1999**, *397*, 601–604.
- [36] Ranea, V. A.; Michaelides, A.; Ramírez, R.; de Andres, P. L.; Vergés, J. A.; King, D. A. Water dimer diffusion on Pd{111} assisted by an H-bond donor-acceptor tunneling exchange. *Phys. Rev. Lett.* **2004**, *92*, 136104.
- [37] Tuckerman, M. E.; Marx, D.; Parrinello, M. The nature and transport mechanism of hydrated hydroxide ions in aqueous solution. *Nature* **2002**, *417*, 925–929.
- [38] Li, X.-Z.; Walker, B.; Michaelides, A. Quantum nature of the hydrogen bond. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 6369–6373.
- [39] Chen, J.; Li, X. Z.; Zhang, Q. F.; Michaelides, A.; Wang, E. G. Nature of proton transport in a water-filled carbon nanotube and in liquid water. *Phys. Chem. Chem. Phys.* **2013**, *15*, 6344–6349.
- [40] Li, X. Z.; Probert, M. I. J.; Alavi, A.; Michaelides, A. Quantum nature of the proton in water-hydroxyl overlayers on metal surfaces. *Phys. Rev. Lett.* **2010**, *104*, 066102.
- [41] Paesani, F.; Voth, G. A. The properties of water: Insights from quantum simulations. *J. Phys. Chem. B* **2009**, *113*, 5702–5719.
- [42] Thiel, P. A.; Madey, T. E. The interaction of water with

- solid surfaces: Fundamental aspects. *Surf. Sci. Rep.* **1987**, *7*, 211–385.
- [43] Henderson, M. A. The interaction of water with solid surfaces: Fundamental aspects. *Surf. Sci. Rep.* **2002**, *46*, 1–308.
- [44] Hodgson, A.; Haq, S. Water adsorption and the wetting of metal surfaces. *Surf. Sci. Rep.* **2009**, *64*, 381–451.
- [45] Kasemo, B. Biological surface science. *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 451–459.
- [46] Odelius, M.; Bernasconi, M.; Parrinello, M. Two dimensional ice adsorbed on mica surface. *Phys. Rev. Lett.* **1997**, *78*, 2855–2858.
- [47] Meng, S.; Zhang, Z. Y.; Kaxiras, E. Tuning solid surfaces from hydrophobic to superhydrophilic by submonolayer surface modification. *Phys. Rev. Lett.* **2006**, *97*, 036107.
- [48] Cheh, J.; Gao, Y.; Wang, C. L.; Zhao, H.; Fang, H. P. Ice or water: Thermal properties of monolayer water adsorbed on a substrate. *J. Stat. Mech.* **2013**, *2013*, P06009.
- [49] Feibelman, P. J. DFT versus the “real world” (or, waiting for Godft). *Top. Catal.* **2010**, *53*, 417–422.
- [50] Meng, S.; Wang, E. G.; Gao, S. W. A molecular picture of hydrophilic and hydrophobic interactions from *ab initio* density functional theory calculations. *J. Chem. Phys.* **2003**, *119*, 7617–7620.
- [51] Smith, R. S.; Huang, C.; Wong, E. K. L.; Kay, B. D. Desorption and crystallization kinetics in nanoscale thin films of amorphous water ice. *Surf. Sci.* **1996**, *367*, L13–L18.
- [52] Wang, C. L.; Lu, H. J.; Wang, Z. G.; Xiu, P.; Zhou, B.; Zuo, G. H.; Wan, R. Z.; Hu, J.; Fang, H. P. Stable liquid water droplet on a water monolayer formed at room temperature on ionic model substrates. *Phys. Rev. Lett.* **2009**, *103*, 137801.
- [53] Zhu, C. Q.; Li, H.; Huang, Y. F.; Zeng, X. C.; Meng, S. Microscopic insight into surface wetting: Relations between interfacial water structure and the underlying lattice constant. *Phys. Rev. Lett.* **2013**, *110*, 126101.
- [54] Choi, C. L.; Feng, J.; Li, Y. G.; Wu, J.; Zak, A.; Tenne, R.; Dai, H. J. WS₂ nanoflakes from nanotubes for electrocatalysis. *Nano Res.* **2013**, *6*, 921–928.
- [55] Voiry, D.; Yamaguchi, H.; Li, J. W.; Silva, R.; Alves, D. C. B.; Fujita, T.; Chen, M. W.; Asefa, T.; Shenoy, V. B.; Eda, G. et al. Enhanced catalytic activity in strained chemically exfoliated WS₂ nanosheets for hydrogen evolution. *Nat. Mater.* **2013**, *12*, 850–855.
- [56] Jaramillo, T. F.; Jørgensen, K. P.; Bonde, J.; Nielsen, J. H.; Horch, S.; Chorkendorff, I. Identification of active edge sites for electrochemical H₂ evolution from MoS₂ nanocatalysts. *Science* **2007**, *317*, 100–102.
- [57] Wang, M.; Ren, F.; Cai, G. X.; Liu, Y. C.; Shen, S. H.; Guo, L. J. Activating ZnO nanorod photoanodes in visible light by Cu ion implantation. *Nano Res.* **2014**, *7*, 353–364.
- [58] Song, S. M.; Wang, W. Z.; Jiang, D.; Zhang, L.; Li, X. M.; Zheng, Y. L.; An, Q. Bi₂WO₆ quantum dot-intercalated ultrathin montmorillonite nanostructure and its enhanced photocatalytic performance. *Nano Res.* **2014**, *7*, 1497–1506.
- [59] Ling, X. Y.; Yan, R. X.; Lo, S.; Hoang, D. T.; Liu, C.; Fardy, M. A.; Khan, S. B.; Asiri, A. M.; Bawaked, S. M.; Yang, P. D. Alumina-coated Ag nanocrystal monolayers as surface-enhanced Raman spectroscopy platforms for the direct spectroscopic detection of water splitting reaction intermediates. *Nano Res.* **2014**, *7*, 132–143.
- [60] Yagi, M.; Kaneko, M. Molecular catalysts for water oxidation. *Chem. Rev.* **2001**, *101*, 21–35.
- [61] Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.* **2009**, *38*, 253–278.
- [62] Chen, X. B.; Shen, S. H.; Guo, L. J.; Mao, S. S. Semiconductor-based photocatalytic hydrogen generation. *Chem. Rev.* **2010**, *110*, 6503–6570.
- [63] Osterloh, F. E. Inorganic nanostructures for photoelectrochemical and photocatalytic water splitting. *Chem. Soc. Rev.* **2013**, *42*, 2294–2320.
- [64] Guo, Q.; Xu, C. B.; Ren, Z. F.; Yang, W. S.; Ma, Z. B.; Dai, D. X.; Fan, H. J.; Minton, T. K.; Yang, X. M. Stepwise photocatalytic dissociation of methanol and water on a TiO₂(110) surface. *J. Am. Chem. Soc.* **2012**, *134*, 13366–13373.
- [65] Chiashi, S.; Hanashima, T.; Mitobe, R.; Nagatsu, K.; Yamamoto, T.; Homma, Y. Water encapsulation control in individual single-walled carbon nanotubes by laser irradiation. *J. Phys. Chem. Lett.* **2014**, *5*, 408–412.
- [66] Soper, A. K.; Bruni, F.; Ricci, M. A. Water confined in Vycor glass. II. Excluded volume effects on the radial distribution functions. *J. Phys. Chem.* **1998**, *109*, 1486–1494.
- [67] Weik, M. Low-temperature behavior of water confined by biological macromolecules and its relation to protein dynamics. *Eur. Phys. J. E-Soft Matter Biol. Phys.* **2003**, *12*, 153–158.
- [68] Koga, K.; Gao, G. T.; Tanka, H.; Zeng, X. C. Formation of ordered ice nanotubes inside carbon nanotubes. *Nature* **2001**, *412*, 802–805.
- [69] Kolesnikov, A. I.; Zanotti, J.-M.; Loong, C.-K.; Thiyaagarajan, P.; Moravsky, A. P.; Loutfy, R. O.; Burnham, C. J. Anomalous soft dynamics of water in a nanotube: A revelation of nanoscale confinement. *Phys. Rev. Lett.* **2004**, *93*, 035503.
- [70] Bergman, R.; Swenson, J. Dynamics of supercooled water in confined geometry. *Nature* **2000**, *403*, 283–286.
- [71] Su, X. C.; Lianos, L.; Shen, Y. R.; Somorjai, G. A. Surface-induced ferroelectric ice on Pt(111). *Phys. Rev. Lett.* **1998**, *80*, 1533.

- [72] Meng, S.; Chakarov, D. V.; Kasemo, B.; Gao, S. W. Two dimensional hydration shells of alkali metal ions at a hydrophobic surface. *J. Chem. Phys.* **2004**, *121*, 12572.
- [73] Meng, S.; Gao, S. W. Formation and interaction of hydrated alkali metal ions at the graphite-water interface. *J. Chem. Phys.* **2006**, *125*, 014708.
- [74] Matsui, H.; Tadokoro, M. Eigen-like hydrated protons traveling with a local distortion through the water nanotube in new molecular porous crystals $\{[M^{III}(H_2bim)_3](TMA) \cdot 20H_2O\}_n$ (M = Co, Rh, Ru). *J. Chem. Phys.* **2012**, *137*, 144503.
- [75] Zhao, Y.; Li, H.; Zeng, X. C. First-principles molecular dynamics simulation of atmospherically relevant anion solvation in supercooled water droplet. *J. Am. Chem. Soc.* **2013**, *135*, 15549–15558.
- [76] Loris, R.; Langhorst, U.; De Vos, S.; Decanniere, K.; Bouckaert, J.; Maes, D.; Transue, T. R.; Steyaert, J. Conserved water molecules in a large family of microbial ribonucleases. *Proteins-Struct., Funct., Bioinf.* **1999**, *36*, 117–134.
- [77] Murata, K.; Mitsuoka, K.; Hirai, T.; Walz, T.; Agre, P.; Heymann, J. B.; Engel, A.; Fujiyoshi, Y. Structural determinants of water permeation through aquaporin-1. *Nature* **2000**, *407*, 599–605.
- [78] Pal, S. K.; Peon, J.; Zewail, A. H. Biological water at the protein surface: Dynamical solvation probed directly with femtosecond resolution. *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 1763–1768.
- [79] Zhong, D. P.; Pal, S. K.; Zewail, A. H. Biological water: A critique. *Chem. Phys. Lett.* **2011**, *503*, 1–11.
- [80] Kropman, M. F.; Bakker, H. J. Dynamics of water molecules in aqueous solvation shells. *Science* **2001**, *291*, 2118–2120.
- [81] Das, D.; Samanta, G.; Mandal, B. K.; Chowdhury, T. R.; Chanda, C. R.; Chowdhury, P. P.; Basu, G. K.; Chakraborti, D. Arsenic in groundwater in six districts of West Bengal, India. *Environ. Geochem. Health* **1996**, *18*, 5–15.
- [82] Bhattacharya, P.; Mukherjee, A.; Mukherjee, A. B. Arsenic in groundwater of India. *Enc. Environ. Health* **2011**, 150–164.
- [83] Devi, N. L.; Chandra, Y. I.; Qi, S. Recent status of arsenic contamination in groundwater of northeastern India - A review. *Rep. Op.* **2009**, *1*, 22–32.
- [84] Pal, T.; Mukherjee, P. K.; Sengupta, S.; Bhattacharyya, A. K.; Shome, S. Arsenic pollution in groundwater of West Bengal, India - An insight into the problem by subsurface sediment analysis. *Gondwana Res.* **2002**, *5*, 501–512.
- [85] Rodriguez-Lado, L.; Sun, G. F.; Berg, M.; Zhang, Q.; Xue, H. B.; Zheng, Q. M.; Johnson, C. A. Groundwater arsenic contamination throughout China. *Science* **2013**, *341*, 866–868.
- [86] Michael, H. A. An arsenic forecast for China. *Science* **2013**, *341*, 852–853.
- [87] Yu, G. Q.; Sun, D. J.; Zheng, Y. Health effects of exposure to natural arsenic in groundwater and coal in China: An overview of occurrence. *Environ. Health Perspect.* **2007**, *115*, 636–642.
- [88] Frost, F.; Franke, D.; Pierson, K.; Woodruff, L.; Raasina, B.; Davis, R.; Davies, J. A seasonal study of arsenic in groundwater, Snohomish County, Washington, USA. *Environ. Geochem. Health* **1993**, *15*, 209–214.
- [89] Hudak, P. F. Distribution of arsenic concentrations in groundwater of the Seymour Aquifer, Texas, USA. *Int. J. Environ. Health Res.* **2008**, *18*, 79–82.
- [90] Barringer, J. L.; Reilly, P. A.; Eberl, D. D.; Blum, A. E.; Bonin, J. L.; Rosman, R.; Hirst, B.; Alebus, M.; Cenno, K.; Gorska, M. Arsenic in sediments, groundwater, and streamwater of a glauconitic Coastal Plain terrain, New Jersey, USA - Chemical “fingerprints” for geogenic and anthropogenic sources. *Appl. Geochem.* **2011**, *26*, 763–776.
- [91] Ghanem, M.; Samhan, S.; Carlier, E.; Ali, W. Groundwater pollution due to pesticides and heavy metals in north West Bank. *J. Environ. Prot.* **2011**, *2*, 429–434.
- [92] Dsikowitzky, L.; Nordhaus, I.; Jennerjahn, T. C.; Khrycheva, P.; Sivatharshan, Y.; Yuwono, E.; Schwarzbauer, J. Anthropogenic organic contaminants in water, sediments and benthic organisms of the mangrove-fringed Segara Anakan Lagoon, Java, Indonesia. *Mar. Pollut. Bull.* **2011**, *62*, 851–862.
- [93] Thompson, B.; Adelsbach, T.; Brown, C.; Hunt, J.; Kuwabara, J.; Neale, J.; Ohlendorf, H.; Schwarzbach, S.; Spies, R.; Taberski, K. Biological effects of anthropogenic contaminants in the San Francisco Estuary. *Environ. Res.* **2007**, *105*, 156–174.
- [94] Feng, L. H.; Zhang, X. C.; Luo, G. Y. Research on the risk of water shortages and the carrying capacity of water resources in Yiwu, China. *Hum. Ecol. Risk Assess.* **2009**, *15*, 714–726.
- [95] Pomeranz, K. The great Himalayan watershed: Water shortages, mega-projects and environmental politics in China, India, and Southeast Asia. *Asia Pac. J.* **2009**, 30-2-09.
- [96] Li, Y.-S.; Raso, G.; Zhao, Z.-Y.; He, Y.-K.; Ellis, M. K.; McManus, D. P. Large water management projects and schistosomiasis control, Dongting Lake Region, China. *Emerg. Infect. Dis.* **2007**, *13*, 973–979.
- [97] Cerci, Y. Exergy analysis of a reverse osmosis desalination plant in California. *Desalination* **2002**, *142*, 257–266.
- [98] Caron, D. A.; Garneau, M.-E.; Seubert, E.; Howard, M. D. A.; Darjany, L.; Schnetzer, A.; Cetinić, I.; Filteau, G.; Lauri, P.; Jones, B. et al. Harmful algae and their potential impacts on desalination operations off southern California. *Water Res.* **2010**, *44*, 385–416.
- [99] Lattemann, S.; Höpner, T. Environmental impact and impact

- assessment of seawater desalination. *Desalination* **2008**, *220*, 1–15.
- [100] Hutton, G. Global Costs and Benefits of Drinking-Water Supply and Sanitation Interventions to Reach the MDG Target and Universal Coverage; World Health Organization: Geneva, Switzerland, 2012.
- [101] Gross, B.; van Wijk, C.; Mukherjee, N. Linking Sustainability with Demand, Gender and Poverty; Water and Sanitation Program, The World Bank, IRC International Water and Sanitation Centre: Delft, The Netherlands, 2000.
- [102] Daughton, C. G. Non-regulated water contaminants: Emerging research. *Environ. Impact Assess. Rev.* **2004**, *24*, 711–732.
- [103] Richardson, S. D. Disinfection by-products and other emerging contaminants in drinking water. *TrAC Trends Anal. Chem.* **2003**, *22*, 666–684.
- [104] Richardson, S. D.; Ternes, T. A. Water analysis: Emerging contaminants and current issues. *Anal. Chem.* **2011**, *83*, 4614–4648.
- [105] Barrett, J. R. Chemical contaminants in drinking water: Where do we go from here? *Environ. Health Perspect.* **2014**, *122*, A80.
- [106] Richardson, S. D. New disinfection by-product issues: Emerging DBPs and alternative routes of exposure. *Global NEST J.* **2005**, *7*, 43–60.
- [107] Boorman, G. A.; Dellarco, V.; Dunnick, J. K.; Chapin, R. E.; Hunter, S.; Hauchman, F.; Gardner, H.; Cox, M.; Sills, R. C. Drinking water disinfection byproducts: Review and approach to toxicity evaluation. *Environ. Health Perspect.* **1999**, *107*, 207–217.
- [108] Krasner, S. W.; Weinberg, H. S.; Richardson, S. D.; Pastor, S. J.; Chinn, R.; Scilimenti, M. J.; Onstad, G. D.; Thruston, A. D. Occurrence of a new generation of disinfection byproducts. *Environ. Sci. Technol.* **2006**, *40*, 7175–7185.
- [109] Iriarte, U.; Álvarez-Uriarte, J. I.; López-Fonseca, R.; González-Velasco, J. R. Trihalomethane formation in ozonated and chlorinated surface water. *Environ. Chem. Lett.* **2003**, *1*, 57–61.
- [110] Rigobello, E. S.; Dantas, A. D. B.; Bernardo, L. D.; Vieira, E. M. Removal of diclofenac by conventional drinking water treatment processes and granular activated carbon filtration. *Chemosphere* **2013**, *92*, 184–191.
- [111] Adams, C.; Wang, Y.; Loftin, K.; Meyer, M. Removal of antibiotics from surface and distilled water in conventional water treatment processes. *J. Environ. Eng.* **2002**, *128*, 253–260.
- [112] Binnie, C.; Kimber, M.; Smethurst, G. Basic Water Treatmentm, 3rd ed.; Thomas Telford Publishing, Thomas Telford, Ltd: London, 2002.
- [113] Guzzella, L.; Feretti, D.; Monarca, S. Advanced oxidation and adsorption technologies for organic micropollutant removal from lake water used as drinking-water supply. *Water Res.* **2002**, *36*, 4307–4318.
- [114] Fritzmann, C.; Löwenberg, J.; Wintgens, T.; Melin, T. State-of-the-art of reverse osmosis desalination. *Desalination* **2007**, *216*, 1–76.
- [115] Elimelech, M.; Phillip, W. A. The future of seawater desalination: Energy, technology and the environment. *Science* **2011**, *333*, 712–717.
- [116] Xu, J.; Ruan, G. L.; Chu, X. Z.; Yao, Y.; Su, B. W.; Gao, C. J. A pilot study of UF pretreatment without any chemicals for SWRO desalination in China. *Desalination* **2007**, *207*, 216–226.
- [117] Yip, N. Y.; Tiraferri, A.; Phillip, W. A.; Schiffman, J. D.; Hoover, L. A.; Kim, Y. C.; Elimelech, M. Thin-film composite pressure retarded osmosis membranes for sustainable power generation from salinity gradients. *Environ. Sci. Technol.* **2011**, *45*, 4360–4369.
- [118] Gupta, V. K.; Ali, I. Water treatment by membrane filtration techniques. In *Environmental Water: Advances in Treatment, Remediation and Recycling*; Gupta, V. K.; Ali, I., Eds.; Elsevier B.V.: Amsterdam, The Netherlands, 2013; pp 135–154.
- [119] Kumar, P.; Sharma, N.; Ranjan, R.; Kumar, S.; Bhat, Z. F.; Jeong, D. K. Perspective of membrane technology in dairy industry: A review. *Asian-Australas. J. Anim. Sci.* **2013**, *26*, 1347–1358.
- [120] Rao, A. P.; Desai, N. V.; Rangarajan, R. Interfacially synthesized thin film composite RO membranes for seawater desalination. *J. Membr. Sci.* **1997**, *124*, 263–272.
- [121] Paul, D. R. The role of membrane pressure in reverse osmosis. *J. App. Polym. Sci.* **1972**, *16*, 771–782.
- [122] Paul, D. R. Reformulation of the solution-diffusion theory of reverse osmosis. *J. Membr. Sci.* **2004**, *241*, 371–386.
- [123] Gerard, R.; Hachisuka, H.; Hirose, M. New membrane developments expanding the horizon for the application of reverse osmosis technology. *Desalination* **1998**, *119*, 47–55.
- [124] Sidney, L.; Srinivasa, S. Seawater demineralization by means of an osmotic membrane. In *Saline Water Conversion-II*; Gould, R. F., Ed.; American Chemical Society: Washington, D. C., 1963; pp 117–132.
- [125] McCutcheon, J. R.; Elimelech, M. Influence of membrane support layer hydrophobicity on water flux in osmotically driven membrane processes. *J. Membr. Sci.* **2008**, *318*, 458–466.
- [126] Tang, Z. H.; Qiu, C. Q.; McCutcheon, J. R.; Yoon, K.; Ma, H. Y.; Fang, D. F.; Lee, E.; Kopp, C.; Hsiao, B. S.; Chu, B. Design and fabrication of electrospun polyethersulfone nanofibrous scaffold for high-flux nanofiltration membranes.

- J. Polym. Sci., Part B-Polym. Phys.* **2009**, *47*, 2288–2300.
- [127] Arena, J. T.; McCloskey, B.; Freeman, B. D.; McCutcheon, J. R. Surface modification of thin film composite membrane support layers with polydopamine: Enabling use of reverse osmosis membranes in pressure retarded osmosis. *J. Membr. Sci.* **2011**, *375*, 55–62.
- [128] Bui, N.-N.; Lind, M. L.; Hoek, E. M. V.; McCutcheon, J. R. Electrospun nanofiber supported thin film composite membranes for engineered osmosis. *J. Membr. Sci.* **2011**, *385–386*, 10–19.
- [129] Loeb, S. The Loeb-Sourirajan membrane: How it came about. In ACS Symposium Series - Synthetic Membranes: Desalination; Turbak, A. F., Ed.; American Chemical Society: Washington, D. C., 1981; pp 1–9.
- [130] Lien, H.-L.; Wilkin, R. T. High-level arsenite removal from groundwater by zero-valent iron. *Chemosphere* **2005**, *59*, 377–386.
- [131] He, F.; Zhao, D. Y.; Paul, C. Field assessment of carboxymethyl cellulose stabilized iron nanoparticles for *in situ* destruction of chlorinated solvents in source zones. *Water Res.* **2010**, *44*, 2360–2370.
- [132] Henn, K. W.; Waddill, D. W. Utilization of nanoscale zero-valent iron for source remediation—A case study. *Remediation* **2006**, 57–77.
- [133] Dubey, S. P.; Dwivedi, A. D.; Kim, I.-C.; Sillanpaa, M.; Kwon, Y.-N.; Lee, C. Synthesis of graphene–carbon sphere hybrid aerogel with silver nanoparticles and its catalytic and adsorption applications. *Chem. Eng. J.* **2014**, *244*, 160–167.
- [134] He, J. S.; Siah, T.-S.; Chen, J. P. Performance of an optimized Zr-based nanoparticle-embedded PSF blend hollow fiber membrane in treatment of fluoride contaminated water. *Water Res.* **2014**, *56*, 88–97.
- [135] Xiong, R.; Wang, Y. R.; Zhang, X. X.; Lu, C. H. Facile synthesis of magnetic nanocomposites of cellulose@ultrasmall iron oxide nanoparticles for water treatment. *RSC Adv.* **2014**, *4*, 22632–22641.
- [136] Saharan, P.; Chaudhary, G. R.; Lata, S.; Mehta, S. K.; Mor, S. Ultra fast effective treatment of dyes from water with the synergistic effect of Ni doped ZnO nanoparticles and ultrasonication. *Ultrason. Sonochem.* **2015**, *22*, 317–325.
- [137] Che, H. X.; Yeap, S. P.; Ahmad, A. L.; Lim, J. K. Layer-by-layer assemble of iron oxide magnetic nanoparticles decorated silica colloid for water remediation. *Chem. Eng. J.* **2014**, *243*, 68–78.
- [138] Cao, J.; Li, J. C.; Liu, L.; Xie, A. J.; Li, S. K.; Qiu, L. G.; Yuan, Y. P.; Shen, Y. H. One-pot synthesis of novel Fe₃O₄/Cu₂O/PANI nanocomposites as absorbents in water treatment. *J. Mater. Chem. A* **2014**, *2*, 7953.
- [139] Bhaumik, M.; Choi, H. J.; McCrindle, R. I.; Maity, A. Composite nanofibers prepared from metallic iron nanoparticles and polyaniline: High performance for water treatment applications. *J. Colloid Interf. Sci.* **2014**, *425*, 75–82.
- [140] Liang, S.; Qi, G. G.; Xiao, K.; Sun, J. Y.; Giannelis, E. P.; Huang, X.; Elimelech, M. Organic fouling behavior of superhydrophilic polyvinylidene fluoride (PVDF) ultrafiltration membranes functionalized with surface-tailored nanoparticles: Implications for organic fouling in membrane bioreactors. *J. Membr. Sci.* **2014**, *463*, 94–101.
- [141] Yu, L.; Peng, X. J.; Ni, F.; Li, J.; Wang, D. S.; Luan, Z. K. Arsenite removal from aqueous solutions by γ -Fe₂O₃-TiO₂ magnetic nanoparticles through simultaneous photocatalytic oxidation and adsorption. *J. Hazard. Mater.* **2013**, *246–247*, 10–17.
- [142] Weng, X. L.; Lin, S.; Zhong, Y. H.; Chen, Z. L. Chitosan stabilized bimetallic Fe/Ni nanoparticles used to remove mixed contaminants-amoxicillin and Cd (II) from aqueous solutions. *Chem. Eng. J.* **2013**, *229*, 27–34.
- [143] Chalasani, R.; Vasudevan, S. Cyclodextrin-functionalized Fe₃O₄@TiO₂: Resuable, magnetic nanoparticles for photocatalytic degradation of endocrine-disrupting chemicals in water supplies. *ACS Nano* **2013**, *7*, 4093–4104.
- [144] Chai, L. Y.; Wang, Y. Y.; Zhao, N.; Yang, W. C.; You, X. Y. Sulfate-doped Fe₃O₄/Al₂O₃ nanoparticles as a novel adsorbent for fluoride removal from drinking water. *Water Res.* **2013**, *47*, 4040–4049.
- [145] Wang, H. T.; Lin, K.-Y.; Jing, B. X.; Krylova, G.; Sigmon, G. E.; McGinn, P.; Zhu, Y. X.; Na, C. Z. Removal of oil droplets from contaminated water using magnetic carbon nanotubes. *Water Res.* **2013**, *47*, 4198–4205.
- [146] Zelmanov, G.; Semiat, R. Boron removal from water and its recovery using iron (Fe³⁺) oxide/hydroxide-based nanoparticles (NanoFe) and NanoFe-impregnated granular activated carbon as adsorbent. *Desalination* **2014**, *333*, 107–117.
- [147] Das, S. K.; Khan, M. M. R.; Parandhaman, T.; Laffir, F.; Guha, A. K.; Sekaran, G.; Mandal, A. B. Nano-silica fabricated with silver nanoparticles: Antifouling adsorbent for efficient dye removal, effective water disinfection and biofouling control. *Nanoscale* **2013**, *5*, 5549–5560.
- [148] Ayati, A.; Ahmadpour, A.; Bamoharram, F. F.; Tanhaei, B.; Manttari, M.; Sillanpaa, M. A review on catalytic applications of Au/TiO₂ nanoparticles in the removal of water pollutant. *Chemosphere* **2014**, *107*, 163–174.
- [149] Qu, X. L.; Alvarez, P. J. J.; Li, Q. L. Applications of nanotechnology in water and wastewater treatment. *Water Res.* **2013**, *47*, 3931–3946.

- [150] Vadahanambi, S.; Lee, S.-H.; Kim, W.-J.; Oh, I.-K. Arsenic removal from contaminated water using three-dimensional graphene-carbon nanotube-iron oxide nanostructures. *Environ. Sci. Technol.* **2013**, *47*, 10510–10517.
- [151] Zhang, Z. Y.; Kong, J. L. Novel magnetic Fe₃O₄@C nanoparticles as adsorbents for removal of organic dyes from aqueous solution. *J. Hazard. Mater.* **2011**, *193*, 325–329.
- [152] Tang, S. C. N.; Lo, I. M. C. Magnetic nanoparticles: Essential factors for sustainable environmental applications. *Water Res.* **2013**, *47*, 2613–2632.
- [153] Yang, Z.; Yan, H.; Yang, H.; Li, H. B.; Li, A. M.; Cheng, R. S. Flocculation performance and mechanism of graphene oxide for removal of various contaminants from water. *Water Res.* **2013**, *47*, 3037–3046.
- [154] Kassae, M. Z.; Motamedi, E.; Mikhak, A.; Rahnemaie, R. Nitrate removal from water using iron nanoparticles produced by arc discharge vs. reduction. *Chem. Eng. J.* **2011**, *166*, 490–495.
- [155] Ali, I. New generation adsorbents for water treatment. *Chem. Rev.* **2012**, *112*, 5073–5091.
- [156] Hua, M.; Zhang, S. J.; Pan, B. C.; Zhang, W. M.; Lv, L.; Zhang, Q. X. Heavy metal removal from water/wastewater by nanosized metal oxides: A review. *J. Hazard. Mater.* **2012**, *211–212*, 317–331.
- [157] Auffan, M.; Achouak, W.; Rose, J.; Roncato, M. A.; Chaneac, C.; Waite, D. T.; Masion, A.; Woicik, J. C.; Wiesner, M. R.; Bottero, J. Y. Relation between the redox state of iron-based nanoparticles and their cytotoxicity toward *Escherichia coli*. *Environ. Sci. Technol.* **2008**, *42*, 6730–6735.
- [158] Brunet, L.; Lyon, D. Y.; Hotze, E. M.; Alvarez, P. J. J.; Wiesner, M. R. Comparative photoactivity and antibacterial properties of C₆₀ fullerenes and titanium dioxide nanoparticles. *Environ. Sci. Technol.* **2009**, *43*, 4355–4360.
- [159] Li, Q. L.; Mahendra, S.; Lyon, D. Y.; Brunet, L.; Liga, M. V.; Li, D.; Alvarez, P. J. J. Antimicrobial nanomaterials for water disinfection and microbial control: Potential applications and implications. *Water Res.* **2008**, *42*, 4591–4602.
- [160] Morones, J. R.; Elechiguerra, J. L.; Camacho, A.; Holt, K.; Kouri, J. B.; Ramirez, J. T.; Yacaman, M. J. The bactericidal effect of silver nanoparticles. *Nanotechnol.* **2005**, *16*, 2346–2353.
- [161] Larimer, C.; Ostrowski, N.; Speakman, J.; Nettleship, I. The segregation of silver nanoparticles in low-cost ceramic water filters. *Mater. Charact.* **2010**, *61*, 408–412.
- [162] Dankovich, T. A.; Gray, D. G. Bactericidal paper impregnated with silver nanoparticles for point-of-use water treatment. *Environ. Sci. Technol.* **2011**, *45*, 1992–1998.
- [163] Liga, M. V.; Bryant, E. L.; Colvin, V. L.; Li, Q. L. Virus inactivation by silver doped titanium dioxide nanoparticles for drinking water treatment. *Water Res.* **2011**, *45*, 535–544.
- [164] Apalangya, V.; Rangari, V.; Tiimob, B.; Jeelani, S.; Samuel, T. Development of antimicrobial water filtration hybrid material from bio source calcium carbonate and silver nanoparticles. *Appl. Surf. Sci.* **2014**, *295*, 108–114.
- [165] Saifuddin, N.; Nian, C. Y.; Zhan, L. W.; Ning, K. X. Chitosan-silver nanoparticles composite as point-of-use drinking water filtration system for household to remove pesticides in water. *Asian J. Biochem.* **2011**, *6*, 142–159.
- [166] Auffan, M.; Rose, J.; Bottero, J. Y.; Lowry, G. V.; Jolivet, J. P.; Wiesner, M. R. Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective. *Nat. Nanotechnol.* **2009**, *4*, 634–641.
- [167] Auffan, M.; Rose, J.; Wiesner, M. R.; Bottero, J. Y. Chemical stability of metallic nanoparticles: A parameter controlling their potential cellular toxicity *in vitro*. *Environ. Pollut.* **2009**, *157*, 1127–1133.
- [168] Kang, S.; Mauter, M. S.; Elimelech, M. Physicochemical determinants of multiwalled carbon nanotube bacterial cytotoxicity. *Environ. Sci. Technol.* **2008**, *42*, 7528–7534.
- [169] Lowry, G. V.; Gregory, K. B.; Apte, S. C.; Lead, J. R. Transformations of nanomaterials in the environment. *Environ. Sci. Technol.* **2012**, *46*, 6893–6899.
- [170] Boverhof, D. R.; David, R. M. Nanomaterial characterization: Considerations and needs for hazard assessment and safety evaluation. *Anal. Bioanal. Chem.* **2010**, *396*, 953–961.
- [171] Blaise, C.; Gagne, F.; Ferard, J. F.; Eullaffroy, P. Ecotoxicity of selected nano-materials to aquatic organisms. *Environ. Toxicol.* **2008**, *23*, 591–598.
- [172] Lanone, S.; Rogerieux, F.; Geys, J.; Dupont, A.; Maillot-Marechal, E.; Boczkowski, J.; Lacroix, G.; Hoet, P. Comparative toxicity of 24 manufactured nanoparticles in human alveolar epithelial and macrophage cell lines. *Part. Fibre Toxicol.* **2009**, *6*, 14.
- [173] Zhang, W.; Rittmann, B.; Chen, Y. S. Size effects on adsorption of hematite nanoparticles on *E. coli* cells. *Environ. Sci. Technol.* **2011**, *45*, 2172–2178.
- [174] Yin, L. Y.; Cheng, Y. W.; Espinasse, B.; Colman, B. P.; Auffan, M.; Wiesner, M. R.; Rose, J.; Liu, J.; Bernhardt, E. S. More than the ions: The effects of silver nanoparticles on *Lolium multiflorum*. *Environ. Sci. Technol.* **2011**, *45*, 2360–2367.
- [175] Franklin, N. M.; Rogers, N. J.; Apte, S. C.; Batley, G. E.; Gadd, G. E.; Casey, P. S. Nanoparticulate ZnO, bulk ZnO, and ZnCl₂ to a freshwater microalga (*Pseudokirchneriella subcapitata*): The importance of particle solubility. *Environ. Sci. Technol.* **2007**, *41*, 8484–8490.

- [176] Hildebrand, H.; Kuhnel, D.; Potthoff, A.; Mackenzie, K.; Springer, A.; Schirmer, K. Evaluating the cytotoxicity of palladium/magnetite nano-catalysts intended for wastewater treatment. *Environ. Pollut.* **2010**, *158*, 65–73.
- [177] Schultz, A. G.; Boyle, D.; Chamot, D.; Ong, K. J.; Wilkinson, K. J.; McGeer, J. C.; Sunahara, G.; Goss, G. G. Aquatic toxicity of manufactured nanomaterials: Challenges and recommendations for future toxicity testing. *Environ. Chem.* **2014**, *11*, 207–226.
- [178] Ma, H. B.; Williams, P. L.; Diamond, S. A. Ecotoxicity of manufactured ZnO nanoparticles - A review. *Environ. Pollut.* **2013**, *172*, 76–85.
- [179] Peulen, T.-O.; Wilkinson, K. J. Diffusion of nanoparticles in a biofilm. *Environ. Sci. Technol.* **2011**, *45*, 3367–3373.
- [180] Reidy, B.; Haase, A.; Luch, A.; Dawson, K. A.; Lynch, I. Mechanisms of silver nanoparticle release, transformation and toxicity: A critical review of current knowledge and recommendations for future studies and applications. *Mater.* **2013**, *6*, 2295–2350.
- [181] Praetorius, A.; Scheringer, M.; Hungerbühler, K. Development of environmental fate models for engineered nanoparticles - A case study of TiO₂ nanoparticles in the Rhine River. *Environ. Sci. Technol.* **2012**, *46*, 6705–6713.
- [182] Lowry, G. V.; Espinasse, B. P.; Badireddy, A. R.; Richardson, C. J.; Reinsch, B. C.; Bryant, L. D.; Bone, A. J.; Deonarine, A.; Chae, S.; Therezien, M. et al. Long-term transformation and fate of manufactured Ag nanoparticles in a simulated large scale freshwater emergent wetland. *Environ. Sci. Technol.* **2012**, *46*, 7027–7036.
- [183] Westerhoff, P.; Nowack, B. Searching for global descriptors of engineered nanomaterial fate and transport in the environment. *Acc. Chem. Res.* **2013**, *46*, 844–853.
- [184] Gavankar, S.; Suh, S.; Keller, A. F. Life cycle assessment at nanoscale: Review and recommendations. *Int. J. Life Cycle Assess.* **2012**, *17*, 295–303.
- [185] Cornelis, G.; Hund-Rinke, K.; Kuhlbusch, T.; van den Brink, N.; Nickel, C. Fate and bioavailability of engineered nanoparticles in soils: A review. *Crit. Rev. Env. Sci. Technol.* **2014**, *44*, 2720–2764.
- [186] Chalew, T. E. A.; Ajmani, G. S.; Huang, H. O.; Schwab, K. J. Evaluating nanoparticle breakthrough during drinking water treatment. *Environ. Health Persp.* **2013**, *121*, 1161–1166.
- [187] Zhu, Y. Q.; Fan, L.; Yang, B.; Du, J. Z. Multifunctional homopolymer vesicles for facile immobilization of gold nanoparticles and effective water remediation. *ACS Nano* **2014**, *8*, 5022–5031.
- [188] Westerhoff, P.; Song, G. X.; Hristovski, K.; Kiser, M. A. Occurrence and removal of titanium at full scale wastewater treatment plants: Implications for TiO₂ nanomaterials. *J. Environ. Monit.* **2011**, *13*, 1195.
- [189] Rottman, J.; Sierra-Alvarez, R.; Shadman, F. Real-time monitoring of nanoparticle retention in porous media. *Environ. Chem. Lett.* **2013**, *11*, 71–76.
- [190] Rahman, T.; Millwater, H.; Shipley, H. J. Modeling and sensitivity analysis on the transport of aluminum oxide nanoparticles in saturated sand: Effects of ionic strength, flow rate, and nanoparticle concentration. *Sci. Total Environ.* **2014**, *499*, 402–412.
- [191] Wu, N.; Wyart, Y.; Liu, Y.; Rose, J.; Moulin, P. An overview of solid/liquid separation methods and size fractionation techniques for engineered nanomaterials in aquatic environment. *Environ. Technol. Rev.* **2013**, *2*, 55–70.
- [192] Westerhoff, P. K.; Kiser, M. A.; Hristovski, K. Nanomaterial removal and transformation during biological wastewater treatment. *Environ. Eng. Sci.* **2013**, *30*, 109–117.
- [193] Ferreira da Silva, B.; Perez, S.; Gardinalli, P.; Singhal, R. K.; Mozeto, A. A.; Barcelo, D. Analytical chemistry of metallic nanoparticles in natural environments. *TrAC-Trend. Anal. Chem.* **2011**, *30*, 528–540.
- [194] von der Kammer, F.; Ferguson, P. L.; Holden, P. A.; Masion, A.; Rogers, K. R.; Klaine, S. J.; Koelmans, A. A.; Horne, N.; Unrine, J. M. Analysis of engineered nanomaterials in complex matrices (environment and biota): General considerations and conceptual case studies. *Environ. Toxicol. Chem.* **2012**, *31*, 32–49.
- [195] Weinberg, H.; Galyean, A.; Leopold, M. Evaluating engineered nanoparticles in natural waters. *TrAC-Trend. Anal. Chem.* **2011**, *30*, 72–83.
- [196] Dreyer, D. R.; Miller, D. J.; Freeman, B. D.; Paul, D. R.; Bielawski, C. W. Elucidating the structure of poly(dopamine). *Langmuir* **2012**, *28*, 6428–6435.
- [197] Kasemset, S.; Lee, A.; Miller, D. J.; Freeman, B. D.; Sharma, M. M. Effect of polydopamine deposition conditions on fouling resistance, physical properties, and permeation properties of reverse osmosis membranes in oil/water separation. *J. Memb. Sci.* **2013**, *425*, 208–216.
- [198] McCloskey, B. D.; Park, H. B.; Ju, H.; Rowe, B. W.; Miller, D. J.; Chun, B. J.; Kin, K.; Freeman, B. D. Influence of polydopamine deposition conditions on pure water flux and foulant adhesion resistance of reverse osmosis, ultrafiltration, and microfiltration membranes. *Polymer* **2010**, *51*, 3472–3485.
- [199] Miller, D. J.; Araujo, P. A.; Correia, P. B.; Ramsey, M. M.; Kruihof, J. C.; van Loosdrecht, M. C. M.; Freeman, B. D.; Paul, D. R.; Whiteley, M.; Vrouwenvelder, J. S. Short-term adhesion and long-term biofouling testing of polydopamine

- and poly(ethylene glycol) surface modifications of membranes and feed spacers for biofouling control. *Water Res.* **2012**, *46*, 3737–3753.
- [200] McCloskey, B. D.; Park, H. B.; Ju, H.; Rowe, B. W.; Miller, D. J.; Freeman, B. D. A bioinspired fouling-resistant surface modification for water purification membranes. *J. Memb. Sci.* **2012**, *413–414*, 82–90.
- [201] Tang, Z. H.; Qiu, C. Q.; McCutcheon, J. R.; Yoon, K.; Ma, H. Y.; Fang, D. F.; Lee, E.; Kopp, C.; Hsiao, B. S.; Chu, B. Design and fabrication of electrospun polyethersulfone nanofibrous scaffold for high-flux nanofiltration membranes. *J. Polym. Sci. B Polym. Phys.* **2009**, *47*, 2288–2300.
- [202] Bui, N.-N.; McCutcheon, J. R. Hydrophilic nanofibers as new supports for thin film composite membranes for engineered osmosis. *Environ. Sci. Technol.* **2013**, *47*, 1761–1769.
- [203] Huang, L.; Bui, N.-N.; Manickam, S. S.; McCutcheon, J. R. Controlling electrospun nanofiber morphology and mechanical properties using humidity. *J. Polym. Sci. B Polym. Phys.* **2011**, *49*, 1734–1744.
- [204] Jackson, E. A.; Hillmyer, M. A. Nanoporous membranes derived from block copolymers: From drug delivery to water filtration. *ACS Nano* **2010**, *4*, 3548–3553.
- [205] Phillip, W. A.; O'Neill, B.; Rodwogin, M.; Hillmyer, M. A.; Cussler, E. L. Self-assembled block copolymer thin films as water filtration membranes. *ACS App. Mater. Int.* **2010**, *2*, 847–853.
- [206] Yeo, J.; Kim, S. Y.; Kim, S.; Ryu, D. Y.; Kim, T.-H.; Park, M. J. Mechanically and structurally robust sulfonated block copolymer membranes for water purification applications. *Nanotechnol.* **2012**, *23*, 245703.
- [207] Wandera, D.; Himstedt, H. H.; Marroquin, M.; Wickramasinghe, S. R.; Husson, S. M. Modification of ultrafiltration membranes with block copolymer nanolayers for produced water treatment: The roles of polymer chain density and polymerization time on performance. *J. Memb. Sci.* **2012**, *403*, 250–260.
- [208] Karunakaran, M.; Nunes, S. P.; Qiu, X. Y.; Yu, H. Z.; Peinemann, K.-V. Isoporous PS-b-PEO ultrafiltration membranes via self-assembly and water-induced phase separation. *J. Memb. Sci.* **2014**, *453*, 471–477.
- [209] Marques, D. S.; Vainio, U.; Chaparro, N. M.; Carlo, V. M.; Behzad, A. R.; Pitera, J. W.; Peinemann, K.-V.; Nunes, S. P. Self-assembly in casting solutions of block copolymer membranes. *Soft Mat.* **2013**, *9*, 5557–5564.
- [210] Nunes, S. P.; Behzad, A. R.; Peinemann, K.-V. Self-assembled block copolymer membranes: From basic research to large scale manufacturing. *J. Mater. Res.* **2013**, *28*, 2661–2665.
- [211] Dorin, R. M.; Phillip, W. A.; Sai, H.; Werner, J.; Elimelech, M.; Wiesner, U. Designing block copolymer architectures for targeted membrane performance. *Polymer* **2014**, *55*, 347–353.
- [212] Phillip, W. A.; Dorin, R. M.; Werner, J.; Hoek, E. M. V.; Wiesner, U.; Elimelech, M. Tuning structure and properties of graded triblock terpolymer-based mesoporous and hybrid films. *Nano Lett.* **2011**, *11*, 2892–2900.
- [213] Gu, Y. B.; Dorin, R. M.; Wiesner, U. Asymmetric organic-inorganic hybrid membrane formation via block copolymer-nanoparticle co-assembly. *Nano Lett.* **2013**, *13*, 5323–5328.
- [214] Hoheisel, T. N.; Hur, K.; Wiesner, U. B. Block copolymer-nanoparticle hybrid self-assembly. *Prog. Polym. Sci.* **2015**, *40*, 3–32.
- [215] Warren, S. C.; Messina, L. C.; Slaughter, L. S.; Kamperman, M.; Zhou, Q.; Gruner, S. M.; DiSalvo, F. J.; Wiesner, U. Ordered mesoporous materials from metal nanoparticle-block copolymer self-assembly. *Science* **2008**, *320*, 1748–1752.
- [216] Bokare, A. D.; Chikate, R. C.; Rode, C. V.; Paknikar, K. M. Iron-nickel bimetallic nanoparticles for reductive degradation of azo dye Orange G in aqueous solution. *Appl. Catal. B* **2008**, *79*, 270–278.
- [217] Fang, Z. Q.; Qiu, X. H.; Chen, J. H.; Qiu, X. Q. Debromination of polybrominated diphenyl ethers by Ni/Fe bimetallic nanoparticles: Influencing factors, kinetics, and mechanism. *J. Hazard. Mater.* **2011**, *185*, 958–969.
- [218] Cao, J.; Xu, R. F.; Tang, H.; Tang, S. S.; Cao, M. H. Synthesis of monodispersed CMC-stabilized Fe-Cu bimetal nanoparticles for *in situ* reductive dechlorination of 1, 2, 4-trichlorobenzene. *Sci. Total Environ.* **2011**, *409*, 2336–2341.
- [219] Choi, K.; Lee, W. Enhanced degradation of trichloroethylene in nano-scale zero-valent iron Fenton system with Cu(II). *J. Hazard. Mater.* **2012**, *211*, 146–153.
- [220] Chun, C. L.; Baer, D. R.; Matson, D. W.; Amonette, J. E.; Penn, R. L. Characterization and reactivity of iron nanoparticles prepared with added Cu, Pd, and Ni. *Environ. Sci. Technol.* **2010**, *44*, 5079–5085.
- [221] Joo, S. H.; Feitz, A. J.; Waite, T. D. Oxidative degradation of the carbothioate herbicide, molinate, using nanoscale zero-valent iron. *Environ. Sci. Technol.* **2004**, *38*, 2242–2247.
- [222] Keenan, C. R.; Sedlak, D. L. Ligand-enhanced reactive oxidant generation by nanoparticulate zero-valent iron and oxygen. *Environ. Sci. Technol.* **2008**, *42*, 6936–6941.
- [223] Lee, C.; Keenan, C. R.; Sedlak, D. L. Polyoxometalate-enhanced oxidation of organic compounds by nanoparticulate zero-valent iron and ferrous ion in the presence of oxygen. *Environ. Sci. Technol.* **2008**, *42*, 4921–4926.

- [224] Hooshyar, Z.; Bardajee, G. R.; Ghayeb, Y. Sonication enhanced removal of nickel and cobalt ions from polluted water using an iron based sorbent. *J. Chem.* **2012**, *2013*, 786954.
- [225] Hug, S. J.; Leupin, O. Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction. *Environ. Sci. Technol.* **2003**, *37*, 2734–2742.
- [226] Liu, T. Z.; Tsang, D. C. W.; Lo, I. M. C. Chromium(VI) reduction kinetics by zero-valent iron in moderately hard water with humic acid: Iron dissolution and humic acid adsorption. *Environ. Sci. Technol.* **2008**, *42*, 2092–2098.
- [227] Armon, R.; Weltch-Cohen, G.; Bettane, P. Disinfection of *Bacillus* spp. spores in drinking water by TiO₂ photocatalysis as a model for *Bacillus anthracis*. *Water Sci. Technol. Water Supp.* **2004**, *4*, 7–14.
- [228] Antoniou, M. G.; Nicolaou, P. A.; Shoemaker, J. A.; de la Cruz, A. A.; Dionysiou, D. D. Impact of the morphological properties of thin TiO₂ photocatalytic films on the detoxification of water contaminated with the cyanotoxin, microcystin-LR. *Appl. Catal. B Env.* **2009**, *91*, 165–173.
- [229] Zhang, H.; Lv, X. J.; Li, Y. M.; Wang, Y.; Li, J. H. P25-graphene composite as a high performance photocatalyst. *ACS Nano* **2010**, *4*, 380–386.
- [230] Jain, S.; Yamgar, R.; Jayaram, R. V. Photolytic and photocatalytic degradation of atrazine in the presence of activated carbon. *Chem. Eng. J.* **2009**, *148*, 342–347.
- [231] Žabar, R.; Komel, T.; Fabjan, J.; Kralj, M. B.; Trebše, P. Photocatalytic degradation with immobilised TiO₂ of three selected neonicotinoid insecticides: Imidacloprid, thiamethoxam and clothianidin. *Chemosphere* **2012**, *89*, 293–301.
- [232] Tu, W. G.; Zhou, Y.; Zou, Z. G. Versatile graphene-promoting photocatalytic performance of semiconductors: Basic principles, synthesis, solar energy conversion, and environmental applications. *Adv. Func. Mater.* **2013**, *23*, 4996–5008.
- [233] Bae, E. Y.; Choi, W. Y. Highly enhanced photoreductive degradation of perchlorinated compounds on dye-sensitized metal/TiO₂ under visible light. *Environ. Sci. Technol.* **2003**, *37*, 147–152.
- [234] Kubacka, A.; Fernández-García, M.; Colón, G. Advanced nanoarchitectures for solar photocatalytic applications. *Chem. Rev.* **2012**, *112*, 1555–1614.
- [235] Su, R.; Tiruvalam, R.; He, Q.; Dimitratos, N.; Kesavan, L.; Hammond, C.; Lopez-Sanchez, J. A.; Bechstein, R.; Kiely, C. J.; Hutchings, G. J. et al. Promotion of phenol photodecomposition over TiO₂ using Au, Pd, and Au-Pd nanoparticles. *ACS Nano* **2012**, *6*, 6284–6292.
- [236] Zhang, W. J.; Zhou, C. J.; Zhou, W. C.; Lei, A. H.; Zhang, Q. L.; Wan, Q.; Zou, B. S. Fast and considerable adsorption of methylene blue dye onto graphene oxide. *Bull. Environ. Contam. Toxicol.* **2011**, *87*, 86–90.
- [237] Ion, A. C.; Alpatova, A.; Ion, I.; Culetu, A. Study on phenol adsorption from aqueous solutions on exfoliated graphitic nanoplatelets. *Mater. Sci. Eng. B.* **2011**, *176*, 588–595.
- [238] Lu, K.; Zhao, G. X.; Wang, X. K. A brief review of graphene-based material synthesis and its application in environmental pollution management. *Chinese Sci. Bull.* **2012**, *57*, 1223–1234.
- [239] Zhao, G. X.; Li, J. X.; Ren, X. M.; Chen, C. L.; Wang, X. K. Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management. *Environ. Sci. Technol.* **2011**, *45*, 10454–10462.
- [240] Sun, Y. B.; Wang, Q.; Chen, C. L.; Tan, X. L.; Wang, X. K. Interaction between Eu(III) and graphene oxide nanosheets investigated by batch and extended X-ray absorption fine structure spectroscopy and by modeling techniques. *Environ. Sci. Technol.* **2012**, *46*, 6020–6027.
- [241] Hu, M.; Mi, B. X. Layer-by-layer assembly of graphene oxide membranes via electrostatic interaction. *J. Membr. Sci.* **2014**, *469*, 80–87.
- [242] O'Hern, S. C.; Boutilier, M. S. H.; Idrobo, J. C.; Song, Y.; Kong, J.; Laoui, T.; Atieh, M.; Karnik, R. Selective ionic transport through tunable subnanometer pores in single-layer graphene membranes. *Nano Lett.* **2014**, *14*, 1234–1241.
- [243] Yeh, C.-N.; Raidongia, K.; Shao, J. J.; Yang, Q.-H.; Huang, J. X. On the origin of the stability of graphene oxide membranes in water. *Nature Chem.* **2015**, *7*, 166–170.
- [244] Nair, R. R.; Wu, H. A.; Jayaram, P. N.; Grigorieva, I. V.; Geim, A. K. Unimpeded permeation of water through Helium-leak-tight graphene-based membranes. *Science* **2012**, *335*, 442–444.
- [245] Greenlee, L. F.; Hooker, S. A. Development of stabilized zero valent iron nanoparticles. *Desalin. Water Treat.* **2012**, *37*, 114–121.
- [246] Greenlee, L. F.; Torrey, J. D.; Amaro, R. L.; Shaw, J. M. Kinetics of zero valent iron nanoparticle oxidation in oxygenated water. *Environ. Sci. Technol.* **2012**, *46*, 12913–12920.
- [247] Bhattacharyya, D. Functionalized membranes and environmental applications. *Clean Technol. Envir.* **2007**, *9*, 81–83.
- [248] Pendergast, M. M. Separation performance and interfacial properties of nanocomposite reverse osmosis membranes. *Desalination* **2013**, *308*, 180–185.
- [249] Pendergast, M. M.; Hoek, E. M. V. A review of water treatment membrane nanotechnologies. *Energy Environ. Sci.* **2011**, *4*, 1946–1971.

- [250] Han, Y.; Xu, Z.; Gao, C. Ultrathin graphene nanofiltration membrane for water purification. *Adv. Funct. Mater.* **2013**, *23*, 3693–3700.
- [251] Bedford, N. M.; Pelaez, M.; Han, C. S.; Dionysiou, D. D.; Steckl, A. J. Photocatalytic cellulosic electrospun fibers for the degradation of potent cyanobacteria toxin microcystin-LR. *J. Mater. Chem.* **2012**, *22*, 12666–12674.
- [252] Byun, S.; Davies, S. H.; Alpatova, A. L.; Corneal, L. M.; Baumann, M. J.; Tarabara, V. V.; Masten, S. J. Mn oxide coated catalytic membranes for a hybrid ozonation-membrane filtration: Comparison of Ti, Fe and Mn oxide coated membranes for water quality. *Water Res.* **2011**, *45*, 163–170.
- [253] Choi, J. H.; Jegal, J.; Kim, W. N. Fabrication and characterization of multi-walled carbon nanotubes/polymer blend membranes. *J. Memb. Sci.* **2006**, *284*, 406–415.
- [254] Dotzauer, D. A.; Bhattacharjee, S.; Wen, Y.; Bruening, M. L. Nanoparticle-containing membranes for the catalytic reduction of nitroaromatic compounds. *Langmuir* **2009**, *25*, 1865–1871.
- [255] Gui, M. H.; Smuleac, V.; Ormsbee, L. E.; Sedlak, D. L.; Bhattacharyya, D. Iron oxide nanoparticle synthesis in aqueous and membrane systems for oxidative degradation of trichloroethylene from water. *J. Nanopart. Res.* **2012**, *14*, 861.
- [256] Lee, H. S.; Im, S. J.; Kim, J. H.; Kim, H. J.; Kim, J. P.; Min, B. R. Polyamide thin-film nanofiltration membranes containing TiO₂ nanoparticles. *Desalination* **2008**, *219*, 48–56.
- [257] Lind, M. L.; Suk, D. E.; Nguyen, T. V.; Hoek, E. M. V. Tailoring the structure of thin film nanocomposite membranes to achieve seawater RO membrane performance. *Environ. Sci. Technol.* **2010**, *44*, 8230–8235.
- [258] Liang, S.; Xiao, K.; Mo, Y. H.; Huang, X. A novel ZnO nanoparticle blended polyvinylidene fluoride membrane for anti-irreversible fouling. *J. Memb. Sci.* **2012**, *394*, 184–192.
- [259] Smuleac, V.; Varma, R.; Sikdar, S.; Bhattacharyya, D. Green synthesis of Fe and Fe/Pd bimetallic nanoparticles in membranes for reductive degradation of chlorinated organics. *J. Memb. Sci.* **2011**, *379*, 131–137.
- [260] Taurozzi, J. S.; Arul, H.; Bosak, V. Z.; Burban, A. F.; Voice, T. C.; Bruening, M. L.; Tarabara, V. V. Effect of filler incorporation route on the properties of polysulfone-silver nanocomposite membranes of different porosities. *J. Memb. Sci.* **2008**, *325*, 58–68.
- [261] Xu, J.; Dozier, A.; Bhattacharyya, D. Synthesis of nanoscale bimetallic particles in polyelectrolyte membrane matrix for reductive transformation of halogenated organic compounds. *J. Nanopart. Res.* **2005**, *7*, 449–467.
- [262] Yang, Y. N.; Zhang, H. X.; Wang, P.; Zheng, Q. Z.; Li, J. The influence of nano-sized TiO₂ fillers on the morphologies and properties of PSF UF membrane. *J. Memb. Sci.* **2007**, *288*, 231–238.
- [263] Zhu, C. Q.; Li, H.; Zeng, X. C.; Wang, E. G.; Meng, S. Quantized water transport: Ideal desalination through graphyne-4 membrane. *Sci. Rep.* **2013**, *3*, 3163.
- [264] Guillot, B. A reappraisal of what we have learnt during three decades of computer simulations on water. *J. Mol. Liq.* **2002**, *101*, 219–260.
- [265] Yoo, S.; Zeng, X. C.; Xantheas, S. S. On the phase diagram of water with density functional theory potentials: The melting temperature of ice Ih with the Perdew-Burke-Ernzerhof and Becke-Lee-Yang-Parr functionals. *J. Chem. Phys.* **2009**, *130*, 221102.