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Nanoscience and Nanotechnology for Water Remediation: An Earnest Hope toward Sustainability

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Nanoscience and Nanotechnology for Water Remediation: An Earnest Hope toward Sustainability

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Water pollution and global freshwater crisis is the most alarming concern of 21st century, as they threaten the sustainability and ecological balance of the environment. The growth of global population, climate change, and expansion of industrial processes are the main causes of this crisis. Therefore, effective remediation of polluted water by the means of detoxification and purification are of paramount importance. To this end, nanoscience and nanotechnology have emerged as a viable option that hold tremendous potential toward advancement of wastewater treatment methods to enhance treatment efficiency along with augmenting water supply via utilization of unconventional water sources. Materials at the nano level have shown great promise toward water treatment applications owing to their unique physicochemical properties. In this focus article, we highlight the role of fundamental new properties at the nano scale and material properties that are drastically increased due to the nano dimension (e.g. volume-surface ratio) and highlighting their impact and potential toward water treatment. We identify and discuss how nano-properties could improve the three main domains of water remediation: the individuation of pollutants, their adsorption and catalytic degradation. After discussing on all the benefitial aspects we further refelct on the key challenges associated with nanomaterials for water treatment. Looking at the current state-of-the-art, the potential as well as the challenges of nanomatrerials we believe that in the future we will see a significant impact of those materials on many water redemiation challenges.

1. Introduction

Water stands as the fundamental resource crucial for the existence and development of all living organisms.[1-2] Despite covering approximately 71% of the Earth's surface, only a mere 0.5% constitutes freshwater suitable for drinking. The contemporary era, marked by technological advancements and overpopulation, has led to unprecedented environmental challenges, including global warming, water pollution, and ocean acidification. These issues stem from the adverse impacts of rapid growth in industrial and agricultural sectors worldwide.[3-6] As a consequence, freshwater resources are depleting due to the extensive release and infiltration of wastewaters into natural water reserves.[7-8] The United Nations estimates that the global population will surpass 10 billion by 2050, and that 2 billion people lack or have limited access to safe drinking water already in 2024.[9] Moreover, hazardous contaminants in water significantly disrupt the balance of aquatic ecosystems. Therefore, proper disposal, separation, and detoxification of wastewater are imperative for preserving ecological symbiosis.[10-14]

The primary sources of water pollutants include industrial waste, oil spills, nuclear waste leakage, mining activities, and agricultural products, which introduce toxic chemicals into natural water bodies.[15-20] These pollutants can be broadly categorized into inorganic and organic types based on their chemical compositions. Inorganic pollutants, comprising toxic heavy metals and radioactive elements, pose greater threats due to their charged nature, resulting in high solubility and mobility in water.[21-23] Additionally, these contaminants can accumulate in the food chain and in the human body where a narrow range lies between deficiency and toxicity, posing a grave risk due to their toxicity and lethality even at lower concentrations.[24-26] On the other hand, organic pollutants, such as hydrocarbons, black waters, insecticides and herbicides, agricultural waste products, dyes, oils and pharmaceuticals, persistently enter the environment in large volumes.[27-29] Despite being, for the most part, less persistent than inorganic pollutants, their continuous generation makes them pseudo-persistent in environmental ecosystems.

In response to the health and environmental risks, various water treatment techniques, including filtration, chemical precipitation, and coagulation, have been developed.[30-33] These techniques employ a plethora of different materials characterized by different properties, such as oxidizing agents, coagulants, flocculants, ion

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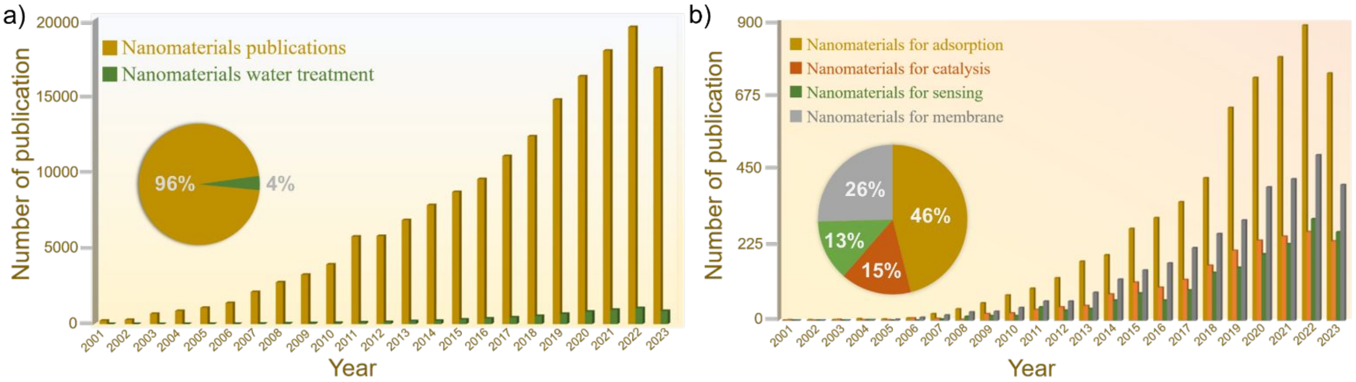

Figure 1: Chronological evolution of the nanomaterials-field and/or nanomaterials for water treatment: a) comparison between overall publications in nanomaterials and nanomaterials for water treatment; b) numerical comparison between publication trend for various water treatment processes by nanomaterials.

exchange resins, and pH-adjusting substances. However, these methods face limitations such as expensive facilities, high maintenance and complex instrumentations, or require materials that are too costly or which production is environmentally unsustainable, making them often unsustainable, in particular in developing countries.[34-36] Novel, simpler methods with improved performance from both energetic and economic perspectives are deeply needed. To this end, recent advancements in chemistry and material science has the potential to advance water treatment technology.

In particular, emergence of nanoscience and nanotechnology over the past decades have played a key role in shaping of current environmental remediation science and technology.[37-42] To begin with, it is important to understand the scopes and differences between nanoscience and nanotechnology. Typically, nanoscience represents a broad multidisciplinary area of scientific research, manipulation with particles and structures in the dimensions of 1-100 nm.[43] Nanoscience deals with precise control over nanoscale assembly of atoms and molecules into the larger structures, which determines the extent of different physiochemical properties such as the thermal, optical, electrical, mechanical properties of the nanomaterials. The field of nanoscience allows mutual cooperation of physicists, chemists, biologists, and material scientists to understand and solve critical scientific challenges.[44-46] On the other hand, nanotechnology is generally attributed as the application of nanoscience materials. Hence, it works in continuation with nanoscience toward engineering and manufacturing of nanomaterials and nanomaterials-based devices for practical applications.[47]

The transformation from bulk material to nano-scale inevitably induces unique materials' characteristics such as size- and surface-dependent physiochemical behaviours, size-dependent quantum effects.[48-49] Consequently, nanomaterials found to have unique electronic, optical and mechanical properties. Overall, the properties can be divided into two large groups: *i*) enhanced properties and *ii*) emergent novel properties.

***i*) Enhancement of bulk properties** – Typically the bulk counterparts have these properties, however, the reduction in size to the nano-level induces exponential enhancement of these properties (e.g. surface area, number of catalytic centres, number of binding sites and as a result reactivity, superparamagnetic properties).

***ii*) Emergence of novel properties** – Typically, bulk materials do not have these properties and they are appearing at the nano-scale. For instance, quantum effects in nanoparticles (size-dependent position of energy levels of QDs and as a result the sift of absorbed light wavelength, plasmon resonance of Au and Ag nanoparticles and its size-dependent shift).

As a result, nanoscience comprises a huge research interest with many applications (Figure 1) but surprisingly water treatment applications as so far underexplored (Figure 1). Till date, the enhancement in nano-properties have been mostly exploited for water treatment, presenting vast unexplored opportunities and a lot of space for further improvements both in nanoscience and nanotechnology for water treatment.

It is worth mentioning that the property gain can vary significantly among different nanomaterials, highlighting the impact of material nature on the focus of investigation. For instance, surface area increases significantly for almost all materials when switching from bulk to the nano scale. In contrast, properties like melting point or fluorescence exhibit diverse changes. Organic nanoparticles show a substantial change in melting point compared to bulk, while metal nanoparticles show no change. Quantum dots display tunable size-dependent fluorescence, whereas there is no such dependence for the organic molecules. Therefore, adequate information and control over such material-property relationships are crucial for the development of efficient nanomaterials for water treatment.

Therefore, in this focus article, we wish to reflect the state-of-art as well as a critical assessment of the benefits and challenges of using nanomaterials and nanotechnology for water remediation.

2. The promise of "nano" in water treatment

The unique chemical, physical and optical properties of nanomaterials and their judicious utilization via nanotechnology have opened new horizons in water treatment research and technologies (Figure 2).[50-58] For instance, the enhanced light absorbing ability of functional nanomaterials made them as excellent platform for photothermal water treatment in solar desalination, nano-photonics based membrane distillation, disinfection applications and so on.[59-64] Moreover, traditional water treatment methods involve utilization of toxic chemicals as disinfectants that possess critical threat from generation of carcinogenic by-products, and iron- and aluminium-based coagulants in large volume which are typically dumped into landfills after use and rarely regenerated.[65-68] To this end, employing nanomaterials in water treatment not only reduce the potential toxicity footprints, but also enhance the overall working capacity and sustainability via multicycle regeneration with unaltered performance.

Individual or combined merits of enhanced and emergent nano-properties render extraordinary water remediation abilities in terms of adsorptive, catalytic and sensory properties.[57-61] Hence, it is important to reflect the origin of such properties and why "nano" materials help to address existing challenges.

Adsorptive properties. Nanomaterials have emerged as an important platform for adsorbing water pollutants owing to their unique properties such as;

High surface area and tunable surface properties: The high surface area that originate from the high surface volume-surface ratio together with tunable surface properties provides high number of active sites for the adsorption of water pollutants and enhanced sorbate-sorbent interaction.[69-71] Hence, a small amount of nanomaterial can exhibit very high adsorption kinetics and removal capacity.

Particle size: The smaller size and closer intraparticle distance allow the nanoparticles to reach and adequately interact with micro/nano-scaled water pollutants at the molecular level. With greater extent of interaction, the nanomaterials´ ability toward adsorbing a wide range of contaminants from water enhances.

Porosity: The higher porosity of nanomaterials compared to their bulks found to enhance the interaction at both internal and external surface, leading to improved adsorption capacity and diffusion rates. In this regard, porous nanomaterials such as activated carbon nanofibers, zeolite, metal-organic frameworks (MOFs) etc. offer tunable porous structure and pore surface that allow control over sorption kinetics and capacity.[72-77]

Moreover, the properties of nano-sorbents can be judicially tuned for target-specific pollutants adsorption via precise structure–property relationship establishments. For instance, significant pitfalls of conventional water treatment methods have been associated with several toxic ionic contaminants (perchlorate, nitrate etc.), heavy metal based oxo-anions (e.g. chromate, arsenate, selenite) and emerging pollutants including per- and polyfluoroalkyl substances (PFAS) etc. owing to their poor selectivity and lack of active functional sites.[78-80] To this end, nanomaterials found to offer superior selectivity toward targeted ionic pollutants and enhanced catalytic activity toward cleave of the C–F bond and sorptive efficiency for removal of PFAS. Further, nano-adsorbents can be easily integrated with other macroscopic structures or into existing water treatment by loading into porous granules or via coating filter media. The culminative or individual merit of these adsorptive properties make nanomaterials superior in real-time water treatment applications.

Catalytic properties. Nanomaterials with a high surface-to-volume ratio can induce high degree of catalytic activity owing to the presence of greater number of catalytically active sites and their facile accessibility compared to their bulk counter parts.[81] In addition, the higher reactivity of nano-catalysts resulted in improved degradation or transformation of environmental pollutants with better kinetics and selectivity than that of their bulk materials.[82-84]

Typically, catalytic degradation processes involve following stages: adsorption of the pollutant molecules, absorption of the irradiated light, and eventually charge transport and separation and degradation of polutant.[85] From the fundamental-perspective, the reason behind the superior photocatalytic efficiency of nano-catalyst materials can be attributed to two main nano-properties.

Quantum size effect: Upon decreasing the particle size to below nanoscale range, one of the immediate effects occurs to the particles is quantum confinement.[86] Depending upon the electronic properties and the size of the materials, the CB and VB are converting into different energy levels, inducing positive electric potential in VB and negative electric potential in CB. Consequently, the oxidation and reduction potential of the holes and the electrons get increased, resulting in improved oxidation reactivity of nano-photocatalysts (e.g., ZnO and TiO_2). [87]

Higher surface area: Increased surface area improve efficiency of the first step of photocatalytic degradation – adsorption of pollutant, and the last steps – charge separation and catalytic degradation. The reactivity is typically governed by the time required to reach the holes and electrons to the catalyst surface.[88] At the nanoscale range, the particle diameter becomes considerably small which renders a much rapid charge transport from the interior to the surface of the nanoparticles, reduces the possibilities of electron–hole recombination and commence the redox reaction. For example, the photocatalytic efficiency of ZnO and TiO_2 nanoparticles are found to be much higher with decrease of particle size.[89-90]

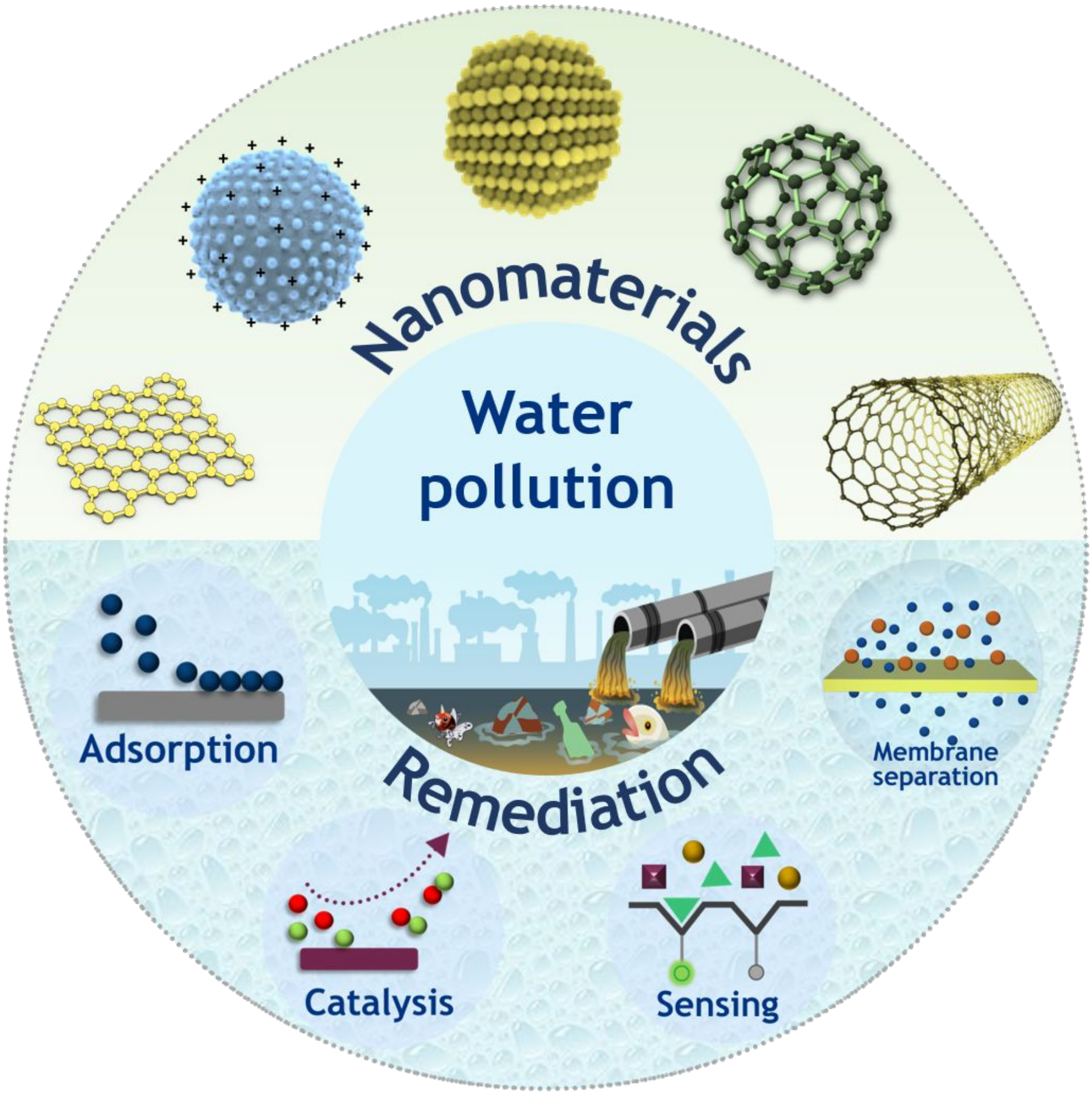

Figure 2: Schematic illustration of various nanomaterials and their potential applicability in different water remediation processes.

It is worth noting that the catalytic activates of Nano-materials can be significantly influenced by several factors including i) size, ii) shape, iii) the preparation medium, iv) the reaction conditions, and v) the distribution of the nanoparticles. Precise monitoring of all these factors are crucial in order to achieve ultimate control over the catalytic properties.[86]

Sensory properties. Precise monitoring of water pollutants is regarded as one of the toughest scientific and technological challenge because of the extremely low micropollutants concentrations along with the higher complexity of natural waters and wastewater systems. To this end, nanomaterials have shown tremendous potential toward selective sensing of various water pollutants with higher efficiency and detection limits. From the fundamental point of view, the higher surface area, surface activity and the electronic properties of nanomaterials play a crucial role in their effectiveness for sensing applications.

Surface-effects: The higher surface area of nanomaterials provides huge number of active/functional sites available for interactions with the targeted analytes, resulting in improved signal-to-noise ratio. Such improved signal-to-noise ratios are critical toward sensing of pollutants with very low/diluted concentrations, and decreasing the limit of detection. Moreover, the increased surface area allows greater adsorption of pollutants and consequently enhancing the sensitivity of the sensor.

Electronic effects: Size-dependent quantum effects allow tuning the electronic structure via adjusting the particle size, leading to unique optical properties. Such strategy is often employed in fluorescence-based sensory prob where the presence of targeted pollutants can be monitored via the change in fluorescence intensity or wavelength. In addition, the semiconducting nanomaterials are widely used for electrochemical sensing in which the electrical conductivity and the energy-bandgap can be precisely controlled via tuning the size, composition and functionalization of the nanomaterials, yielding in higher selectivity of the sensory probe.

Overall, water remediation is a very diverse topic as different aquatic systems present different levels and types of pollutants which necessitates development of target specific nanomaterials and technologies with high precision. From the design and selection perspective, judicious choice of respective building units for both nanomaterials (at molecular level) and nanotechnologies (at macroscopic level) holds huge potential toward efficient development of high-performance water treatment methods or devices.[91-93] It is important to point out that two nanomaterials with similar elemental composition can exhibit completely different water treatment efficiency and effectiveness upon alteration of their physiochemical parameters such as shape, size, surface functionality etc.[94-95] In addition, the nano-effects in nanocrystalline materials can be also fine-tuned by tuning the molecular building units as well as the synthetic parameters during synthesis or post-synthesis processing, resulting in alteration of adsorptive, magnetic, and catalytic activities.[96-98] Controlled manipulation of surface functionalization of nanoparticles has shown tremendous potential not only to improve stability and dispersibility of nanoparticles, but also effective transformation of nanomaterials into macroscopic structure development in the form of hybrid composites, membranes etc. for real-time applicability.[99-103] Moreover, surface functionalization can induce higher binding affinity and selectivity toward target contaminants, resulting in improved catalytic and oxidative activity, sorption capacity, paramagnetism and antimicrobial activity. On the other hand, the core-shell structure of nanomaterials affords additional advantages toward multifunctionality via controlling the stability, reactivity, and tunability at the nanoscale.[104] Hence, in-depth understanding and appropriate selection of various shapes, sizes and surface functionalities along with the core-shell nanostructures can yield in highly efficient nanomaterials and nanotechnologies.

3. Chemistry of nanoparticles in aqueous environment

The systematic correlation of the nanoparticle physicochemical properties under water of with their performances is the key toward improved water treatments. Upon entering into water, the immediate interactions occur at the solid-liquid interface between the nanoparticle surface and water medium, which consequently control the nano-abilities of the material in the immerged state.[105] The solid-liquid interfacial interactions between the nanoparticles and water medium are governed by the surface hydrophobicity and hydrophilicity along with the zeta potential of the nanoparticles (Figure 3). The water treatment performance of a nanomaterials significantly depends on its affinity toward water.[106-107] Again, nanoparticle surface plays crucial role as the amount of polar or Lewis acidic/basic functional groups present on the surface determines the extent of hydrogen bonding interactions with water molecules and thus controls the overall affinity toward water. From the nano-perspective, the nano-effect allows higher degree of facial hydrophilic/hydrophobic interactions which helps the nanoparticles to be dispersed easily in water medium, resulting in greater extent of contact with the contaminants and higher efficiency compared to their bulk components.

Moreover, structural and physical properties such as lattice defects, surface curvature and roughness etc. also play crucial roles toward interfacial interactions and solubility of nanoparticles. The overall behaviour of nanoparticles in aqueous medium typically governed by their chemical stability and dispersion stability of the materials.[108-109] In particular, dispersion stability of nanoparticles determines the exposure duration in water, whereas the chemical stability controls the overall physiochemical properties under water.[110] Dispersion stability of nanoparticles is the key factor in determining the exposure and fate of these materials in aquatic environment. It is well established that the size-variation at nano-scale will allow relatively bigger agglomerates of nanoparticles to act differently from the well dispersed ones.[111] The dispersion stability of nanoparticles can be influenced by several parameters including: their surface properties, solution chemistry (e.g., pH of the medium, ionic composition, ionic strength, nanoparticle concentration etc.) etc.[110] From the molecular point of view, the dispersion stability depends on the interparticle collision frequency and collision efficiency between two nanoparticles. Under aquatic environments, although the interparticle collision frequency can be originated from both Brownian motion and the local mechanical stirring, but Brownian motion prevails toward controlling the aggregation and dispersion extends of the nanoparticles.[112-114] Moreover, the sticking efficiency also depends on the type of interfacial interactions (attractive or repulsive) existing between colliding nanoparticles. For instance, stronger repulsive interaction results in reduced sticking efficiency and higher particle dispersion. On the other hand, stronger attractive interaction induces higher sticking efficiency and higher aggregation of the nanoparticles.

At nano-scale, the type and extent of attractive and repulsive interactions are governed by the existing electrostatic interactions and Van-der-Waals interactions between nanoparticles.[115] The electrostatic interactions occur between two electronically charged/polarized surfaces via electronic cloud diffusion. Hence, the ionic strength and pH of the medium, surface charge, and interparticle distance are the important factors, controlling the degree of electrostatic interactions in water medium.[116] Typically, electrostatic interactions in a homogeneous dispersion of same nanomaterial is repulsive in nature owing to the similar electric surface potential of the nanoparticles. On the other hand, the Van-der-Waals interactions between nanoparticles are constant and

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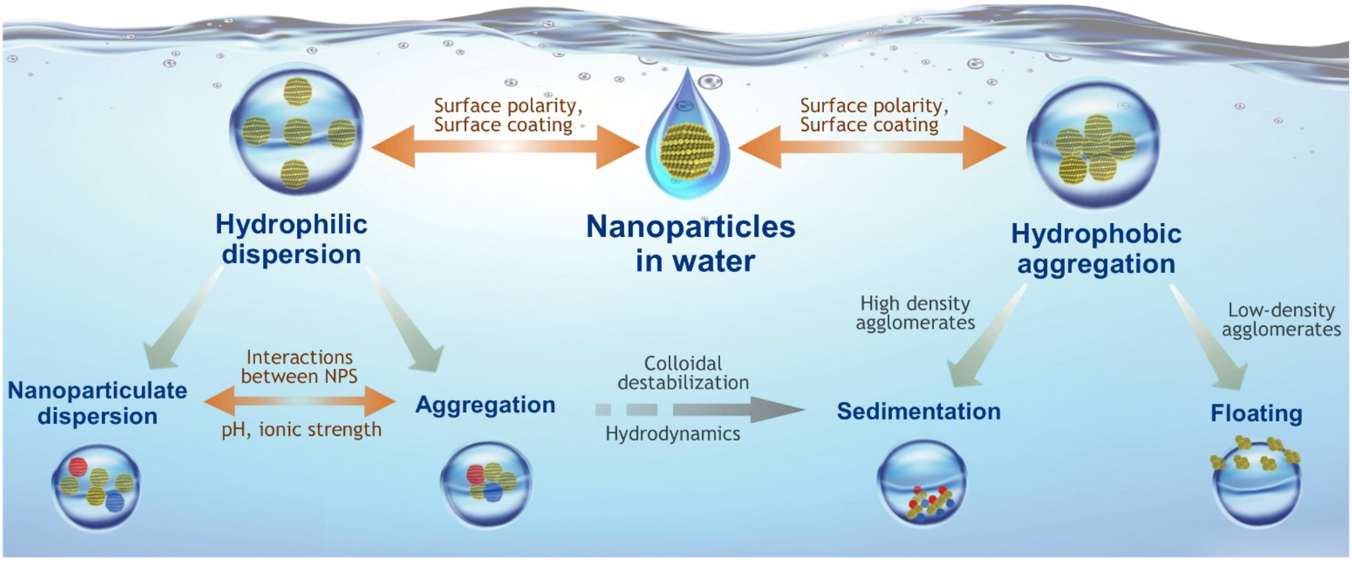

Figure 3: Properties of nanoparticles in water

attractive in nature. Hence, the resultant interaction originated from the repulsive electrostatic interactions and attractive Van-der-Waals interactions determine the extent of colloidal dispersion and dispersion stability at nano-level, thus significantly affecting the remediation potential of the nanomaterials.

4. Water remediation by nanoscience

Nanoscience is actively explored toward improvement of existing water treatment processes and even to developed new processes. However, for the real-world water treatment scenario, it is important to precisely define the target pollutants, their behaviour and safe-limits in order to develop sustainable and affordable nano-remediation technologies. Target-specific designing of nanomaterials via fine-tuning of their size, electronic properties and functionalities have shown tremendous promises in terms of selectivity and sensitivity toward several environmental contaminants even at very low concentration levels. Thus, defining the permitted level of the concentration is important for appropriate selection of nanomaterials toward developing the efficient water treatment process.

In the following subsequent section, we will highlight the key role of nanoscience toward water pollutants remediation.

4.1 Adsorption & Separation

Among the commonly utilized nano-adsorbents, carbon nanotubes (CNTs) are accounted as a promising alternative of activated carbon owing to their ability in effective removal of both toxic organic and inorganic water pollutants.[117-121] Owing to the advantage of controlled pore size distribution and high surface-active site to volume ratio, CNTs have already shown improvement in pollutants removal efficiency than that of the traditional powdered or granular activated carbons (Figure 4).[122] In particular, CNTs found to have active binding sites toward bulky organic pollutants adsorption which promotes selective interaction between CNTs and the incoming pollutants via intermolecular electrostatic interactions, π-π bonding, hydrogen bonding etc. Extensive studies have revealed that the pollutants removal depend upon both the type of sorbate molecules and the surface functional groups.[123] Moreover, their characteristic π-rich surface can act as both electron donor or acceptor toward toxic polar aromatic pollutants such as phenols and nitroaromatics (Figure 4).[124] While hydrophobic graphitic surfaces found to exhibit higher removal toward organic pollutants, adsorption of inorganic pollutants such as toxic metal ions primarily dominated by the surface functionalities via electrostatic interactions, which can be reversed controllably via tuning the pH of the medium, enabling reusability of the nanomaterial (Figure 4).[125-126] Since, CNTs are associated with significantly higher cost compared to the activated carbon materials, current research has been dedicated toward energy-economically sustainable materials development for pollutants preconcentration.

To this end, another allotropy of carbon, namely Graphene has emerged as a cost-effective alternative which can be synthesized by exfoliation of graphite.[122] In the last few decades, there has been significant utilization of graphene and graphene-based materials, such as graphene oxide (GO), in water pollutant remediation applications. This is attributed to their unique structural features, enabling the efficient remediation of a broad range of water pollutants.[127-130] Compared to CNTs, graphenes and its derivatives offer several advantages as sorbents for water treatment. Firstly, the single-layered graphene intrinsically possesses two accessible basal planes for effective interactions with the incoming pollutants whereas in case of CNTs, the inner walls are not available for the incoming pollutants. Secondly, GO based materials involves simpler synthetic methods which avoids utilization of metallic catalysts and energy intensive purification steps, resulting in more sustainable environmental footprints.[122] Moreover, these materials found to exhibit significant improvements in sorption capacity compared to their bulk carbon materials and pristine graphene analogues. In this regard, water treatment via GO-based materials have shown tremendous potential owing to their intrinsic functionalized surface area (rich with polar oxygen-groups) which not only imparts high reactivity toward polar pollutants, but also avoids the additional treatments by toxic acids to introduce hydrophilic character.[130] A variety of studies have demonstrated the utilization of the combined merit of polar functionalities and high surface area of GO toward effective removal of toxic inorganic species such as metal ions (Pb(II), Cd(II), Zn(II), Hg(II) etc.) from water via electrostatic interactions and coordinative binding.[131-134] Both GO and graphene nanosheets (GNs) can be hybridized with other functional materials such as metal oxides to produce hybrid composite materials which enables high target specificity toward contaminants.[122]

Apart from the carbon-based nano-materials, nanosized metal oxides such as nano-TiO_2, nanomagnetites Fe_3O_4 have emerged as affordable sorbents for efficient remediation of toxic heavy metals and radionuclides.[135-137] Similar to the organic counterparts, these nanomaterials also offer high surface area and tunable surface structures such as edges, corners, vacancies, crystallographic facets etc. which can be strategically controlled in order to maximize the adsorption performance. In addition, the development of nanomagnetites which possess superparamagnetic properties, enables easy segregation of the sorbent material after water treatment via a weak magnetic field.[138-139] This unique feature allows development of next-generation nanoparticles with core-shell structures where the shell allows introduction of desired functionalities and the magnetic core helps in the rapid particle separation.[139] However, the significant surface energy of the metal oxides at the nanometer level inevitably leads to particle agglomeration because of their strong van der Waals interactions, resulting in reduced performance in terms of both sorption capacity and selectivity.[140] An effective way to prevail over these technical bottlenecks is to hybridize the metal oxide nanoparticles with different porous supports to form hierarchical macroscopic objects. The commonly utilized supports include synthetic polymer hosts, cross-linked ion-exchange resins, porous manganese oxide complex, Al_2O_3 membrane etc.[122] However, fabrication of these hybrid sorbent materials is still at the nascent phase and several technical limitations need to be addressed including slow fabrication process and performance optimization via interplay between the nanoparticles and the porous support of the composite materials.

4.2 Photocatalytic degradation

Nanomaterials with a high surface-to-volume ratio can induce high degree of catalytic activity owing to the presence of greater catalytically active sites and their facile accessibility compared to their bulk counter parts.[81,141] Hence, much scientific attention has been paid toward development of photocatalytically active nanomaterials which can operate under visible or UV light in water. There are two prime mechanistic theories for the photocatalysis: 1) single-step oxidative degradation of organic molecules via initiation of free radicals, induced by the generation of electron (e^-)-hole (h^+) pairs at the nano-catalyst surface; and 2) adsorption followed by photocatalytic degradation where the organic molecule initially gets adsorbed on the photocatalyst surface and subsequently photo-degraded via the generated radicals or the superficial electron-hole pairs (Figure 4).[142-143] Moreover, the photodegradation kinetics and the overall performance can be governed by the nature of catalyst surface, size of the nanoparticles, accessibility of the surface-active sites and adsorption ability toward the organic molecules.[144]

To this end, semiconductor materials have exhibited tremendous promise as photocatalyst for various organic pollutants treatment.[145] The electronic structure of the semiconductor materials and the difference between their energy levels, namely valence band (VB) and conduction band (CB), known as bandgap, determines the photocatalytic activity of the material. Upon irradiation by photons having energy ≥ bandgap, electrons from the VB get excited and jump to CB, creating a positively charged hole in the VB. In semiconductor materials, both the electrons and the holes act as reducing and oxidizing species respectively toward the incoming pollutant molecules. It is important to note that the crystallinity, photon absorption efficiency, rate of electron–hole pairs separation of the photocatalyst also play crucial role in determining the overall efficacy of the photocatalyst. In this regard, TiO_2 has gained much scientific attention over other semiconducting materials owing to its´ promising chemical properties, higher physiochemical stability and low cost. Further, hetero-atom doping (e.g. carbon, nitrogen, sulphur) in TiO_2 have shown promise toward photocatalytic degradation. Multi-doped TiO_2 composite materials are found to exhibit great efficiency toward photocatalytic reduction of toxic heavy-metal ions, such as chromium (VI)) in water.[146] Moreover, the metal sulfides (e.g. WS_2, MoS_2, CoS_2, ZnS etc.) and their heterojunction composites (e.g. $ZnIn_2S_4/TiO_2$) have shown tremendous potential toward photocatalytic degradation of water pollutants.[147] In addition, in pursuit of eco-friendlier and sustainable options, metal-free 2D materials including various g-C_3N_4 nanosheets, black phosphorus (BP), and their heterojunction composite materials such as oxygen-enriched porous g-C_3N_4 nanosheets assembled with black phosphorus, have been investigated toward water remediation owing to their broad visible light absorption range, chemical stability, high surface area and non-toxic nature.[148-149]

Other catalytic methods including electrocatalysis, photoelectrocatalysis and piezocatalysis have also been widely

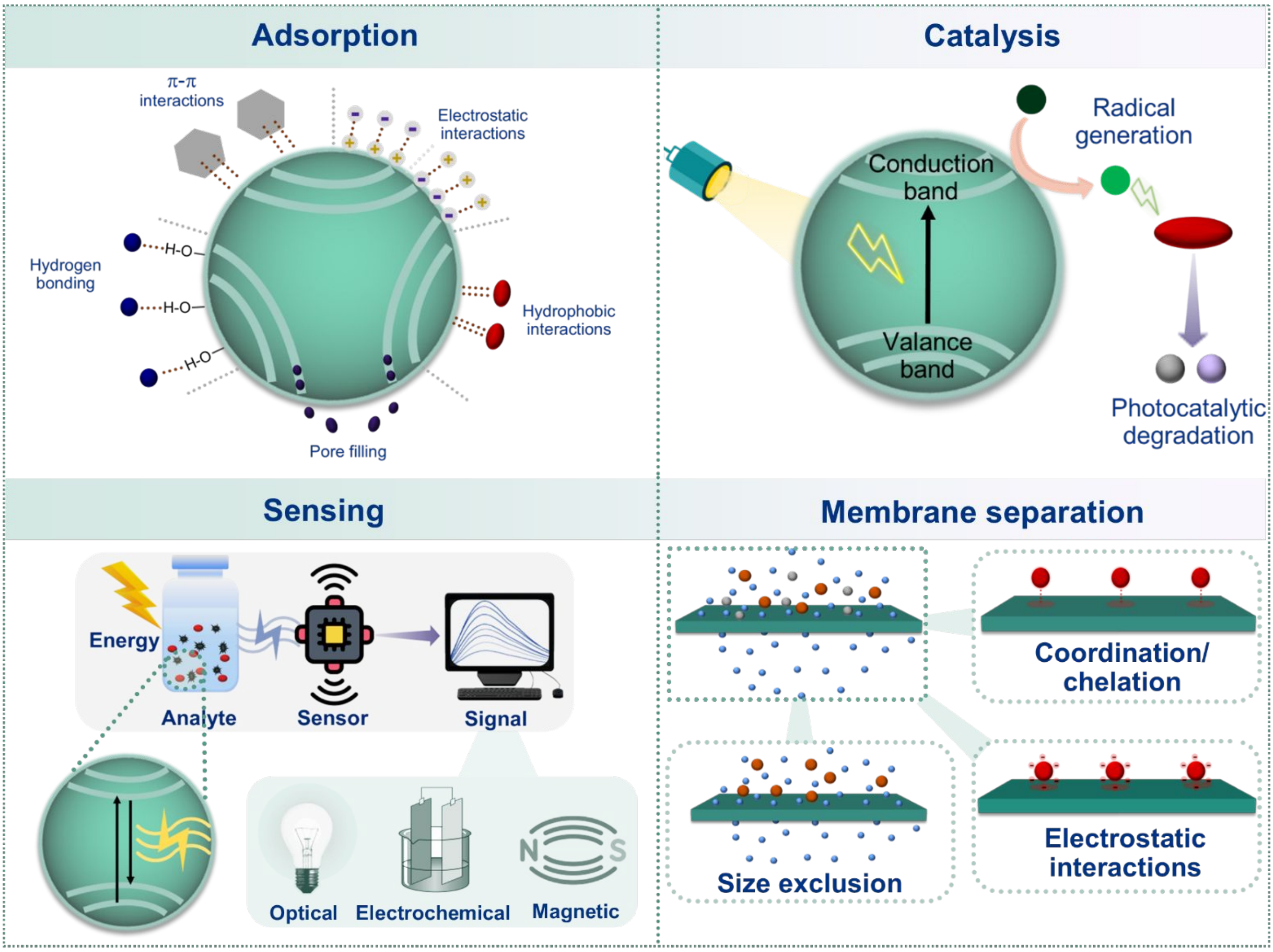

Figure 4. Schematic illustrations of nano-scale mechanistic insights of different water remediation processes.

studied. To this end, metal-oxide electrode materials such as cobalt oxide (Co_3O_4) and bimetallic oxide electrodes (e.g. Co_3O_4–La_2O_3) have been proven to act as exceptional catalysts for conducting heterogeneous catalysis processes owing to their unique structural and electronic properties.[150]

Moreover, photoelectrocatalytic processes have emerged as a viable advanced oxidation method for mineralization and decomposition of various aquatic pollutants. Several materials including TiO_2, zinc oxide, bismuth vanadium oxide ($BiVO_4$) and their composite materials have exhibited significant photoelectrocatalytic activity toward degradation of organic pollutants.[151] Importantly, precise control over semiconducting properties and electronic band structure of the catalyst holds paramount importance in dictating the in oxidation (photoanode) or reduction (photocathode) efficiency. In the quest of improved efficiency and eco-sustainability, piezocatalytic processes have been explored in recent times. In particular, Bi-based materials have attracted huge attention owing to their both photocatalytic and piezocatalytic activity that elegantly blend the advantages of both processes, resulting in improved degradation efficiency. Among different materials, Bi-based materials have attracted much attention owing to their layered structures comprising $(Bi_2O_2)^{2+}$ layers and interlayer ions that offers lesser eco-toxicity footprints. Moreover, Bi-catalysts can perform piezoelectric activity even under mechanical vibration because of the lone-pair electrons of $Bi^{3+,}$ providing a sustainable alternative as lead-free piezoelectric materials.

From the material designing perspective, several controlling factors including bandgap, carrier transport, chemical stability and surface area are highly important. Although, significant efforts being devoted toward development of photocatalysts with small bandgaps, rapid recombination of the charge carriers (hole-electron) can happen because of the small bandgap, thus affecting the photocatalytic activity. Hence, precise control to achieve a fine balance between bandgap and charges recombination is of paramount importance in order to develop efficient photocatalyst.[152]

4.3 Sensing

From the mechanistic point of view, sensors operate via three main signal transduction, namely optical, magnetic and electrochemical, sensing (Figure 4). Depending upon the structural, electronic and physiochemical properties of the nanomaterials along with the type of analyte and the interfacial interaction between the sensor and the analyte, different signal transduction methods can be employed.

Nanomaterials such as CNTs, dye-doped nanoparticles, Quantum dots (QDs), carbon nanostructures (carbon nanotubes, graphene etc.), magnetic nanoparticles, metal nanoparticles etc. are widely utilized as nano-sensor materials owing to their the unique optical, electrochemical and magnetic properties.[148] For example, QDs offer a wide absorption range with a narrow and stable fluorescence emission range which can be tuned via tuning the chemical compositions and particle size and shape, resulting in targeted multiplex detection with single excitation source.[153-155] In addition, strategic inclusion of organic dyes into porous silica or polymeric nanoparticles found to induce in high luminesce properties owing to the confined effect on the dye molecules.[156] On the other hand, noble metal nanoparticles such as nano-Au, nano-Ag have been extensive exploited as sensory probs owing to their wide range of shapes, facile surface functionalization and high extinction coefficients ($\varepsilon > 3\times10^{11}$ M^{-1} cm^{-1}).[157] The colloidal solutions of nano-Au, nano-Ag particles exhibit size dependent chromism behaviour. For instance, the spherical nano-Au particles with diameter in between ~5-50 nm range exhibit intense red colour in the solution phase, however, it transforms into purple by increasing the particle size up to ~100 nm. In the same line, a wide range of nanostructured metal oxide materials including iron oxides, zirconium oxides, titanium oxides, cerium oxides, tin oxides, zinc oxides etc. have been explored toward effective recognition of aquatic pollutants.

In addition, magnetic metal oxides such as maghemite (γ-Fe_3O_4), magnetite (Fe_3O_4) also have attracted significant attention toward water remediation processes owing to their ease in structural functionalization and less energy-economic footprints.[158] Apart from the QDs and metal oxides, functional organic materials such as CNTs and graphene are employed as sensory prob owing to their high electrical and thermal conductivity, and excellent mechanical strength. In particular, these materials have shown excellent improvement in sensitivity and electrochemical detection limits for glassy carbon electrodes toward several analytes.[159-160]

5. Water remediation by membrane separation

Membrane-based nanotechnology is one of the most crucial components for the global water treatment and purification paradigm.[161] Although membrane-based separations doesn´t directly deal with nano-properties at atomic or molecular level, it involves utilization of nanoscience, nanomaterials and nanocomposites toward development of membrane-based nanotechnology water treatment and separation processes. Nanomaterials presents several advantages in membrane-based nanotechnology:

Enhanced pore structure. Incorporation of nanomaterials into water-treatment membranes allows fine tuning of the membrane-pore structures at the nanoscale which subsequently can yield in improved permeability and selectivity of the membrane, enabling effective pollutants separation from water.

Improved flux rates. Judicious choice of the nanomaterials, polymer matrix and the support layer can lead to better water flux rate through the membrane, enabling higher interaction between the contaminants and the active materials. Such strategy is highly critical for methods such as nanofiltration and ultrafiltration where very high-water flow is desired.

Selective filtration. The liberty in flexible designing of both nanomaterials and the membranes allow control over the functionalization and porosity of the membrane which enables selective removal/separation of the targeted contaminants from water (Figure 4).

The separation performance of water-treatment membranes significantly governed by the physiochemical properties of the membrane material, thus dictating the trade-off between solute rejection and solvent permeation.[162] Amongst different membrane nanotechnologies, thin film nanocomposite (TFNC) membranes, aligned CNT membranes and biomimetic membranes have shown tremendous promise in overcoming the above-mentioned trade-off. In case of both biomimetic (also known as aquaporin) and CNTs-based membranes, the intrinsic nanochannels assist in preferential water diffusion with very high permeation rates, yielding in high volume of purified water.[163-165] Such selectivity and high flux are attributed to the nanosized channels with unique hourglass shape, size and surface composition of the nanotubes. In fact, it is observed that even with very lower loading of aligned CNTs and aquaporins, the resultant water flux along the membrane is much higher than that of the commercially available reverse osmosis (RO) membranes.[166-167] Such high flux found to significantly reduce the energy-economic footprints in seawater desalination and wastewater treatment by RO. In addition to high flux water channels, aquaporins can provide advantages of selective ion channels which can selectively pull out ions from the water.

Lately, there has been an introduction of various nanoparticles into polymeric thin films to create TFNC membranes, aiming to harness the additional nano-scale properties of nanomaterials Fabrication of TFNC membranes with nanoparticles during interfacial polymerization or via surface attachment found to improve the separation performance, antimicrobial activity and antifouling properties of the membrane.[168-169] Moreover, the separation performance of TFNC membranes can be also tuned via tuning the size and composition of the nanoparticles, enabling target-specific membrane designing for efficient treatment of a wide-range of aquatic pollutants. TFNC membranes fabricated from zeolite nanoparticle have shown promise in water treatment via molecular sieving properties of zeolites.[170] The zeolite nanoparticles found to enhance the permeability of the membrane owing to their nano-scale, hydrophilic pores that induce preferential water flux while rejecting hydrated ions. Moreover, significant efforts have been devoted toward development of reactive nano-composite membranes which mainly formulated with nano-TiO_2 particles, combined with either polymeric membranes or ceramic membranes.[171] Such reactive nano-composite membrane found to exhibit simultaneous dual-treatment, i.e. separation and catalytic degradation of aquatic contaminants along with improved membrane fouling properties.

Another important aspect of membrane nanotechnology is controlling the fouling properties of the membranes during water treatment processes. To address this issue, various nanomaterials including TiO_2-nanoparticles, nano-alumina, CNTs have been utilized as additional support in polymeric membranes via surface self-assembly.[172-173] However, installation of these nanomaterials via covalent bonding have been regarded as the most effective method in order to maximizes the nanomaterial utilization and generation of active sites. The incorporation of the nanomaterials inevitably increases the fouling resistance of the nanocomposite membranes, owing to the antimicrobial activity and surface hydrophilicity of the nanomaterials.

The integration of nanotechnology with water treatment membranes provide wide opportunities in enhanced membrane performance in terms of both improved fouling resistance and selective removal. Strategic utilization of functional membranes via nanotechnology has shown great potential in enhancing the water permeability, catalytic activity, flux recovery and robustness (chemical, physical, thermal and mechanical) of the water treatment methods over the current state-of-the-art. For example, Ceramic membranes with reactive surfaces exhibited good potential toward selective pollutants removal in nanofiltration and reverse-osmosis methods with high durability. Moreover, introduction of photocatalytically active and antimicrobial nanoparticles in such membranes found to shown significant self-cleaning and catalytic water treatment performance. The mixed-matrix-membranes offer enhanced mechanical stability, fouling resistance, filtration performances as individual matrix or as a support-matrix for TFNC membranes. Integration of each of these membranes with nanotechnology-enabled water treatments promises to provide great platforms toward practically viable alternatives.[13,160]

6. Challenges

Importantly, despite the huge potential of nanomaterials in water treatment, the attractive nano-properties come with intrinsic challenges that have to be addressed.[174-181]

Environmental toxicity: The entry of nanomaterials into aquatic and terrestrial environments inevitably induces additional toxicity that threatens environmental symbiosis. The type and extent of ecotoxicity of nanomaterials vastly depends upon the type of nanomaterials, their chemical composition, functionalization and the fate of the nanomaterial in water. Because of their smaller size and high surface reactivity, nanomaterials often undergo significant bioaccumulations by the aquatic organisms which consequently leading to biomagnification in the food chain, potentially impacting higher trophic levels. Moreover, nanoparticles can undergo disintegration under water which may cause release of toxic particles, ions and other by-products that could potentially induce different toxicological effects than the original nanoparticles. For example, silver or lead nanoparticles may release toxic ions upon disintegration, which can also be extremely dangerous to aquatic organisms, disrupting the balance of microbial-systems and affect the overall health of ecosystems.

Agglomeration: Because of their higher surface reactivity nanoparticles often found to agglomerate to form larger particles or clusters under water, significantly limiting their potential toward water treatment processes. Upon formation of the larger agglomerate particles, the effective surface area and surface reactivity of the nanomaterials decrease, thus decreasing the water treatment performance. Moreover, agglomerated nanoparticles exhibit lower mobility under water and can quickly settle down which reduces their ability to reach and interact with targated pollutants in water.

Recyclability: While nanomaterials can offer exciting properties, several of them can contribute in hindering their effective recovery and reuse from water. As mentioned before, agglomerated nanoparticles can form larger particles that settle quickly, making it challenging to separate them from the water for recycling. Moreover, several nanomaterials tend to lose their surface properties over successive usage cycles, resulting in significant decrease water treatment performance and their overall recyclability. Finally, nanomaterials can undergo structural degradation over multicycle usage under harsh water conditions which not only reduce their recyclability performance, but also induce acute toxicity to the water body. Hence, development of environmentally friendly and energy-efficient methods for recovering and reusing nanoparticles in water treatment that can be implimented at real-world scale still is a significant challenge.

Property controlability: Presice controlling the nano-properties hold the key for the success of nanomaterials in water treatment. However, achieving higher controllability at the nanoscale range poses several challenges. For example, the standout feature of nanomaterials lies on their high surface area and surface activities which contributes in efficient sorptive interaction or catalytic activity toward water pollutants. However, these same properties can make the nanomaterials undergo interparticulate binding with other particles/bio-organisms and/or agglomeration within the same nanoparticles. Controlability over surface functional properties of nanomaterials under water is extremely difficult. Hence, the target-specificity of the nanomaterilas can be significantly affected as the reactive surface-functionalities can interact/bind with other molecules and get saturated even before interacting with the water pollutants. Moreover, precise control over structural defects and the defect densities are crucial yet higly challenging in order to control the nano-properties. Addressing these challenges demands multidisciplinary approach that allows precise understanding of the environmental deamands and delopment of next generation nanomaterials.

Complex characterization: Nanomaterials´ characterization in water medium presents additional challenges due to the complex interactions between the nanomaterials and the advanced characterization techniques required for it. The properties and behaviour of nanomaterials can be significantly influenced by water chemistry, temperature, and the presence of other dissolved or suspended substances. Moreover, the agglomerating ability of nanomaterials can significantly affect the dispersion stability of the nanoparticles in water, thus rending in higher complexity in characterization. The compositional complexity of real-world water matrix creates additional challenges toward analytical techniques performing under water. On the other hand, standardization of nano-properties in water matrix are often challenging and require highly qualified experts. Accounting on these challenges, the characterization techniques under water are often found to be relatively expensive and trained expert are need it.

Cost: From the real-world applicability scinario, the economic feasiblity and commercialization of a 'nano' product is a key concern. The synthetic methods of nanomaterials can be complex and require expensive equipments and expertise which can lead to high production costs, especially for large-scale manufacturing. Moreover, utilization of costly raw materials and complexicity associated with the surface functionalization or modification renders in increased costs in terms of materials synthesis and processing. Hence, continued scientific and technological efforts must be devoted toward overcoming these cost- barriers in order to push real-world utilization of nanomaterials.

Conclusion

Sustainable access to clean and drinking water is one of the most crucial challenges of the 21st century which necessitates development of next-generation water treatment approaches and technological reforms. Continued development of nanoscience and nanotechnology promises to provide ideal platform toward novel and efficient water treatment methods. Thanks to the scientific and technological efforts devoted over the last few decades, significant progress has been made toward fundamental understanding and development of nanoscience and nanotechnology. Despite several advantages and unique properties, nanomaterials still suffer from several key challenges that need to be solved in order to establish their long-term sustainability and industrialization. Significant attention must be devoted toward development of green-synthesis of nanomaterials that associates with minimal toxicity footprints toward environment. Moreover, current research direction also focusses on designing and development of multifunctional nanomaterials that can address multiple water treatment challenges simultaneously. From the practical applicability point of view, it is important to exploring ways toward integration of nanomaterials with the existing water treatment technologies in order to enhance the overall treatment efficiency. Significant efforts being made to overcome the issues associated with large-scale production of nanomaterials, which in combination with improved cost and reproducibility can show the way toward sustainability production and profitable commercialization. Moreover, current research and methodologies possess serious pitfalls in recycling the nanoparticles and nano-composite materials owing to operational difficulties. Apart from magnetic separation-based techniques, most of the nano-materials integrated methods lack fast, affordable and energy-efficient NPs removing and recycling techniques. Future research should focus on development of energy-efficient recycling processes for nanomaterials in water. Moreover, systematic evaluation of the nanomaterial´s fate in the environment should get much attention in future research in order to achieve environmental sustainability. From the practical implementation point of view, integration of nanotechnology-enabled water treatment methods with other existing techniques, like biological and chemical purification can pave the way toward more efficient water purification methods. Considering, nano-engineered water-treatment methods possess dificulty in mass-scale adaptation, signifiant research and development efforts must be devoted toward hybridization of traditional methods (e.g. desalination) and the emerging nano-engineered water-treatment methods.

Conflicts of interest

There are no conflicts to declare.

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