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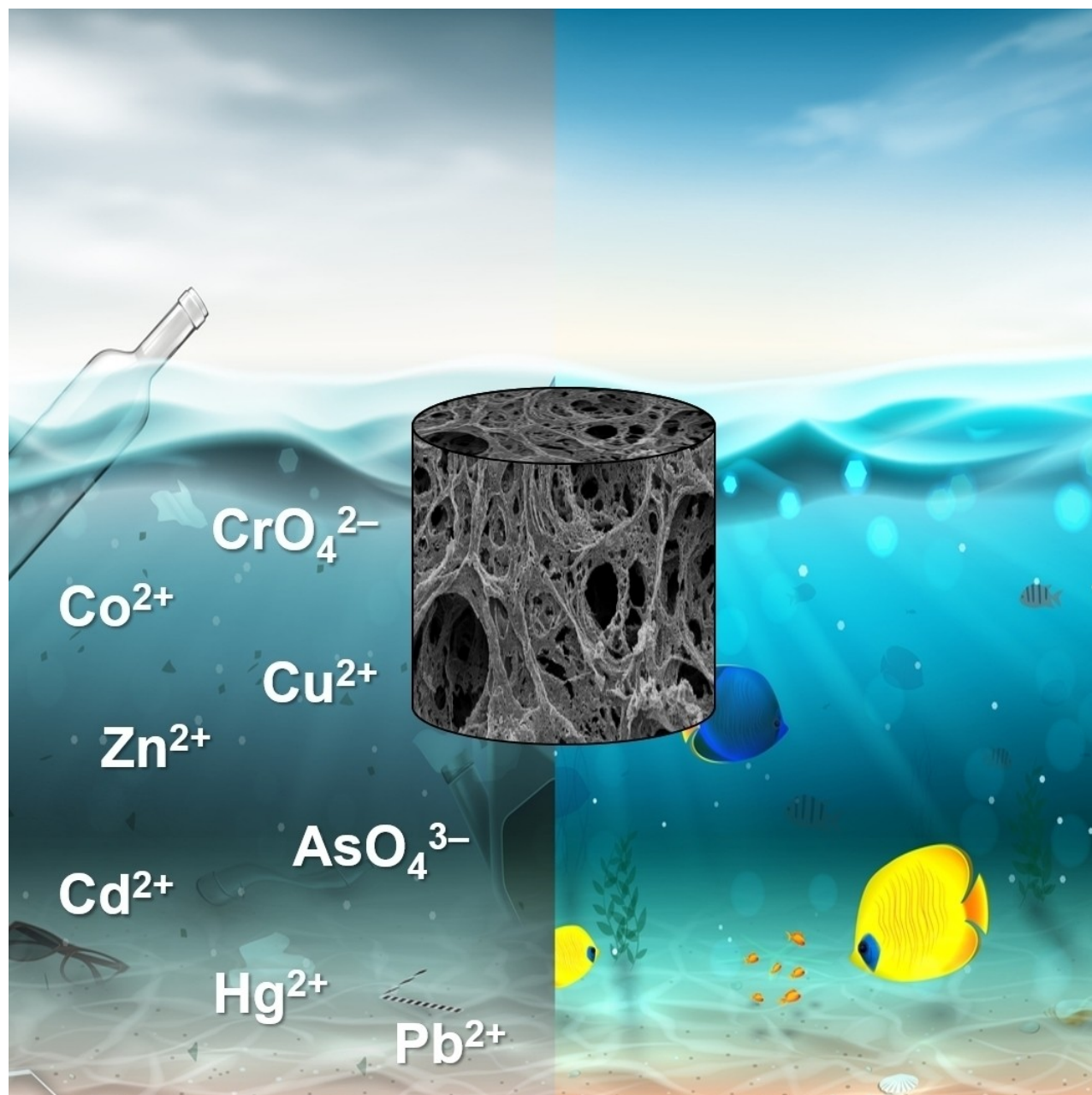
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Graphene-Based Macromolecular Assemblies for Scavenging Heavy Metals

Shamik Chowdhury[a] and Sharadwata Pan*[b]

The integration of graphene or graphene oxide nanosheets into three-dimensional (3D) graphene-based macromolecular assemblies (GMAs), in the form of sponges, beads, fibres, films, and crumpled nanosheets, has greatly advanced their environmental remediation applications. This is attributed to the outstanding physicochemical characteristics and superlative mechanical features of 3D GMAs, including precise and physically linked permeable networks, enormous surface area, profound porosity, and high-class sturdiness, amongst others. In this review, the recent advancements towards the exploration of 3D GMAs as an exciting new class of high-performance adsorbents, for eliminating toxic heavy metal ions from both wastewater and freshwater, are systematically summarized and discussed, from both fundamental and applied perspectives. In particular, the numerous surface modification techniques that are actively pursued to enrich the metal adsorption capacity of 3D GMAs, are comprehensively examined. Additionally, associated challenges are pointed out and tactical research strategies and improvements are proposed, with an eye on the conceivable future.

1. Introduction

Environmental contamination is a global menace, affecting ecosystems as well as human well-being, to an incredible extent. Particularly threatening to the flora and fauna, both in freshwater and marine ecosystems, is the indiscriminate and uncontrolled discharge of heavy metal ions, such as Cu^{2+}, CrO_4^{2-}, $Cr_2O_7^{2-}$, Cd^{2+}, Pb^{2+}, AsO_4^{3-}, Hg^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+}.[1,2,3] This stems majorly from manufacturing and industrial facilities, as well as other anthropogenic activities, which can be credited to the rapid industrial progress, and an insatiable appetite for value-added goods and services.[4,5,6] In response to this global setback, extraordinary efforts are currently underway, towards efficient removal of heavy metal ions from aqueous matrices.

To date, a wide range of strategies has been attempted in this regard, including employment of coagulants,[7] flocculants,[8] precipitants,[9] resins,[10] sorbents,[11] and membranes,[12] amongst others. Among these, the applicability of adsorbents possessing enormous surface area and intense porosity has garnered maximum interest, because of their outstanding saturation capacity, ultrafast removal rate, simple, reliable, and predictable operation requiring minimal operator attention, as well as self-capability to acclimatize under extreme conditions.[13,14] Indeed, a variety of diverse materials has been rigorously explored as adsorbents for removing heavy metals from aquatic compartments, which can be broadly classified into five major categories: (i) agricultural residues (like rice husk, orange peels, watermelon rinds, peanut shells, sugarcane bagasse, etc.),[15,16,17] (ii) synthetic polymers (such as polypyrrole, polypropylene, polyaniline, polystyrene, and polyacrylamide),[1,18] (iii) naturally-occurring soil and mineral deposits (like zeolites, sand, peat, organo clays, etc.),[11,19,20,21] (iv) aquatic and terrestrial biomass (like neem leaves, hyacinth roots, green algae, etc.),[11,22,23] and (v) municipal and industrial wastes (like spent tea leaves, egg shells, fly ash, etc.).[11,17,24] In spite of their many advantages, some of these materials have limited adsorption efficiency due to pore congestion.[25] A more common problem is that most of these adsorbents exhibit poor retrieval performance, insufficient recyclability, as well as issues corresponding to disposal post usage. Consequently, there is a pressing need for better, inexpensive adsorbents, which can overcome these drawbacks.

On this front, the challenges have been alleviated to a considerable degree with the inception of two-dimensional (2D) materials, primarily graphene.[26,27,28] The applicability of graphene-based adsorbents has been noted especially for the elimination of a wide array of noxious contaminants from aqueous media.[29,30,31,32,33] This is largely possible attributing to their beneficial structural features, including enormous specific surface area, intrinsic hydrophobicity, outstanding mechanical properties and superior chemical resistance, amongst others.[29,34,35] Despite these merits, graphene as a bulk material demonstrates a strong propensity to agglomerate, owing to its vigorous hydrophobic nature, or could even restack into graphite as a consequence of the robust van der Waals interactions between the neighboring sheets,[35,36] thereby reducing its application potential.[37]

To tackle the above challenges, the self-congregation of graphene or graphene oxide (GO) nanosheets into 3D macromolecular assemblies, and subsequent serviceable structures (in the form of sponges, beads, fibers, films, and crumpled nanosheets), has emerged as the optimal solution in recent years.[38,39,40,41] The transformation of graphene and GO to 3D macrostructures grossly minimizes the restacking probability, and simplifies their processing difficulties.[35,39] Most importantly, all these novel 3D graphene-based macromolecular assemblies (GMAs) demonstrate massively interconnected networks, vigorously reduced compactness, huge surface area, profound porosity, extremely high permeability, and high-class sturdiness, all of which make them versatile adsorbents for eliminating heavy metal ions from water,[35,39] with remarkable sorption competence.[38,42,43]

The current review provides a critical outline of the contemporary advancements in the exploration and application of 3D GMAs as adsorbents towards a wide variety of toxic heavy metal ions. In addition, the review comprehensively examines the diverse surface modification schemes that have been conceived to magnify the metal adsorption capacity of 3D

[a] Dr. S. Chowdhury
School of Environmental Science and Engineering
Indian Institute of Technology Kharagpur
West Bengal 721 302 (India)
[b] Dr. S. Pan
School of Life Sciences Weihenstephan
Technical University of Munich
85354 Freising (Germany)
E-mail: sharadwata.pan@tum.de

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GMAs. While keeping the aforementioned perspectives in hindsight, it also detects the key knowledge gaps in the domain, and lays out novel strategic research guidelines that would drive innovations and applications in this rapidly evolving cross-disciplinary field of topical interest.

2. 3D GMAs for Scavenging Heavy Metals From Aqueous Phase

2.1. Self-Assembled 3D GMAs

Attributing to their geometrical anisotropy, GO nanosheets can self-assemble into 3D GMAs of different morphologies, by various processing techniques,[41] as summarized in Figure 1. For instance, GO dispersions can self-assemble, *via* noncovalent interactions, i.e., hydrogen bonding, hydrophobic association, and electrostatic attraction, into mechanically robust, highly porous ($>90\%$ v/v), low density (typically <200 mg.cm^{-3}) sponges (also referred to as aerogels), either through hydrothermal treatment under mild conditions, or cross-linking and/or chemical reduction with the aid of a chemical agent.[35] Additionally, upon wet spinning, the lyotropic liquid crystalline behavior of GO in polar solvents enforces it to assemble into fibers and beads.[44,45] Further, the GO sheets can be transformed into crumpled graphene balls, with high compressive strength and improved stability in water, *via* aerosol-assisted spray drying.[49] Although most of the aforementioned methods lead to 3D GMAs with randomly oriented pores, the major advantage of solution-processed self-assembly of GO is manifested in the contexts of its relative ease of synthesis, as well as scalability for practical usage.[41] As such, it is the most widely practiced approach for producing 3D GMAs for adsorption-mediated removal of heavy metal ions.

A typical example is that of Chen et al.,[50] who explored the possibility of constructing graphene sponges (GSs) through chemical reduction-induced self-assembly of GO in the presence of structurally diverse mercapto compounds, including mercaptoacetic acid, mercaptoethanol, ethanethiol, 2-phenyl-ethanethiol, and glycine. While all the selected mercapto compounds effectively reduced GO to graphene, only mercaptoacetic acid and mercaptoethanol could assemble the reduced GO (rGO) nanosheets into 3D porous macroarchitectures (Figure 2A). This is conceivable since the sulfhydryl (—SH) groups in both mercaptoacetic acid and mercaptoethanol can react with the hydroxyl or epoxy functional groups on the GO nanosheets, leading to their covalent attachment to the GO nanosheets. Subsequently, the carboxyl group of mercaptoacetic acid (or hydroxyl group of mercaptoethanol) compel the flexible, rGO sheets to partially overlap and interlock with each other through hydrogen bonds, resulting in the formation of a 3D porous scaffold (Figure 2B). This self-supporting mechanically resilient GS had an average porosity of over 90% (Figure 2C), and therefore demonstrated admirable adsorption potential towards a wide range of heavy metal ions, including Pb^{2+}, Cu^{2+} and Cd^{2+}. Similarly, applying ethylenediamine as a reducing agent, Zhao et al.[51] prepared an ultralight GS, which benefitting from its fairly large surface area (351 m^2.g^{-1}) and continuous open-pore geometry, displayed a superior adsorption propensity for UO_2^{2+} ions in aqueous media (approximately 239 mg.g^{-1} at $25\,^{\circ}$C) (Figure 2D–F).

Attractively, Chen et al.[52] covalently crosslinked the oxygen functionalities of GO with the hydroxyl and amine groups of chitosan (CS) to produce sponges with larger pores (Figure 3A, B), in order to improve the mass transfer rate and reduce the diffusion resistance within the bulk material. Batch adsorption tests revealed that the GO–CS composite sponge holds tremendous potential to treat wastewater and freshwater for toxic heavy metal ions, such as Pb^{2+} and Cu^{2+}. In another exciting contribution, Fang and Chen[53] integrated GO nanosheets with the aid of Mg—Al—CO$_3^{2-}$ layered double hydroxide (LDH) as binders (Figure 3C–F). Owing to lattice-lattice cation-π and/or charge-mediated hydrogen bonding interactions between the positively charged stacks of LDH and the negatively charged basal planes of GO, a highly stretchable and hydrophilic 3D GMA was obtained. These unique characteristics of the GO–LDH composite sponge assisted in adsorbing up to 96 mg.g^{-1} of Cd^{2+} ions from polluted water. Impressively, Pakulski et al.[54] formulated a highly porous GO sponge *via* a

Shamik Chowdhury is an Assistant Professor in the School of Environmental Science and Engineering at the Indian Institute of Technology Kharagpur, India. He obtained his B.Tech. from the West Bengal University of Technology (Kolkata, India) and M.Tech. (Gold Medalist) from the National Institute of Technology (Durgapur, India), both in biotechnology. He then earned his Ph.D. (2017) in Environmental Engineering from the National University of Singapore, Singapore (Supervisor: Prof. Rajasekhar Balasubramanian). His current research activities focus on the design and development of advanced functional materials, with an emphasis on 2D materials, for sustainable energy applications and environmental remediation.

Sharadwata Pan is a Scientific Staff and Project Lead at the Technical University of Munich (TUM) in Germany. He completed his dual degree: bachelors and masters with a major in Biotechnology in 2007. He followed it up with a dual-badged, interdisciplinary Ph.D. from Indian Institute of Technology (IIT) Bombay, India and Monash University, Australia in 2015. Following short stays at IIT Bombay and IIT Delhi, India as a Research Associate, he moved to TUM, Germany as a TUFF Postdoctoral Fellow in 2016. Since 2017, he is based at TUM. He is formally trained in bioengineering and experimental soft matter physics, with a principal focus on industrial materials research and product development.
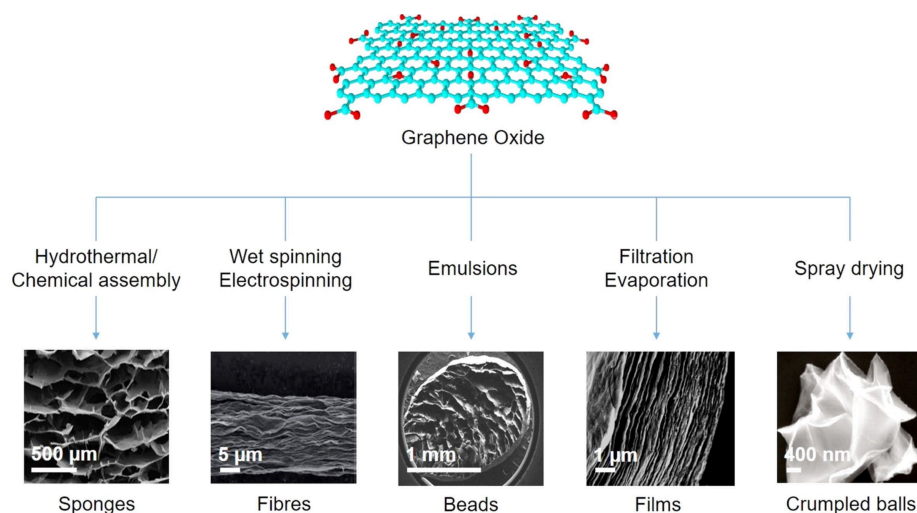
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Figure 1. Processing techniques for the self-assembly of 2D graphene-based nanosheets into 3D GMAs. Scanning electron microscopy images reproduced from Xie et al.,[44] Copyright 2013, with permission from Springer Nature (sponges); Xu et al.,[45] Copyright 2013, with permission from John Wiley and Sons (fibres); Bao et al.,[46] Copyright 2016, with permission from the Royal Society of Chemistry (beads); Wallace et al.,[47] Copyright 2010, with permission from the Royal Society of Chemistry (films); and Luo et al.,[48] Copyright 2011, with permission from the American Chemical Society (crumpled balls).
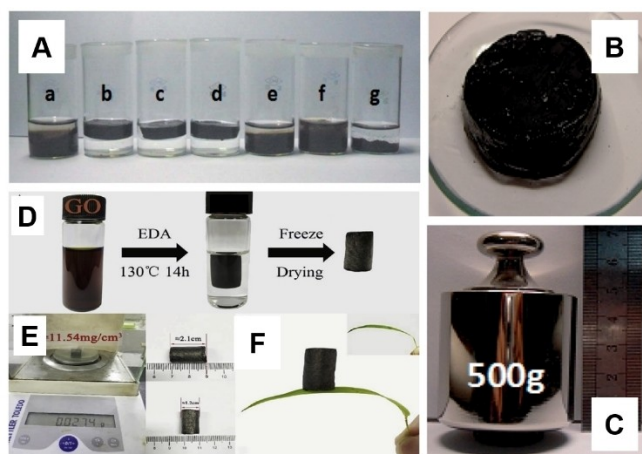

Figure 2. (A) Digital image of GO dispersions after heating at 70–80 °C for 30 min in the presence of 0.01 mL mercaptoacetic acid (a), 0.05 mL mercaptoacetic acid (b), 0.1 mL mercaptoacetic acid (c), 0.1 mL mercaptoethanol (d), 0.1 mL ethanethiol (e), 0.1 mL glycine (f), and 0.1 mL 2-phenyl-ethanethiol (g). Higher concentrations of mercaptoacetic acid resulted in GSs with improved stability. (B) Digital photograph of a GS obtained *via in situ* chemical reduction of GO sheets, by mercaptoacetic acid, and their subsequent self-assembly. (C) Digital picture of the GS in (B) supporting a 500 g counterpoise. Reproduced from Chen et al.,[50] Copyright 2013, with permission of the Royal Society of Chemistry. (D) Schematic of the preparation of GS using ethylenediamine (EDA) as the reducing agent. (E) Estimation of specific mass of the as-prepared GS. (F) Digital image of the GS in (E) propped up on a bamboo leaf. Reproduced from Zhao et al.,[51] Copyright 2019, with permission of Elsevier.
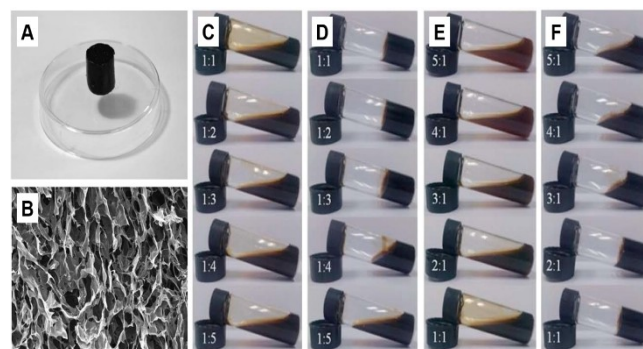

Figure 3. (A) Digital image of the as-prepared GO–CS sponge. (B) Scanning electron micrograph of the GO–CS sponge, revealing a well interconnected network of macropores throughout the bulk material. Reproduced from Chen et al.,[52] Copyright 2013, with permission of the Royal Society of Chemistry. Digital images of homogeneous mixtures of GO (5 mg.mL^{-1} dispersion in water) and LDH (5 mg.mL^{-1}→1 mg.mL^{-1} for 1:1→1:5 samples) before (C) and after (D) ultrasonic treatment. Digital images of homogeneous mixtures of LDH (5 mg mL^{-1}) and GO aqueous dispersion (1 mg.mL^{-1}→5 mg.mL^{-1} for 5:1→1:1 samples) before (E) and after (F) ultrasonic treatment. When the GO concentration was fixed at 5 mg.mL^{-1}, the GO sheets cross-linked into a stable monolith at an LDH : GO ratio ≥ 1 : 3. Similarly, when the amount of LDH was fixed at 5 mg.mL^{-1}, a stable monolith was formed only when the concentration of GO was ≥ 2.5 mg.mL^{-1}. Evidently, the degree of crosslinking can be reasonably controlled by varying either the concentration of GO or LDH. Reproduced from Fang and Chen,[53] Copyright 2014, with permission of the Royal Society of Chemistry.

condensation reaction between GO and branched polyethylenimine (BPEI), under mild conditions. The amine moieties of BPEI not only assisted in the self-congregation of the GO nanosheets, but also served as auxiliary molecular traps. As a result, the hierarchical porous GO–BPEI hybrid sponge could readily adsorb humongous amounts of heavy metal ions from aqueous environments, with the maximum uptake capacity peaking

around 1096, 2051, and 3390 mg.g^{-1} for Cu^{2+}, Cd^{2+} and Pb^{2+}, respectively. Furthermore, the metal-ion-saturated GO–BPEI could be easily separated from the aqueous phase and reclaimed by acid washing. In a similar way, a broad range of natural macromolecules, such as proteins,[55] DNA,[55] cellulose,[56] xanthan gum,[57] sodium alginate,[58] phytic acid,[59] and silk fibroins,[60] as well as synthetic materials, such as polysiloxane[61] and polyacrylic acid,[62] have been employed as crosslinking

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agents to realize high performance GO sponges, for the routine cleanup of metal processing and metalworking effluents.

As most existing methods for the fabrication of 3D GMAs yield disorderly connected porous structures, Mi et al.[63] introduced a unidirectional freeze-drying scheme, for processing GO sponges with well-aligned pore channels. When an aqueous dispersion of GO is subjected to uniaxial freezing conditions, the ensuing unidirectional ice crystals align the colloidal GO sheets sandwiched between them, along their growth route. Upon subsequent freeze drying of the unidirectionally frozen dispersions, the aligned GO sheets form 3D GMAs with well-ordered and unidirectional thin channels (Figure 4). High adsorption capacities and fast adsorption rates towards heavy metal ions makes such freeze-cast porous 3D systems promising candidates for efficient water treatment.[63,65]

Apart from sponges, spheroidal scaffolds with hierarchical porous structures have also been proposed in recent years, to effectively separate heavy metal ions from contaminated waters.[66,67] For instance, Yu et al.[66] manufactured honeycomb-cobweb structured GO/CS microspheres with radially oriented microchannels, through a combination of electrospray processing and freeze-casting, as depicted in Figure 5. This distinctive structural arrangement significantly shortened the diffusion pathways, which in turn facilitated rapid and extensive
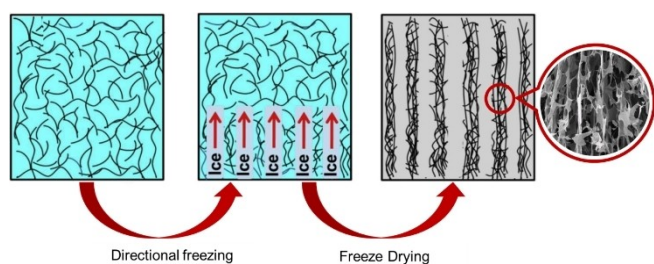
adsorption of several heavy metal ions, including Pb^{2+} (746 mg.g^{-1}), Cu^{2+} (575 mg.g^{-1}) and $Cr_2O_7^{2-}$ (293 mg.g^{-1}), onto the microspheres.

2.2. CVD Grown 3D GMAs

Besides self-assembly techniques, chemical vapor deposition (CVD) of high-quality graphene onto copper or nickel foams, have garnered considerable attention of late.[68,69,70] After selective dissolution of the metallic foams in strong acids, graphene foams (GFs) are subsequently obtained. Contrary to self-assembled 3D GMAs, CVD-processed GFs usually have a well-defined interconnected porous structure with large pores (Figure 6A). This makes them extremely appealing as adsorbents for eliminating heavy metal ions from wastewater. For example, by adopting a versatile ambient pressure CVD scheme, Li et al.[68] created self-supporting 3D GMAs, with fairly high surface area (560 m^2.g^{-1}) and remarkable electrical conductivity (12 S.cm^{-1}), which could effectively separate positively charged heavy metal ions (such as Cd^{2+}, Cu^{2+}, Ni^{2+} and Pb^{2+}) from aqueous solution by electrosorption (Figure 6B,C). In another noteworthy study, Lei et al.[70] built a free-standing GO foam through direct oxidation of CVD-grown GF, as outlined in Figure 6D. Compared to many competing adsorbent materials, the GO foam presented excellent adsorbance towards a multitude of heavy metal ions, including Zn^{2+}, Fe^{3+}, Pb^{2+}, and Cd^{2+}, due to its large specific surface area (578 m^2.g^{-1}) and oxygen-rich surface chemistry (Figure 6E). In addition, the GO foam could be reused over multiple adsorption/desorption cycles, and therefore merits further consideration in removal and recovery of heavy metal ions from industrial wastewaters.
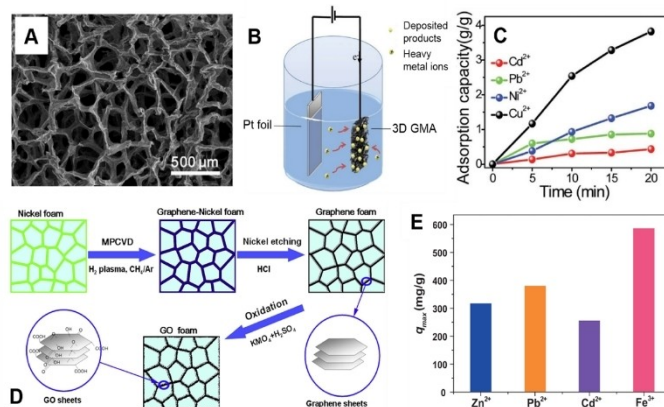

Figure 4. Schematic for processing of 3D GMAs by unidirectional freeze drying of GO dispersions. Reproduced from Liu et al.,[64] Copyright 2016, with permission of Elsevier. Scanning electron microscopy image reproduced from Mi et al.,[63] Copyright 2012, with permission of Elsevier.

Figure 5. Preparation scheme of GO/CS microspheres. Reproduced from Yu et al.,[66] Copyright 2017, with permission of the American Chemical Society.

Figure 6. (A) Scanning electron micrograph of 3D GMA fabricated using ambient pressure CVD. (B) Schematic of the electrolytic deposition of divalent heavy metal ions onto the CVD-processed 3D GMA. The corresponding electrosorption kinetics is presented in (C). Reproduced from Li et al.,[68] Copyright 2013, with permission of Springer Nature. (D) Illustration of the key steps involved in the preparation of GO foam. (E) Maximum metal ion adsorption capacity of the GO foam, as determined from batch equilibrium studies. Reproduced from Lei et al.,[70] Copyright 2013, with permission of Elsevier.

3. Improving Heavy Metal Scavenging Capacity of 3D GMAs

The aforementioned discussions provide credible evidence that a wide spectrum of highly efficient and exceptionally durable 3D GMAs have been rationally designed and developed to combat heavy metal contamination of freshwater sources. The seamlessly interconnected porous channels of 3D GMAs can accommodate enormous amounts of contaminant molecules, resulting in maximum adsorption capacities several orders of magnitude higher than that of the peers, including carbon nanotube (CNT) sponges, biochars and granular activated carbon. Nevertheless, the metal uptake capacity of most of these graphene-based macrostructures is still not acceptable for practical implementation. Consequently, numerous strategies are actively being pursued to enrich the surface chemistry, and enhance the adsorption capabilities of 3D GMAs for heavy metals.

3.1. Heteroatom Doping

The insertion of heteroatoms, such as boron (B), nitrogen (N), phosphorous (P), and sulfur (S), into the 2D graphene building blocks of 3D GMAs, is a relatively straightforward approach to elevate their adsorption affinity towards heavy metal ions. This can be attributed to the fact that the incorporation of heteroatoms, with a different electronegativity from carbon (C) atoms, rearranges the electrons in the honeycomb lattice of the graphene sheets.[71] This in turn increases the population of local active sites in graphene, and consequently, the adsorption capacity of the 3D bulk material. A notable example is that of Zhao et al.,[72] who successfully doped the sp^2 hybridized domains of GS with S atoms *via* a facile, one-pot hydrothermal method, without any post-synthesis modification. When evaluated as an adsorbent using a batch experimental set-up, the S-doped GS (SGS) showed a remarkably high adsorption capacity towards a myriad of heavy metal ions, including Pb^{2+} (404 mg.g^{-1}), Cu^{2+} (228 mg.g^{-1}), Cd^{2+} (6 mg.g^{-1}) and Zn^{2+} (28 mg.g^{-1}). More importantly, employing thiourea as an eluent, the metal ion-loaded SGS could be easily regenerated for repeated use, without any substantial deterioration in the adsorption performance. In addition to single-element doping, co-doping with two different elements may induce synergistic effects, and create even more molecular traps on the graphene plane, resulting in further improvements in the adsorption efficiency. Due to this, Kong et al.[73] hydrothermally synthesized N/S co-doped GSs (NSGSs), using 2,5-dithiobisurea as the co-doping agent. Owing to a strong synergy between the various N and S induced defects in the graphene matrix, the as-prepared NSGSs could effectively remove Cd^{2+} from binary metal-dye solutions, and therefore warrants widespread applications in prevailing wastewater treatment technologies.

3.2. Decoration with Inorganic Nanostructures

Alternatively, decoration with inorganic nanostructures, such as metal oxide nanoparticles,[74,75,76,77] carbon nanoallotropes,[78,79,80] and clay-based nanostructures,[81] can also extend the adsorption efficiency of 3D GMAs, by offering additional sites for interactions with metal ions. Notably, Liu et al.[76] uniformly anchored ultrathin birnessite-type MnO_2 nanosheets on the 3D interconnected networks of GS, via *in situ* growth and a self-assembly scheme. The self-supporting δ-MnO_2@GS with continuous open porosity could rapidly remove significant quantities of Pb^{2+} (644 mg.g^{-1}), Cd^{2+} (250 mg.g^{-1}), and Cu^{2+} (228 mg.g^{-1}) ions, through a combination of physisorption (electrostatic attraction) and chemisorption (ion exchange and surface complexation), and may therefore be readily adopted for separating heavy metal ions from industrial and mining waste effluents. More recently, Yu et al.[77] impregnated GSs with porous Fe_2O_3 nanocubes, and rigorously evaluated the efficacy of the resulting 3D composite macrostructure, for treating arsenic contaminated water. Remarkably, the as-prepared Fe_2O_3@GS material was capable of adsorbing substantial amounts of AsO_2^- (99.7%) and AsO_4^{3-} (97.9%) from realgar tailing wastewater within 4 h. This attribute is indeed beneficial for practical industrial applications, where considerable volumes of wastewater have to be treated and processed in a short period of time. Further, the mesoporous composite sponge can be exploited for decontaminating large volumes of arsenic-laden groundwater, as inferred from continuous flow experiments. Additionally, the effects of common inorganic anions (Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-, SiO_3^{2-} and PO_4^{3-}) in water matrices, as well as natural organic matter (humic acid), was examined on the adsorption performance, in order to conduct a more realistic assessment of the application potential of the Fe_2O_3@GS adsorbent. While the presence of Cl^-, NO_3^-, SO_4^{2-} and humic acid had no significant influence on the adsorption process, CO_3^{2-}, HCO_3^-, SiO_3^{2-} and PO_4^{3-} severely impeded the binding of heavy metal ions to the adsorbent surface (Figure 7). On the basis of these results, it was speculated that adsorption of AsO_2^- and AsO_4^{3-} on Fe_2O_3@GS proceeded *via* surface complexation and electrostatic attraction.

Meanwhile, Sui et al.[78] inserted acid functionalized multi-walled CNTs (MWCNTs–COOH) in between the 2D nanoscale building blocks of GSs, through a facile and sustainable route. The intercalation of MWCNTs–COOH expanded the interlayer spacing between the constituent graphene sheets, and increased their effective surface area. Consequently, the resulting ultralight graphene-MWCNTs–COOH hybrid sponge featured fairly high specific surface area (365 m^2.g^{-1}), ample pore space (1.90 cm^3.g^{-1}) and abundant sites for ion adsorption, thereby manifesting admirable binding capacities for four representative heavy metal ions: 104.9 mg.g^{-1} for Pb^{2+}, 93.3 mg.g^{-1} for Hg^{2+}, 64 mg.g^{-1} for Ag^+ and 33.8 mg.g^{-1} for Cu^{2+}. In another interesting study, Zhan et al.[80] devised a green strategy to fabricate ultralight and robust graphene/polydopamine modified MWCNT (MWCNT-PDA) hybrid sponges (Figure 8, top panel). Owing to its distinct honeycomb-like porous structure,
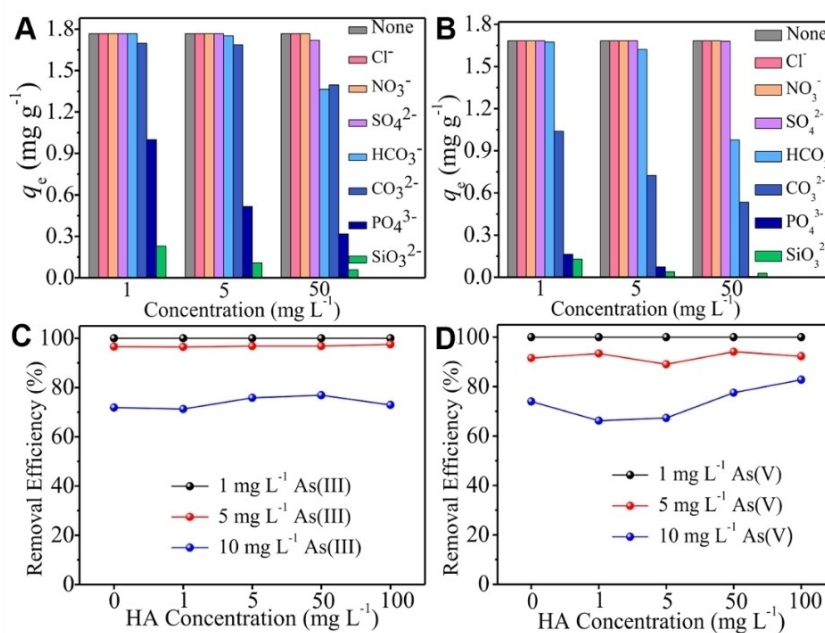
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Figure 7. Effect of inorganic anions and humic acid (HA) on the adsorption of AsO_2^- and AsO_4^{3-} onto Fe_2O_3@GS. Reproduced from Yu et al.,[77] Copyright 2019, with permission of Elsevier.

the 3D graphene/MWCNT-PDA material delivered an incredible adsorptive uptake of 318 and 351 mg.g^{-1} for Cu^{2+} and Pb^{2+}, respectively. Furthermore, on the basis of the surface chemical analysis of the monolithic adsorbent (before and after adsorption) using X-ray photoelectron spectroscopy, it was concluded that the adsorption proceeded *via* complexation and chelation of metal ions with the amine and oxygen functionalities of the hybrid sponge, as illustrated in Figure 8 (bottom panel).

3.3. Functionalization with Organic Molecules

Apart from the aforementioned techniques, surface modification of 3D GMAs by noncovalent attachment of organic polymers[82,83,84] or surfactants,[85] is an equally promising approach to improve their affinity for metal ions, and thus, significantly reform their adsorption capabilities. A representative illustration is the work of Gao et al.,[82] who grafted PDA particles on the 2D constituents of GS, by directly heating a homogenous mixture of GO and dopamine at 60 °C for 6 h. By virtue of the numerous reactive functional groups of PDA, the PDA—GS presented a higher uptake capacity for Pb^{2+} and Cd^{2+}, compared to pristine GS. More importantly, unlike the conventional powdery adsorbents, the free-standing PDA—GS adsorbent can be easily recovered from the aqueous media post decontamination, eliminating the need for tedious and time-consuming unit operations, such as filtration, magnetic separation, and high-speed centrifugation.

4. Summary and Outlook

With the unabated discharge of potentially toxic heavy metal ions from manufacturing and industrial facilities into aquatic environments, the development of robust adsorbents with high adsorption capacity and excellent recyclability, have become a top priority. Among the various adsorbents explored by the scientific community to separate heavy metals from water, 3D macrostructures of graphene and GO are receiving increased attention of late, because of their extraordinary uptake and ultrafast removal capabilities. This essentially stems from the exceptionally high surface area, intense porosity, and physically linked permeable networks of the 3D GMAs. Further, surface engineering of their constituent 2D nanosheets, *via* elemental doping, functionalization with organic/inorganic nanostructures, and hybridization with carbon nanoarchitectures, may yield 3D GMAs with more selective adsorption capabilities, thereby outspreading their application potential in complex matrices. In spite of this extraordinary progress, several fundamental knowledge gaps persist that warrant immediate investigations to facilitate yet more significant advancements, pertaining to this exciting and novel research domain of current global interest. First, most attempts to probe the heavy metal removal capacity of 3D GMAs, are based on single-component laboratory-scale batch studies. In order to comprehend the maximum potential of 3D GMAs for practical applications, their adsorption performance in multiple metal ion systems must be rigorously examined. Needless to say, such assessments must invariably be conducted under continuous flow conditions, since they represent a more industrially relevant approach of exploring the actual process-level performance of any adsorbent. Second, the structural integrity and durability of 3D GMAs
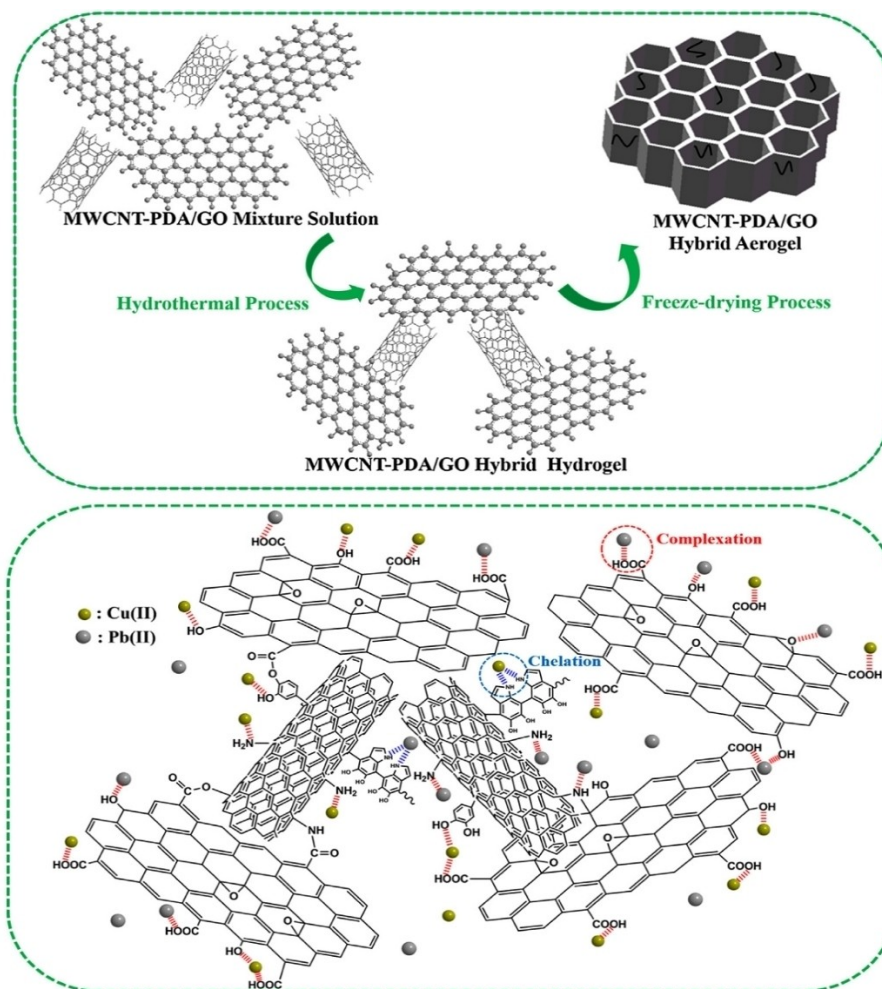
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Figure 8. Top panel: Schematic of the green synthesis of 3D graphene/MWCNT-PDA hybrid sponge. Bottom panel: Illustration of the complexation (red) and chelation (blue) interactions of Pb^{2+} and Cu^{2+} ions with the graphene/MWCNT-PDA hybrid sponge. Reproduced from Zhan et al.,[80] Copyright 2018, with permission of Elsevier.

against rough handling, intrinsic to wastewater treatment facilities, remains relatively unknown. Therefore, to realize a full-scale optimization of the commercial potential of the 3D GMAs, their tensile properties and attrition resistance should be comprehensively investigated. In addition, the insights conferred by their mechanical properties, and their relationship with the punitive aquatic chemistry, should also be carefully considered. Finally, even though numerous tactics have been devised to fabricate highly porous 3D GMAs, it is still a challenge to produce them on a commercial scale. Hence, more concerted efforts should be devoted to conceiving cost-effective and environmentally benign protocols for the mass production of 3D GMAs. We anticipate that the ongoing interdisciplinary research and strategic initiatives by the global scientific community will adequately tackle these bottlenecks, paving the way for widespread adoption and deployment of 3D GMAs, to effectively manage the environmental consequences of heavy metal pollution in the foreseeable future.

Conflict of Interest

The authors declare no conflict of interest.

[1] H. N. M. E. Mahmud, A. K. Obidul Huq, R. binti Yahya, *RSC Adv.* **2016**, *6*, 14778–14791.
[2] J. Li, X. Wang, G. Zhao, C. Chen, Z. Chai, A. Alsaedi, T. Hayat, X. Wang, *Chem. Soc. Rev.* **2018**, *47*, 2322–2356.
[3] S. Sikdar, M. Kundu, *ChemBioEng Rev.* **2018**, *5*, 18–29.
[4] A. Azimi, A. Azari, M. Rezakazemi, M. Ansarpour, *ChemBioEng Rev.* **2017**, *4*, 37–59.
[5] S. Bolisetty, M. Peydayesh, R. Mezzenga, *Chem. Soc. Rev.* **2019**, *48*, 463–487.
[6] J. P. Vareda, A. J. M. Valente, L. Durães, *J. Environ. Manage.* **2019**, *246*, 101–118.
[7] X. Tang, H. Zheng, H. Teng, Y. Sun, J. Guo, W. Xie, Q. Yang, W. Chen, *Desalin. Water Treat.* **2016**, *57*, 1733–1748.

[8] C. Y. Teh, P. M. Budiman, K. P. Y. Shak, T. Y. Wu, *Ind. Eng. Chem. Res.* **2016**, *55*, 4363–4389.

[9] Y. Zhu, W. Fan, T. Zhou, X. Li, *Sci. Total Environ.* **2019**, *678*, 253–266.

[10] A. Bashir, L. A. Malik, S. Ahad, T. Manzoor, M. A. Bhat, G. N. Dar, A. H. Pandith, *Environ. Chem. Lett.* **2019**, *17*, 729–754.

[11] L. Joseph, B.-M. Jun, J. R. V. Flora, C. M. Park, Y. Yoon, *Chemosphere* **2019**, 229, 142–159.

[12] N. Abdullah, N. Yusof, W. J. Lau, J. Jaafar, A. F. Ismail, *J. Ind. Eng. Chem.* **2019**, *76*, 17–38.

[13] S. Chowdhury, S. Pan, R. Balasubramanian, in *Sustainable Agriculture Reviews 34: Date Palm for Food, Medicine and the Environment* (Eds: M. Naushad, E. Lichtfouse), Springer, Cham, **2019**, pp. 247–263.

[14] L. Wang, C. Shi, L. Wang, L. Pan, X. Zhang, J.-J. Zou, *Nanoscale*, **2020**, *12*, 4790–4815.

[15] T. A. H. Nguyen, H. H. Ngo, W. S. Guo, J. Zhang, S. Liang, Q. Y. Yue, Q. Li, T. V. Nguyen, *Bioresour. Technol.* **2013**, *148*, 574–585.

[16] S. Afroze, T. K. Sen, *Water Air Soil Pollut.* **2018**, *229*, 225.

[17] I. Anastopoulos, I. Pashalidis, A. Hosseini-Bandegharaei, D. A. Gianna-koudakis, A. Robalds, M. Usman, L. B. Escudero, Y. Zhou, J. C. Colmenares, A. Núñez-Delgado, É. C. Lima, *J. Mol. Liq.* **2019**, *259*, 111684.

[18] G. Zhao, X. Huang, Z. Tang, Q. Huang, F. Niu, X. Wang, *Polym. Chem.* **2018**, *9*, 3562–3582.

[19] S. Sen Gupta, K. G. Bhattacharyya, *RSC Adv.* **2014**, *4*, 28537–28586.

[20] M. Jimenez-Castaneda, D. Medina, *Water* **2017**, *9*, 235–246.

[21] M. K. Uddin, *Chem. Eng. J.* **2017**, *308*, 438–462.

[22] A. G. Adeniyi, J. O. Ighalo, J. Environ, *Chem. Eng.* **2019**, *7*, 103100.

[23] A. A. Beni, A. Esmaeili, *Environ. Technol. Innov.* **2020**, *17*, 100503.

[24] A. Mittal, M. Teotia, R. K. Soni, J. Mittal, *J. Mol. Liq.* **2016**, *223*, 376–387.

[25] I. Ali, *Chem. Rev.* **2012**, *112*, 5073–5091.

[26] M. Yusuf, F. M. Elfghi, S. A. Zaidi, E. C. Abdullah, M. A. Khan, *RSC Adv.* **2015**, *5*, 50392–50420.

[27] A. I. A. Sherlala, A. A. A. Raman, M. M. Bello, A. Asghar, *Chemosphere* **2018**, *193*, 1004–1017.

[28] C. Liu, Q. Wang, F. Jia, S. Song, *J. Mol. Liq.* **2019**, *292*, 111390.

[29] S. Chowdhury, R. Balasubramanian, *Adv. Colloid Interface Sci.* **2014**, *204*, 35–56.

[30] S. Chowdhury, R. Balasubramanian, P. Das, in *Green Chemistry for Dyes Removal from Wastewater: Research Trends and Applications* (Ed.: S. K. Sharma), John Wiley & Sons Inc., Hoboken, **2015**, pp. 35–82.

[31] F. Perreault, A. F. de Faria, M. Elimelech, *Chem. Soc. Rev.* **2015**, *44*, 5861–5896.

[32] N. Baig, Ihsanullah, M. Sajid, T. A. Saleh, *J. Environ. Manage.* **2019**, *244*, 370–382.

[33] K. Thakur, B. Kandasubramanian, *J. Chem. Eng. Data* **2019**, *64*, 833–867.

[34] R. Balasubramanian, S. Chowdhury, *J. Mater. Chem. A* **2015**, *3*, 21968–21989.

[35] S. Chowdhury, S. Pan, R. Balasubramanian, P. Das in *A New Generation Material Graphene: Applications in Water Technology* (Ed.: M. Naushad), Springer, Cham, **2019**, pp. 43–68.

[36] S. Chowdhury, R. Balasubramanian, *J. CO₂ Util.* **2016**, *13*, 50–60.

[37] C. Xue, M. Gao, Y. Xue, L. Zhu, L. Dai, A. Urbas, Q. Li, *J. Phys. Chem. C* **2014**, *118*, 15332–15338.

[38] Y. Shen, Q. Fang, B. Chen, *Environ. Sci. Technol.* **2015**, *49*, 67–84.

[39] S. Chowdhury, R. Balasubramanian, *Prog. Mater. Sci.* **2017**, *90*, 224–275.

[40] Z. Yuan, X. Xiao, J. Li, Z. Zhao, D. Yu, Q. Li, *Adv. Sci.* **2018**, *5*, 1700626.

[41] N. Yousefi, X. Lu, M. Elimelech, N. Tufenkji, *Nat. Nanotechnol.* **2019**, *14*, 107–119.

[42] B. Y. Z. Hiew, L. Y. Lee, X. J. Lee, S. Thangalazhy-Gopakumar, S. Gan, S. S. Lim, G.-T. Pan, T. C.-K. Yang, W. S. Chiu, P. S. Khiew, *Process Saf. Environ. Prot.* **2018**, *116*, 262–286.

[43] K. C. Lai, L. Y. Lee, B. Y. Z. Hiew, S. Thangalazhy-Gopakumar, S. Gan, *J. Environ. Sci.* **2019**, *79*, 174–199.

[44] X. Xie, Y. Zhou, H. Bi, K. Yin, S. Wan, L. Sun, *Sci. Rep.* **2013**, *3*: 2117.

[45] Z. Xu, H. Sun, X. Zhao, C. Gao, *Adv. Mater.* **2013**, *25*, 188–193.

[46] C. Bao, S. Bi, H. Zhang, J. Zhao, P. Wang, C. Y. Yue, J. Yang, *J. Mater. Chem. A* **2016**, *4*, 9437–9446.

[47] G. G. Wallace, J. Chen, D. Li, S. E. Moulton, J. M. Razal, *J. Mater. Chem.* **2010**, *20*, 3553–3562.

[48] J. Luo, H. D. Jang, T. Sun, L. Xiao, Z. He, A. P. Katsoulidis, M. G. Kanatzidis, J. Murray Gibson, J. Huang, *ACS Nano* **2011**, *5*, 8943–8949.

[49] S. Kavadiya, R. Raliya, M. Schrock, P. Biswas, *J. Nanopart. Res.* **2017**, *19*, 43.

[50] M. Chen, C. Zhang, X. Li, L. Zhang, Y. Ma, L. Zhang, X. Xu, F. Xia, W. Wang, J. Gao, *J Mater. Chem. A* **2013**, *1*, 2869–2877.

[51] D. Zhao, Y. Wang, S. Zhao, M. Wakeel, Z. Wang, R. S. Shaikh, T. Hayat, C. Chen, *Environ. Pollut.* **2019**, *251*, 547–554.

[52] Y. Chen, L. Chen, H. Bai, L. Li, *J. Mater. Chem. A* **2013**, *1*, 1992–2001.

[53] Q. Fang, B. Chen, *J. Mater. Chem. A* **2014**, *2*, 8941–8951.

[54] D. Pakulski, W. Czepa, S. Witomska, A. Aliprandi, P. Pawluć, V. Patroniak, A. Ciesielski, P. Samorí, *J. Mater. Chem. A* **2018**, *6*, 9384–9390.

[55] A. He, B. Lei, C. Cheng, S. Li, L. Ma, S. Sun, C. Zhao, *RSC Adv.* **2013**, *3*, 22120–22129.

[56] N. Yousefi, K. K. W. Wong, Z. Hosseinidoust, H. O. Sørensen, S. Bruns, Y. Zheng, N. Tufenkji, *Nanoscale* **2018**, *10*, 7171–7184.

[57] S. Liu, F. Yao, O. Oderinde, Z. Zhang, G. Fu, *Carbohydr. Polym.* **2017**, *174*, 392–399.

[58] C. Jiao, J. Xiong, J. Tao, S. Xu, D. Zhang, H. Lin, Y. Chen, *Int. J. Biol. Macromol.* **2016**, *83*, 133–141.

[59] B. Tan, H. Zhao, Y. Zhang, X. Quan, Z. He, W. Zheng, B. Shi, *J. Colloid Interface Sci.* **2018**, *512*, 853–861.

[60] S. Wang, H. Ning, N. Hu, K. Huang, S. Weng, X. Wu, L. Wu, J. Liu, Alamusi, *Compos. B. Eng.* **2019**, *163*, 716–722.

[61] G. Zhou, C. Liu, Y. Tang, S. Luo, Z. Zeng, Y. Liu, R. Xu, L. Chu, *Chem. Eng. J.* **2015**, *280*, 275–282.

[62] Q. Han, L. Chen, W. Li, Z. Zhou, Z. Fang, Z. Xu, X. Qian, *Environ. Sci. Pollut. Res.* **2018**, *25*, 34438–34447.

[63] X. Mi, G. Huang, W. Xie, W. Wang, Y. Liu, J. Gao, *Carbon* **2012**, *50*, 4856–4864.

[64] T. Liu, M. Huang, X. Li, C. Wang, C.-X. Gui, Z.-Z. Yu, *Carbon* **2016**, *100*, 456–464.

[65] S. P. Lee, G. A. M. Ali, H. Algarni, K. F. Chong, *J. Mol. Liq.* **2019**, *277*, 175–180.

[66] R. Yu, Y. Shi, D. Yang, Y. Liu, J. Qu, Z.-Z. Yu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 21809–21819.

[67] T. Huang, Y.-W. Shao, Q. Zhang, Y.-F. Deng, Z.-X. Liang, F.-Z. Guo, P.-C. Li, Y. Wang, *ACS Sustain. Chem. Eng.* **2019**, *7*, 8775–8788.

[68] W. Li, S. Gao, L. Wu, S. Qiu, Y. Guo, X. Geng, M. Chen, S. Liao, C. Zhu, Y. Gong, M. Long, J. Xu, X. Wei, M. Sun, L. Liu, *Sci. Rep.* **2013**, *3*, 2125.

[69] G. Chen, Y. Liu, F. Liu, X. Zhang, *Appl. Surf. Sci.* **2014**, *11*, 808–815.

[70] Y. Lei, F. Chen, Y. Luo, L. Zhang, *Chem. Phy. Lett.* **2014**, *593*, 122–127.

[71] Y. Jiang, S. Chowdhury, R. Balasubramanian, *J. Colloid Interface Sci.* **2019**, *534*, 574–585.

[72] L. Zhao, B. Yu, F. Xue, J. Xie, X. Zhang, R. Wu, R. Wang, Z. Hu, S.-T. Yang, J. Luo, *J. Hazard. Mater.* **2015**, *286*, 449–456.

[73] Q. Kong, Q. Wei, S. Preis, Y. Hu, F. Wang, *Environ. Sci. Pollut. Res.* **2018**, *25*, 21164–21175.

[74] H.-P. Cong, X.-C. Ren, P. Wang, S.-H. Yu, *ACS Nano* **2012**, *6*, 2693–2703.

[75] Y. Lei, F. Chen, Y. Luo, L. Zhang, *J. Mater. Sci.* **2014**, *49*, 4236–4245.

[76] J. Liu, X. Ge, X. Ye, G. Wang, H. Zhang, H. Zhou, Y. Zhang, H. Zhao, *J. Mater. Chem. A* **2016**, *4*, 1970–1979.

[77] X. Yu, Y. Wei, C. Liu, J. Ma, H. Liu, S. Wei, W. Deng, J. Xiang, S. Luo, *Chemosphere* **2019**, *222*, 258–266.

[78] Z. Sui, Q. Meng, X. Zhang, R. Ma, B. Cao, *J. Mater. Chem.* **2012**, *22*, 8767–8771.

[79] M. Zhang, B. Gao, X. Cao, L. Yang, *RSC Adv.* **2013**, *3*, 21099–21105.

[80] W. Zhan, L. Gao, X. Fu, S. H. Siyal, G. Sui, X. Yang, *Appl. Surf. Sci.* **2019**, *467—468*, 1122–1133.

[81] Y. Zhang, X. Yan, Y. Yan, D. Chen, L. Huang, J. Zhang, Y. Ke, S. Tan, *RSC Adv.* **2018**, *8*, 4239–4248.

[82] H. Gao, Y. Sun, J. Zhou, R. Xu, H. Duan, *ACS Appl. Mater. Interfaces* **2013**, *5*, 425–432.

[83] Z. Dong, F. Zhang, D. Wang, X. Liu, J. Jin, *J. Solid State Chem.* **2019**, *224*, 88–93.

[84] Z. Wang, F. Lin, L. Huang, Z. Chang, B. Yang, S. Liu, M. Zheng, Y. Lu, J. Chen, *Environ. Pollut.* **2019**, *254*, 112854.

[85] Y. Kuang, R. Yang, Z. Zhang, J. Fang, M. Xing, D. Wu, *Chemosphere* **2019**, *236*, 124416.