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REVIEW ARTICLE

Efficient elimination of environmental pollutants through sorption-reduction and photocatalytic degradation using nanomaterials

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Abstract With the rapid development of industrial, large amounts of different inorganic and organic pollutants are released into the natural environments. The efficient elimination of environmental pollutants, i.e., photocatalytic degradation of persistent organic pollutants into nontoxic organic/inorganic chemicals, *in-situ* solidification or sorption-reduction of heavy metal ions, is crucial to protect the environment. Nanomaterials with large surface area, active sites and abundant functional groups could form strong surface complexes with different kinds of pollutants and thereby could efficiently eliminate the pollutants from the aqueous solutions. In this review, we mainly focused on the recent works about the synthesis of nanomaterials and their applications in the efficient elimination of different organic and inorganic pollutants from wastewater and discussed the interaction mechanism from batch experimental results, the advanced spectroscopy techniques and theoretical calculations. The adsorption and the photocatalytic reduction of organic pollutants and the sorption/reduction of heavy metal ions are generally considered as the main methods to decrease the concentration of pollutants in the natural environment. This review highlights a new way for the real applications of novel nanomaterials in environmental pollution management, especially for the undergraduate students to understand the recent works in the elimination of different kinds of inorganic and organic chemicals in the natural environmental pollution management.

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1 Introduction

With the fast development of industry, large amounts of wastewater containing different kinds of organic pollutants, toxic metal ions, radionuclides and manmade nanoparticles are inevitably released into the natural environment. These contaminants create serious threats to human health and environmental ecology systems [1–6]. Although some toxic organic pollutants could be photocatalytic degraded into less toxic organic molecules by catalysts under the UV-Vis or visible light, it still takes long time to achieve the degradation of organic pollutants [7–10]. However, most kinds of catalysts are difficult to degrade organic pollutants under visible light. It is necessary to synthesize novel nanomaterials which have multi-reactive centers, can harvest visible light and accelerate the separation electrons and holes. Such nanomaterials are ideal catalysts for the photocatalytic degradation of persistent organic pollutants under visible light conditions. Unlike organic pollutants, toxic metal ions are difficult to degrade into ecofriendly substances, but easily to be accumulated into living organisms, fruits, vegetables or plants, which results in higher concentration and thereby are more dangerous to human health [11–17]. Thereby, it is crucial to efficiently eliminate the organic/inorganic pollutants from the wastewater before the wastewater is released into the natural environment.

Up to now, various kinds of techniques such as sorption/

adsorption, photocatalytic degradation, precipitation, (electro)coagulation, (ultra)filtration, extraction, reduction/oxidation, biological degradation/treatment, and membrane methods, have been extensively applied for the decontamination of different kinds of pollutants from large amounts of aqueous solutions [18–23]. The advantages and disadvantages of different methods are summarized in Table 1. From Table 1, one can see that different techniques have different advantages/disadvantages. Different methods are suitable for different kinds of pollutants. However, the sorption method is simple in operation and could be applied in large scale.

Nanomaterials, such as graphene oxides (GO), carbon nanotubes (CNTs), covalent organic frameworks (COF), metal organic frameworks (MOF), carbon nitride (C_3N_4), MXenes, and chitosan-based materials have shown excellent properties in the high sorption, sorption selectivity, reduction/oxidation, photocatalytic reduction, and preconcentration/degradation of different kinds of metal ions and persistent organic pollutants [24–29]. Large amounts of functional groups on the surfaces, plenty of binding sites and high specific surface areas of these nanomaterials attracted extensive researches in multidisciplinary areas, especially in the elimination and preconcentration of metal ions and the degradation of persistent organic pollutants in environmental pollution management. The methods for the preparation and/or surface/structure modification of such nanomaterials have been reported in many relevant papers and the methods for the synthesis and modification are not necessary to be described herein. MOFs are considered as the state of crystalline nano-porous materials which are constructed by the coordination interactions between the cluster nodes/metal ions and organic linkers. The large amounts of amidoxime, carboxyl and hydroxyl groups could form strong inner-sphere surface complexes with metal ions and thereby increases the metal ions' sorption. The amidoxime groups which can act as Lewis acid could form complexes with metal ions which are considered as Lewis base through the Lewis' acid-base interactions [24]. COFs are built by strong covalent bonds and thereby own high chemical stability even under vigorous conditions. The surface property, arrangement and the density of active centers is easily constructed through special organic building unites or by post-synthetic modification to modify functional groups. The special properties of COFs make them suitable materials for the selective binding of metal ions under complicated conditions. MXene is a kind of two-dimensional transition metal carbide/nitride layered materials. MXenes are generally terminated with –OH, –O, –Cl or –F groups, which could provide large amounts of adsorption sites and hydrophilicity surfaces. The large specific surface area, high ion-exchange capacity, abundant active sites, hydrophilicity and controllable interlayer spaces make MXenes suitable materials for the solidification of metal ions, especially the fast calcination at high temperatures to shorten the interlayer spaces. C_3N_4 owns a two-dimensional lamellar structure with moderate energy gap (~2.7 eV) and π conjugated structure, which lead to good visible light absorption. Such property is beneficial for the application of C_3N_4 as catalyst in the photocatalytic degradation of organic pollutants under visible light conditions. The properties, advantages and disadvantages of these novel nanomaterials are summarized in Table 2. One can see that these novel nanomaterials are suitable candidates in the environmental pollution cleanup. In this review, the recent works about the sorption-reduction of metal ions and the photocatalytic degradation of persistent

Table 1 Summary of the advantages and disadvantages of different methods in the elimination of pollutants

Methods	Advantages	Disadvantages
Sorption/adsorption	Easy operation in large scale for separation of metal ions and organic pollutants	Difficult for separation from solutions
Photocatalytic degradation	For the degradation of organic pollutants at low concentration	Difficult for the elimination of metal ions
Precipitation	Different kinds of metal ions could be precipitated simultaneously	The solution pH should be adjusted for precipitation
(Electro)coagulation	Different kinds of pollutants could be coagulated together in the coagulation process	Need further separation of the coagulates and parts of pollutants could still present in solution
(Ultra)filtration	Different kinds of pollutants could be separated through the control of filter size	Can not be used in large scale and high cost
Extraction	Pollutants could be selectively extracted through the addition of special extraction agent	Need special extraction agents which are pollutants themselves and need further treatment
Reduction/oxidation	High valent metal ions could be reduced to low valent and *in-situ* solidified	Only suitable for organic pollutants and metal ion with different valent
Biological degradation	Environmentally friendly methods for the preconcentration of metal ions and degradation of organic pollutants	Need long time for the treatment process and strict condition for microorganism
Membrane separation	Easy operation in the separation of pollutants from one solution to another solution	Is not in large scale and high cost

Table 2 Summary of the advantages and disadvantages of different nanomaterials

Nanomaterials	Advantages	Disadvantages
GO	High sorption capacity; easy surface modification; sufficient functional groups; large surface area; easy modification	Difficult for separation from solutions; high cost in synthesis; poor selectivity; difficult for synthesis in large scale
CNTs	Easy synthesis; high external surface area; high stability in vigorous low or high pH conditions	Relatively high cost in synthesis; low selectivity in sorption; low sorption capacity
COFs	High sorption capacity; high chemical and thermal stability; easy modification with functional groups	High cost for synthesis; difficult for separation; difficult to control the structure and layer stacking
MOFs	Easy synthesis in large scale; easy modification with functional groups; high specific surface area; easy to adjust the pore size	High cost in synthesis; low hydrolytic stability; difficult to be separated from solutions
C_3N_4	Easy synthesis; easy doping to improve the photocatalytic property	Low sorption capacity for metal ions; high photocatalytic degradation of organic pollutants
MXenes	Enough sorption sites; high ion exchangeable ability with metal ions; easy controllable layered structure	High cost in the synthesis; poor selectivity; collapse at high temperature

organic pollutants are summarized, and the perspective of nanomaterials in real applications is also described in the end.

2 Sorption of metal ions and organic pollutants

CNTs have attracted multidisciplinary attention because of their outstanding physicochemical properties since they were firstly discovered in 1991. CNTs are good candidates for the sorption of metal ions through the formation of strong surface complexes and organic pollutants through the π-π interactions, electrostatic attraction etc. Pan and Xing [30] reviewed CNTs as adsorbents for the sorption of organic chemicals, and summarized that the π-π interactions, hydrophobic interactions, electrostatic interactions and hydrogen bonds were the main mechanisms for the uptake of organic pollutants. Rao et al. [31] summarized the sorption of metal ions on CNTs and concluded that the sorption was mainly attributed to chemical interactions between functional groups and metal ions, especially the oxidation of CNTs to introduce different oxygen-containing groups could obviously improve the sorption capacities. Zhao et al. [32,33] synthesized graphene oxides and applied them in the removal of persistent organic pollutants (naphthalene and 1-naphthol) and metal ions (Cd(II) and Co(II) ions) from aqueous solutions under different experimental conditions, and the results showed the maximum sorption capacities of ~2.3 mmol/g for naphthalene and ~2.4 mmol/g for 1-naphthol, and 106.3 mg/g for Cd(II), which were the highest sorption capacities of today's nanomaterials. In Ai's group, the sorption of bisphenol A, tetracycline antibiotics, phenol, 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol on graphene oxides and graphene oxide-based nanomaterials was studied by the batch techniques, advanced spectroscopy measurements and theoretical calculations at molecular level, and the maximum sorption capacity of 255.4 mg/g for bisphenol A was achieved. The density functional theory and molecular dynamics simulation indicated that the sorption of organic pollutants to graphene oxides was mainly driven by hydrophobic effect and ultimately stabilized by hydrogen bonds and π-π interaction, and the adsorption capacity was improved by hydroxyl groups which provided more adsorption sites for the binding of chlorophenol chemicals [34–36]. The adsorption of naphthalene, phenanthrene and pyrence on graphene oxide nanosheets also showed the high sorption capacity of organic chemicals on graphene oxides, and the interaction was mainly dominated by hydrogen bond and π-π interaction [37]. From the above-mentioned experimental results and theoretical calculation, one can see that the sorption of organic pollutants on nanomaterials were mainly dominated by hydrogen bonds, π-π interaction and electrostatic attraction. Wang et al. [38] reviewed graphene oxides and graphene oxide-based nanomaterials as adsorbents for the removal of U(VI), Eu(III), Th(IV), Sr(II) and Cs(I) from solutions from the viewpoint of the batch techniques, advanced spectroscopic analysis and theoretical calculations, and concluded that graphene oxide-based nanomaterials were suitable candidates for the elimination/preconcentration of heavy metal ions from wastewater, and could eliminate metal ions simultaneously. Wang et al. [39] synthesized vanadium carbide MXene for U(VI) capture and found that U(VI) preferred to coordinate with hydroxyl groups via forming bidentate inner-sphere complexes with the sorption capacity of 174 mg/g. They also applied surface-modified Ti_2CT_x MXene for the sequestration of Tc(VII) and Re(VII) from solutions under different pH values and found that the MXene had high selectivity for Tc(VII) and Re(VII) [40]. The sorption of Th(IV) on Ti_2CT_x MXene showed the capacity of 213.2 mg/g with high sorption selectivity in the presence of other competing metal ions, which was much higher than most common inorganic materials [41]. The

$Ti_3C_2T_x$ MXene modified with KH570 showed the adsorption capacity of 147.3 mg/g for Pb(II). The internal MXene hydroxyl groups and carbonyl groups are major responsible for Pb(II) adsorption [42]. The high surface areas and enough pores of MOFs make them excellent candidates for the separation of Sr(II) and Cs(I) through ion-exchange [43,44]. Wang's group in Soochow University synthesized different kinds of MOFs and applied for the separation of metal ions such as Tc(VII), Re(VII), Kr/Xe [45–49], and the results showed that the synthesized MOFs had high sorption capacities in the selective elimination of target metal ions from aqueous solutions in the presence of other metal ions. The elimination of arsenic(V) from solution to MOFs-derived magnetic chestnut shell-like hollow sphere NiO/Ni@C composites showed the adsorption capacity of 454.94 mg/g on NiO/Ni@C400, which was mainly attributed to the rich oxygen-containing functional groups and high specific surface area [50]. The filtration membranes are good materials for the elimination of metal ions [51]. The filtration experiments using nanofibrous membrane with MOFs as adsorbents for the removal of Zn(II), Cd(II), Pb (II), Hg(II) and Zn(II) showed that significant improvement removal efficiency with the increase of membrane thickness [52,53]. The high separation performance and reusability of the membranes and the outstanding stability of the nanofibrous membrane with MOFs suggested the materials as potential candidate for wastewater treatment. The pore within COFs is anchored by the different functional organic unites, and thereby enhances the affinity of metal ions and organic molecules. The high chemostability makes COFs as promising absorbents for the elimination of pollutants under rigorous conditions [54]. Most importantly, COFs were most promising in the preconcentration of metal ions at strong acidic conditions such as pH = 1 for U(VI) separation [55]. A porous aromatic MOF framework exhibited U(VI) adsorption capacity of 300 mg/g [56] and amino substituent COF showed the sorption capacity of 530 mg/g [57]. The adsorption of bisphenol A on magnetic COFs was investigated by batch techniques and theoretical calculations, and the results showed that the BPA molecules were mainly removed via the complexation with phenolic aldehyde groups, the pore structure of the frameworks and aggregation of BPA molecules were the crucial factors for the sorption efficiency [58]. The chitosan-based nanomaterials were also applied for the adsorption of metal ions such as Cu(II), Co(II), Mn(II) from aqueous solutions, and the results showed that the chitosan-based nanomaterials had high sorption capacities for the removal of metal ions from wastewater. The crosslink of chitosan with other biocompatible polymers such as poly(acrylic acid) or poly(ethylene glycol), could enhance the adsorption capacity [59,60]. Ngah et al. [61] reviewed the adsorption of dyes and metal ions by chitosan-based composites and concluded that chitosan was a good adsorbent for the removal of various kinds of anionic and cationic dyes as well as heavy metal ions. The use of cross-linking agent such as glutaraldehyde or some modification process like coating could improve the properties of chitosan in acidic conditions. The sorption of metal ions and dyes is mainly attributed to electrostatic attractions and chelation. The chitosan-based nanomaterials are promising candidates for the efficient elimination of metal ions from wastewater with high stability and high sorption capacity. From the abovementioned results, one can see that nanomaterials showed high sorption capacity for the elimination of organic and inorganic pollutants, especially under vigorous conditions. Through the modification of special functional groups on the surface or in the pores of nanomaterials, the high selectivity of special pollutants could be selectively adsorbed through the formation of strong inner-sphere surface complexes, ion exchange, π-π interaction, hydrogen bond, electrostatic interaction or hydrogen bond etc. The sorption method is the simplest technique for the elimination of metal ions or organic chemicals from aqueous solutions in large scale. The high dispersion of nanomaterials in aqueous solutions makes them difficult to be separated from wastewater. One can modify nanomaterials with magnetic nanoparticles which could separate the nanocomposites efficiently from solutions through magnetic separation technique. The nanomaterials are promising candidates in the preconcentration and solidification of different kinds of environmental pollutants if they are synthesized in large scale at low price in future.

3 Sorption and reduction of high valent metal ions to low valent metal ions

The sorption-reduction strategy of high valent metal ions such as U(VI) to U(IV), Cr(VI) to Cr(III), Se(IV) to Se(II) etc. and then the *in-situ* solidification at solid particle surfaces are important method for the immobilization and reduction of high valent metal ions to low valent metal ions in natural environment. Generally, the high valent metal ions are mobile whereas the low valent metal ions are less mobile and easily form precipitates. Wang et al. [62] applied Ti_2CT_x MXene for the reduction and sequestration of U(VI) from aqueous solutions via a sorption-reduction strategy, and the Ti_2CT_x MXene exhibited excellent U(VI) sorption-reduction over a wide pH range with a sorption capacity of 470 mg/g at pH = 3.0 and the reduced U(VI) formed mononuclear with bidendate binding on MXene. The activation and fast calcination strategies of U(VI) uptake and solidification in the inner channel of MXene was shown in Fig. 1(a). One can see that U(VI) could be solidified in the inner channel after fast calcination at high temperatures. Figures. 1(b) and 1(c) showed the X-ray absorption near-edge structure (XANES) spectra and the corresponding Fourier transforms of extended X-ray absorption fine structure (EXAFS) spectra of U(VI) on Ti-based MXene over a wide pH range. The XANES spectra indicated that U(VI) could be reduced to U(IV) in the pH range of 3–8. However, non-reduction of U(VI) was found on $Ti_3C_2T_x$, suggesting the reduction ability of MXene. The EXAFS analysis (Fig. 1(c)) could provide the information about the species, microstructures, and the coordination information of U(VI) on MXene materials. The application of C_3N_4 for the photoreduction of U(VI) to U(IV) and Cr(VI) to Cr(III) in the presence and absence of bisphenol A (BPA) showed that U(VI) was photocatalytic reduced to U(IV) by photogenerated electrons of conduction band edge whereas Cr(VI) was photocatalytic reduced to Cr(III) by H_2O_2. The reduced U(IV) and Cr(III) further formed precipitation and strong inner-sphere surface complexes on C_3N_4. The BPA was also reduced to organic acid and alcohols in the photocatalytic degradation process and the presence of BPA enhanced the photoreduction of U(VI) and Cr(VI) [63]. The results showed that C_3N_4 is a suitable material for the simultaneous removal of metal ions and organic pollutants in environmental pollution cleanup. Nano zero-valent iron (nZVI) supported nanomaterials is also an ideal material for the sorption-reduction of high valent metal ions as the surface oxygen-containing functional groups of nanomaterials could form strong surface complexes with metal ions and the surface-bound Fe(II) and Fe(0) could play critical role in the reduction of metal ions from high valent to low valent [64]. The reduction of Cr(VI) to Cr(III) in the presence of humic acid by nZVI/Ni bimetal material showed that 99.8% Cr(VI) could be reduced to Cr(III) at pH 5 and the presence of humic acid inhibited the reduction of Cr(VI) [65]. Yang et al. [66] synthesized Fe_3S_4 micro-crystal and applied for the sorption-reduction of U(VI) and Cr(VI). The batch experimental results showed high sorption capacities of 505.4 mg/g for U(VI)

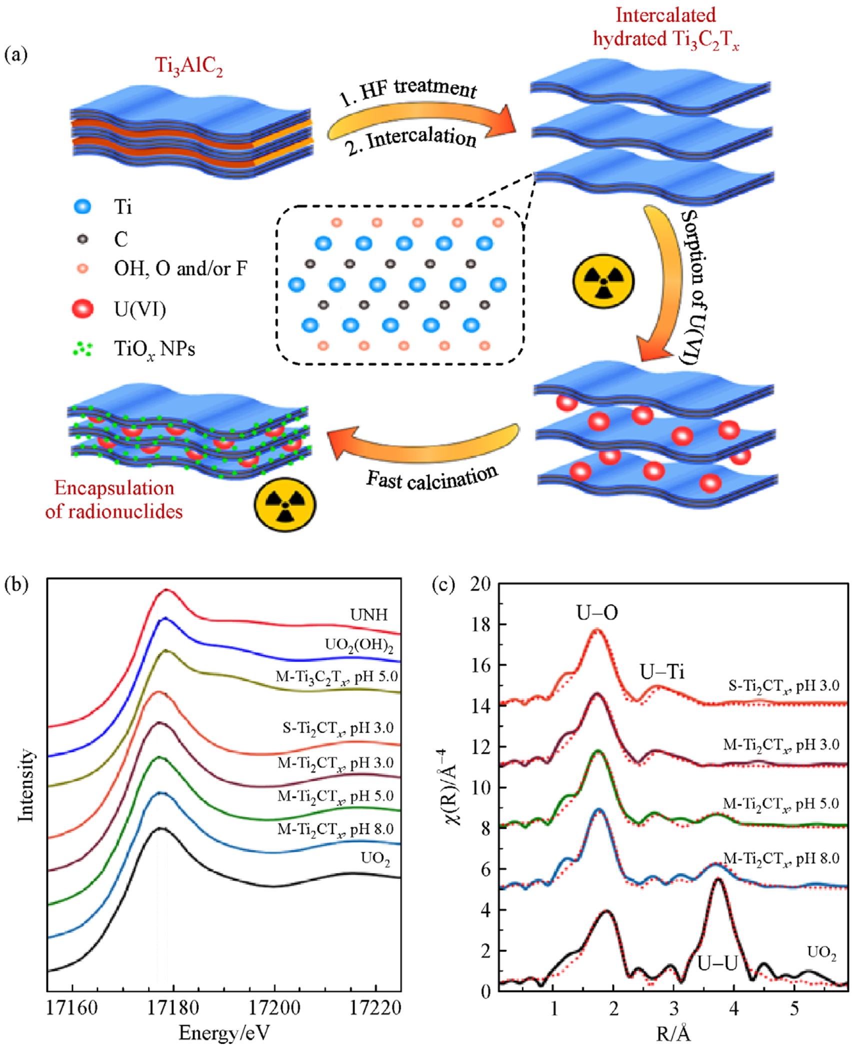

Fig. 1 (a) Hydrated intercalation activation and fast calcination strategy of $Ti_3C_2T_x$ MXene for U(VI) sorption and encapsulation [83] (reprinted with permission from RSC); (b, c) U L_3 edge XANES spectra and the Fourier transforms of k^3-weighted EXAFS spectra of U-loaded MXene samples [62,84] (reprinted with permission from ACS, copyright 2018).

and 274.1 mg/g for Cr(VI) at pH 5.0 for the simultaneous removal of Cr(VI) and U(VI). U(VI) and Cr(VI) could be reduced to less toxic U(IV) and Cr(III) species with the help of reducing Fe(II) and Fe(0) components in Fe_3S_4. However, the nZVI nanoparticles could be easily accumulated and thereby reduced their sorption capacity and reduction efficiency. The dispersion of nZVI on nanomaterials is a suitable way to avoid the aggregation of nZVI. Sheng et al. [67] immobilized nZVI on CNTs and applied for the sorption-reduction of Se(IV), and the X-ray absorption fine structure (XAFS) analysis revealed that Se(IV) was almost reduced to Se(0)/Se(II) by nZVI/CNT composites. Figure 2 shows the X-ray absorption near-edge structures (XANES) and the Fourier transforms of Se (IV) adsorbed nZVI/CNT samples. One can clearly see that Se(0)/Se(II) presented on nZVI and nZVI/CNT samples, however only Se(IV) presented on CNT samples, suggesting the reduction of Se(IV) to Se(II)/Se(0) in the presence of nZVI. Some other materials, such as graphene oxide, layered double hydroxides, were also used to support nZVI for the elimination of different contaminants [68–70], and similar results were reported. Li et al. [71] synthesized nZVI@MOF-74 composites and applied the composites for the removal of U(VI), and the results showed that the improved sorption of U(VI) was attributed to the sorption of U(VI) from MOF-74 and the reduction of U(VI) to U(IV) by nZVI. Although most kinds of nanomaterials showed high sorption capacity for the removal of metal ions and organic molecules, the *in-situ* sorption-reduction strategy is crucial for the immobilization of some kinds of metal ions such as Cr(VI), U(VI), Se(IV) because the low valent metal ions are easily precipitated and then fixed on nanomaterials. The main challenges for the sorption-reduction strategy of metal ions are the sorption capacity and the reduction ability of the different components in the composites. Another problem is the stability of the nanomaterials and the solidification of metal ions on nanomaterials after long time, which may result in the reoxidation of metal ions and releases into the natural environment again.

4 Photocatalytic degradation of organic pollutants

The photocatalytic degradation of persistent organic pollutants under visible light irradiation for the removal of organic pollutants at low concentrations is an efficient way. TiO_2 and TiO_2 modified with different components have been studied extensively for the degradation of organic pollutants. There are many reviews about the modification of TiO_2 for the photocatalytic degradation of organic pollutants. MXene is also a promising photocatalyst for water splitting with high stability and facilitates the migration and separation of photogenerated electro-hole pairs [72]. Iqbal et al. [73] synthesized Ti_3C_2-MXene/bismuth ferrite nanohybrids and applied for the degradation of Congo Red and acetophenone under visible light irradiation, and the 100% Congo Red was photocatalytic degraded within 42 min and 100% acetophenone was degraded in 150 min. C_3N_4 has been studied extensively as heterogeneous photocatalyst for the elimination of various organic and inorganic pollutants because of its metal-free, ubiquitous, visible-light driven and low cost [74–76].

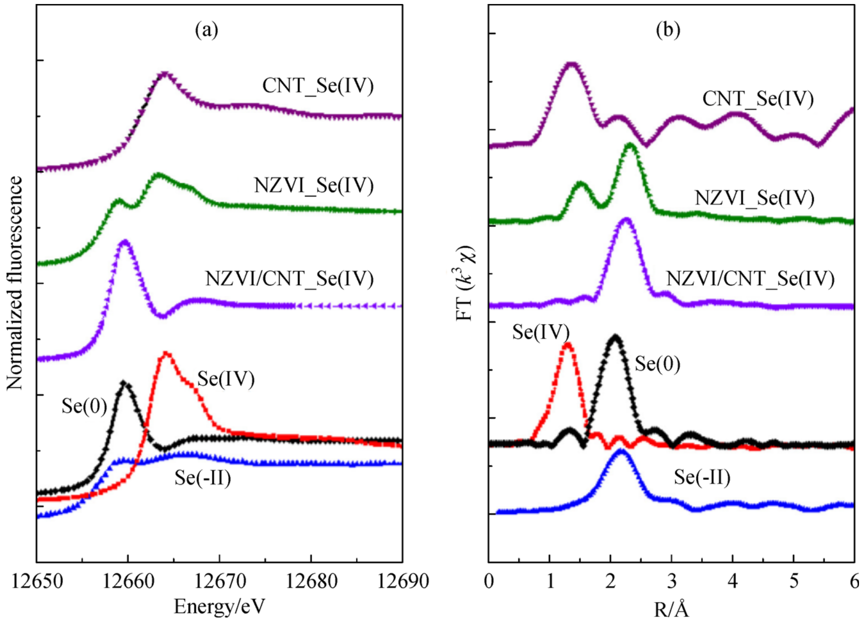

Fig. 2 (a) XANES spectra, and (b) EXAFS spectra of reference samples and reacted samples of Se(IV) on CNT, nZVI and nZVI/CNT samples [67] (reprinted with permission from Elsevier).

$AlVO_4$/g-C_3N_4 nanocomposites were applied for the degradation of methylene blue (MB) from wastewater and the analysis suggested that the enhanced separation of photogenerated electron/hole pairs leading to the effective photocatalytic degradation of MB, and the photogenerated holes and superoxide anion radicals played a major role in the photocatalysis process [77]. The photocatalytic degradation of acetaminophen by TiO_2/g-C_3N_4 nanocomposites under visible-light irradiation showed that $SO_4^{\cdot}$, $^{\cdot}OH$ and H^+ contributed to the eliminating organic compounds. The composites have strong nonselective oxidative ability for the degradation of organic pollutants such as phenol, bisphenol A and carbamazepine [78]. The Ag-decorated phosphorus doped C_3N_4 showed fast photocatalytic degradation of sulfamethoxazole under visible light irradiation. The catalyst was stable and could be reused for at least 6 cycles without losing photocatalytic activity [79]. Sridharan et al. [80] showed that ~98% of dyes and 33% of Cr(VI) were removed by C_3N_4-TiO_2 composites. To ascertain the photocatalytic degradation of organic pollutants, different radical scavengers such as *tert*-butyl alcohol (*t*BA) for $^{\cdot}OH$, $Na_2C_2O_4$ for h^+, N_2 for $O_2^{\cdot-}$ active species are applied to understand the major role of different active species on the photocatalytic degradation processes [29]. After adding different radical scavenger, the contribution of active species can be evaluated from the change of photocatalytic degradation efficiency. The desired photocatalytic efficiency was not easily achieved by the pristine C_3N_4 because of inefficient solar-light absorption, its narrow absorption region and insufficient charge carrier transportation. The photocatalytic reactions are mainly dependent on the morphologies of catalyst, mass transport processes, visible-light absorption and surface distribution of active sites. Thereby, the doping of C_3N_4 to enhance the absorption of low-frequency light, to accelerate the separation of electrons and holes, to introduce multi-reactive centers and to enhance the charge transfer is the most important method to improve the photocatalytic capacity. The proposed mechanism of BPA by C_3N_4 and structure-deficient mesoporous C_3N_4 (DMCN) was depicted in Fig. 3. One can see that the DMCN showed much higher photocatalytic degradation ability than C_3N_4. To improve the photocatalytic efficiency under visible light conditions, the controllable nanomaterial synthesis is the best method to change the energy gap, to increase favorable structural defects and to generate more active species [8,81]. Generally, the doping of other metal ions or the decorated with other metal oxides to change the energy gap, or to change the structural defects or to increase the active sites is a useful method to improve the photocatalytic property under visible light conditions. Also, the reusability and stability of the catalyst should be considered for their application in the photocatalytic degradation of persistent organic pollutants. The photocatalytic degradation of organic pollutants is suitable for the treatment of wastewater or waste solid components at low concentrations. For high concentrations, photocatalytic reduction of organic pollutants may need long time to degrade the organic pollutants totally.

5 Mechanism

In the above sections, we presented some representative works about the sorption of metal ions and organic pollutants, sorption-reduction of metal ions with oxidation/reduction properties, and the photocatalytic degradation of persistent organic pollutants under visible light irradiation. However, the interaction mechanism especially at molecular level was not discussed in detail. The understanding of the interaction mechanism is helpful for us to evaluate the physicochemical properties of pollutants in the natural environment. Herein, different spectroscopy techniques and theoretical calculations are mainly introduced. Density functional theory (DFT) is a useful method to provide the active sites, the structures of reactants, the total energy

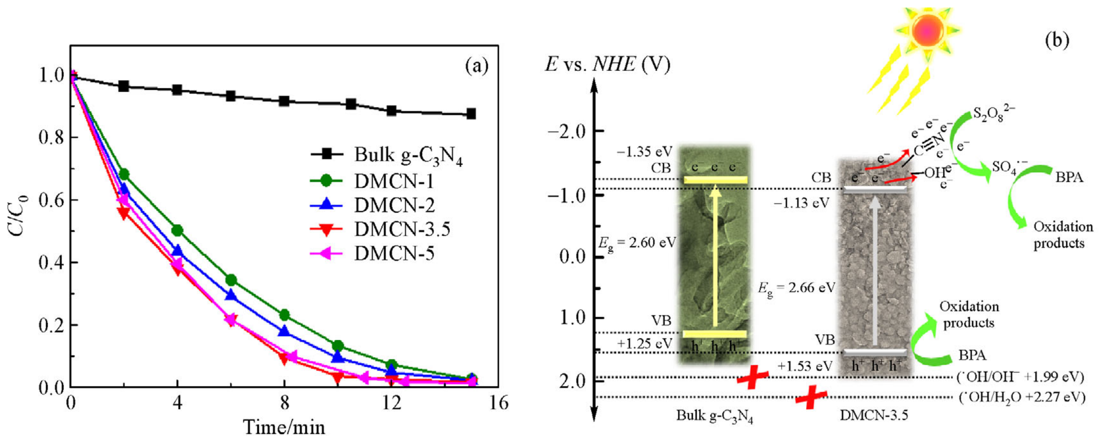

Fig. 3 (a) The photocatalytic degradation of BPA on C_3N_4 and DMCN; (b) the proposed mechanism schematic for the separation and transfer of charge carriers in BPA degradation by DMCN under visible light irradiation [82] (reprinted with permission from RSC).

information and the charge density of the system for the interaction [82,85]. The interaction mechanism can be identified from the analysis of the electronic structures. The whole process such as the intermediates, the transition states, the coordination conditions and the bond distances could also be simulated to understand the whole sorption and photocatalytic degradation processes. The DFT calculation of BPA photocatalytic degradation dual-oxygen-doped porous g-C_3N_4 (OPCN) photocatalysts were shown in Fig. 4. The intermediates, transition states and corresponding energies were calculated in detail, which can evidence the possible pathway for the photocatalytic degradation of BPA. The X-ray photoelectron spectroscopy (XPS) could provide the chemical composition, the oxidation state, the relative concentration and the bonding relationship for the surface and near-surface target metal ions. From the peak shifting, one can understand the interaction of metal ions with different functional groups on nanomaterials. XAFS could provide the information of oxidation/reduction state, coordination number, bond distances and the near-neighbor elements surrounding the target metal ions. From the coordination number and neighbor elements, the microstructure could be achieved at molecular level. The bond distance is helpful to understand the formation of inner-sphere or outer-sphere surface complexes. The oxidation or reduction of metal ions could also be confirmed from the XAFS spectra. Some XAFS spectra about U(VI) and Se(IV) sorption and reduction are shown in Figs. 1 and 2. Comparing to the XAFS spectra of reference samples, one can clearly see that U(VI) is reduced to U(IV), and Se(IV) is reduced to Se(0). The XAFS technique is the sensitive method to understand the valent change of metal ions. For other techniques such as scanning electron microscopy, transmission electron

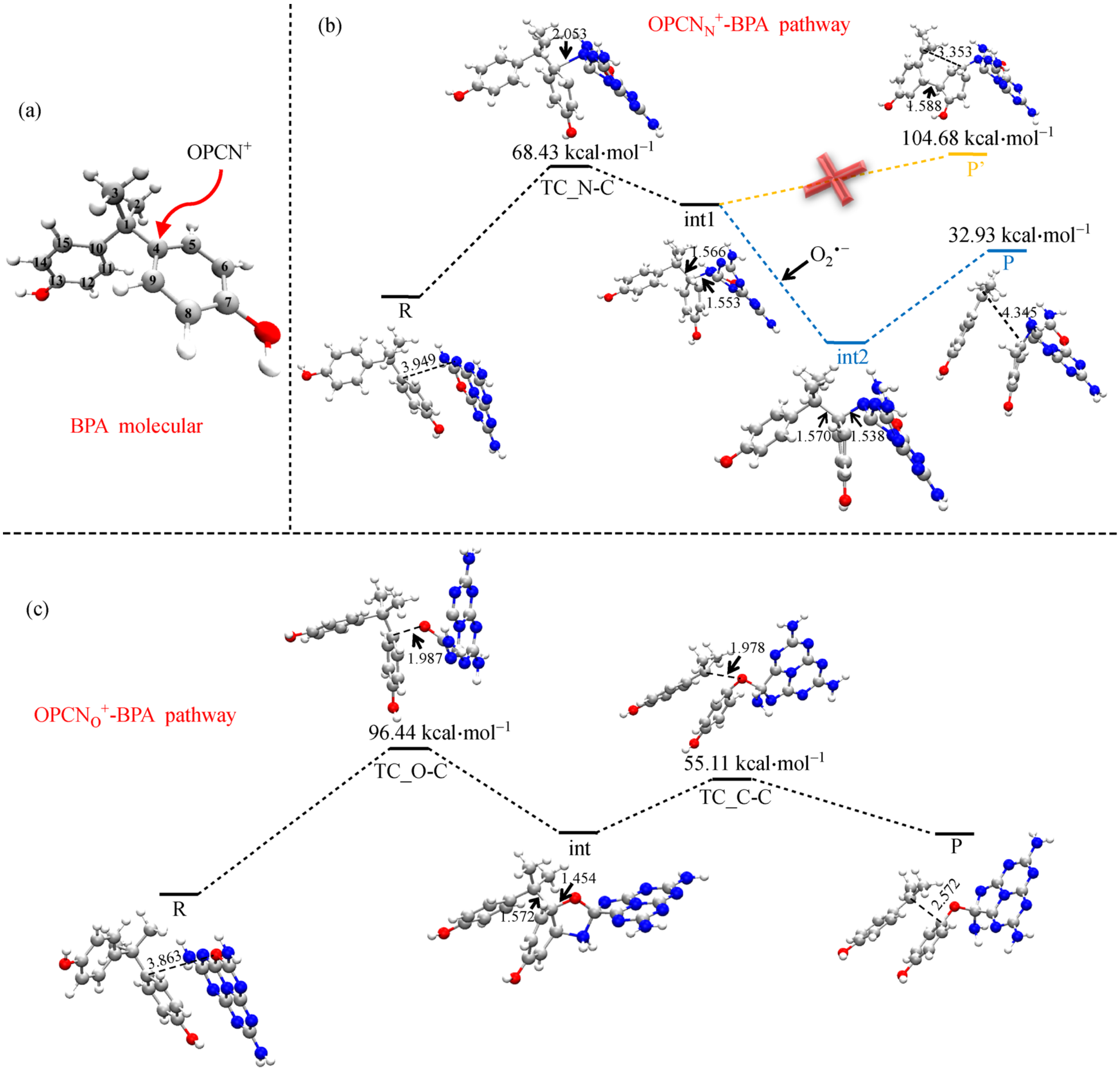

Fig. 4 (a) The active sites of BPA for OPCN attacks. DFT calculated structures of reactants, intermediates and transition state for the degradation of BPA attacked by OPCN catalysts with (b) N atoms or (c) doped O atoms as reactive sites (white, red, gray and blue balls represented H, O, C and N elements, respectively) [29] (reprinted with permission from Elsevier).

microscopy, Fourier transformed infrared spectra, Raman, electron spin resonance (ESR) etc. are also useful methods to characterize the materials and helpful to understand the interaction mechanism. These techniques can be easily found in many published papers, and thereby are not described herein.

6 Conclusions and perspectives

In this paper, the sorption-reduction/solidification of metal ions and adsorption-photocatalytic degradation of organic pollutants by several kinds of manmade nanomaterials are reviewed. The high specific surface area, the abundant functional groups, large amounts of active sites and infects are the advantages of nanomaterials for the high sorption of organic/inorganic pollutants and photocatalytic degradation of organic pollutants. However, the low selectivity, the difficult separation from solutions and aggregation restricted the application of nanomaterials in the preconcentration of metal ions or organic chemicals from solution to solid particles. The poor visible light absorption and low separation of electrons and holes also restricted the photocatalytic efficiency of nanomaterials in the degradation of organic pollutants. For the adsorption selectivity of pollutants from complicated systems, the surface modification with special functional groups is a good method to improve the selectivity. For the improvement of photocatalytic efficiency, the doping of metal/non-metal and structure construction of nanomaterials are efficient to improve the visible-light absorption and electrons/holes separation. It is necessary to say that the synthesis of nanomaterial is still limited in laboratory at high price, which limit their real application in environmental pollution cleanup. With the development of technique, it is possible to synthesize the novel nanomaterials at low price in large scale. This is important for the application of the nanomaterials in environmental pollution management.

As mentioned above, the high price is one important key parameter which restricts the real applications of nanomaterials. Also the aggregation of nanomaterials will decrease their active sites for the binding of pollutants and thereby reduces the sorption capacity of nanomaterials. Some kinds of natural materials such as bentonite, attapulgite, metal oxides have pore structures and strong active sites, which could form composites with nanomaterials. The natural materials also have high sorption capacities and thereby increase the sorption or photocatalytic degradation ability of nanomaterials. Such method could disperse the nanoparticles on natural materials homogeneously and thereby avoids the aggregation of nanomaterials. Such method not only decreases the amounts of nanomaterials used in pollution cleanup, but also stabilizes the nanomaterials on natural materials. In future, the natural-manmade material composites will broaden the application of nanomaterials in environmental pollution management.

In the application of nanomaterials, the nanotoxicity should be considered when applied in pollution management. Although some studies showed the lack of adverse health effect, long-term investigation is necessary to understand the full impact. The separation of nanomaterials from aqueous solutions and their reusability should also be considered when they are applied in real applications.

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References

1. Yao T, Cui T, Wu J, Chen Q, Lu S, Sun K. Preparation of hierarchical porous polypyrrole nanoclusters and their application for removal of Cr(VI) ions in aqueous solution. Polymer Chemistry, 2011, 2(12): 2893–2899
2. Wang X X, Li X, Wang J Q, Zhu H T. Recent advances in carbon nitride-based nanomaterials for the removal of heavy metal ions from aqueous solution. Journal of Inorganic Materials, 2020, 35(3): 260–270
3. Khan A, Wang J, Wang X, Li J, Chen Z, Alsaedi A, Hayat T, Chen Y, Wang X. The role of graphene oxide and graphene oxide-based nanomaterials in the removal of pharmaceuticals from aqueous media: A review. Environmental Science and Pollution Research International, 2017, 24(9): 7938–7958
4. Wang X, Chen L, Wang L, Fan Q, Pan D, Li J, Chi F, Yu S, Xie Y, Xiao C, et al. Synthesis of novel nanomaterials and their application in efficient removal of radionuclides. Science China. Chemistry, 2019, 62(8): 933–967
5. Xu X, Huang Q, Mao Y, Wang X, Wang Y, Hu Q, Wang H, Wang X. Sensors for determination of uranium: A review. Trends in Analytical Chemistry, 2019, 118: 89–111
6. Zhu Y, Bai Z, Wang B, Zhai L, Luo W. Microfluidic synthesis of renewable biosorbent with highly comprehensive adsorption performance for copper(II). Frontiers of Chemical Science and Engineering, 2017, 11(2): 238–251
7. Wang H, Chen Z, Zhang S, Li Q, Wang W, Zhao G, Zhuang L, Hu B, Wang X. Visible-light-driven N_2-g-C_3N_4 as a high stable and efficient photocatalyst for bisphenol A and Cr(VI) removal in binary systems. Catalysis Today, 2019, 335: 110–116
8. Zhang S, Gu P, Ma R, Luo C, Wen T, Zhao G, Cheng W, Wang X. Recent developments in fabrication and structure regulation of visible-light-driven g-C_3N_4-based photocatalysts towards water purification: A critical review. Catalysis Today, 2019, 335: 65–77
9. Pang H, Wu Y, Wang X, Hu B, Wang X. Recent advances in composites of graphene and layered double hydroxides for water remediation: A review. Chemistry, an Asian Journal, 2019, 14(15): 2542–2552
10. Peyravi M. Preparation of adsorptive nanoporous membrane using powder activated carbon: Isotherm and thermodynamic studies. Frontiers of Chemical Science and Engineering, 2019, doi: https://doi.org/10.1007/s11705-019-1800-9

11. Ouni L, Ramazani A, Fardood S T. An overview of carbon nanotubes role in heavy metals removal from wastewater. Frontiers of Chemical Science and Engineering, 2019, 13(2): 274–295
12. Yin L, Hu Y, Ma R, Wen T, Wang X, Hu B, Yu Z, Hayat T, Alsaedi A, Wang X. Smart construction of mesoporous carbon templated hierarchical Mg-Al and Ni-Al layered double hydroxides for remarkably enhanced U(VI) management. Chemical Engineering Journal, 2019, 359: 1550–1562
13. Gu P, Zhao C, Wen T, Ai Y, Zhang S, Chen W, Wang J, Alsaedi A, Hayat T, Wang X, Highly U (VI) immobilization on polyvinyl pyrrolidine intercalated molybdenum disulfide: Experimental and computational studies. Chemical Engineering Journal, 2019, 359: 1563–1572
14. Romanchuk A, Slesarev A, Kalmykov S, Kosynkin D, Tour J. Graphene oxide for effective radionuclide removal. Physical Chemistry Chemical Physics, 2013, 15(7): 2321–2327
15. Pang H, Diao Z, Wang X, Ma Y, Yu S, Zhu H, Chen Z, Hu B, Chen J, Wang X. Adsorptive and reductive removal of U(VI) by *Dictyophora indusiate*-derived biochar supported sulfide NZVI from wastewater. Chemical Engineering Journal, 2019, 366: 368–377
16. Pakulski D, Czepa W, Witomska S, Aliprandi A, Pawluć P, Patroniak V, Ciesielski A, Samorì P. Graphene oxide-branched polyethylenimine foams for efficient removal of toxic cations from water. Journal of Materials Chemistry. A, Materials for Energy and Sustainability, 2018, 6(20): 9384–9390
17. Zhang Z, Dong Z, Wang X, Ying Y, Cao X, Wang Y, Hua R, Feng H, Chen J, Liu Y, et al. Synthesis of ultralight phosphorylated carbon aerogel for efficient removal of U(VI): Batch and fixed-bed column studies. Chemical Engineering Journal, 2019, 370: 1376–1387
18. Liu X, Ma R, Wang X, Ma Y, Yang Y, Zhuang L, Zhang S, Jehan R, Chen J, Wang X. Graphene-based composites for efficient removal of heavy metal ions from aqueous solution: A review. Environmental Pollution, 2019, 252: 62–73
19. Chandra V, Park J, Chun Y, Lee J, Hwang I, Kim K. Water-dispersible magnetite-reduced graphene oxide composites for arsenic removal. ACS Nano, 2010, 4(7): 3979–3986
20. Efome J, Rana D, Matsuura T, Lan C. Insight studies on metal-organic framework nanofibrous membrane adsorption and activation for heavy metal ions removal from aqueous solution. ACS Applied Materials & Interfaces, 2018, 10(22): 18619–18629
21. Yang S, Li Q, Chen L, Chen Z, Pu Z, Wang H, Yu S, Hu B, Chen J, Wang X. Ultrahigh sorption and reduction of Cr(VI) by two novel core-shell Fe_3O_4@MoS_2 and MoS_2@Fe_3O_4 composites. Journal of Hazardous Materials, 2019, 379: 120797
22. Chen W, Lu Z, Xiao B, Gu P, Yao W, Xing J, Asiri A M, Alamry K A, Wang X, Wang S. Enhanced removal of lead ions from aqueous solution by iron oxide nanomaterials with cobalt and nickel doping. Journal of Cleaner Production, 2019, 211: 1250–1258
23. Yin L, Hu B, Zhuang L, Fu D, Li J, Hayat T, Alsaedi A, Wang X. Synthesis of flexible cross-linked cryptomelane-type manganese oxide nanowire membranes and their application for U(VI) and Eu (III) elimination from solutions. Chemical Engineering Journal, 2020, 381: 122744
24. Li J, Wang X, Zhao G, Chen C, Chai Z, Alsaedi A, Hayat T, Wang X. Metal-organic framework-based materials: Superior adsorbents for the capture of toxic and radioactive metal ions. Chemical Society Reviews, 2018, 47(7): 2322–2356
25. Fan L, Luo C, Sun M, Qiu H. Synthesis of graphene oxide decorated with magnetic cyclodextrin for fast chromium removal. Journal of Materials Chemistry, 2012, 22(47): 24577–24583
26. Kassaee M, Motamedi E, Majdi M. Magnetic Fe_3O_4-graphene oxide/polystyrene: Fabrication and characterization of a promising nanocomposite. Chemical Engineering Journal, 2011, 172(1): 540–549
27. Gu P, Zhang S, Zhang C, Wang X, Khan A, Wen W, Hu B, Alsaedi A, Hayat T, Wang X. Two-dimensional MAX-derived titanate nanostructures for efficient removal of Pb(II). Dalton Transactions (Cambridge, England), 2019, 48(6): 2100–2107
28. Wang J, Ai Y, Gu P, Wang X, Li Q, Yu S, Chen Y, Yu Z, Wang X. Efficient elimination of Cr(VI) from aqueous solutions using sodium dodecyl sulfate intercalated molybdenum disulfide. Ecotoxicology and Environmental Safety, 2019, 175: 251–262
29. Zhang S, Liu Y, Gu P, Ma R, Wen T, Zhao G, Li L, Ai Y, Hu C, Wang X. Enhanced photodegradation of toxic organic pollutants using dual-oxygen-doped porous g-C_3N_4: Mechanism exploration from both experimental and DFT studies. Applied Catalysis B: Environmental, 2019, 248: 1–10
30. Pan B, Xing B S. Adsorption mechanisms of organic chemicals on carbon nanotubes. Environmental Science & Technology, 2008, 42(24): 9005–9013
31. Rao G P, Lu C, Su F. Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review. Separation and Purification Technology, 2007, 58(1): 224–231
32. Zhao G, Jiang L, He Y, Li J, Dong H, Wang X, Hu W. Sulfonated graphene for persistent aromatic pollutant management. Advanced Materials, 2011, 23(34): 3959–3963
33. Zhao G, Li J, Ren X, Chen C, Wang X. Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management. Environmental Science & Technology, 2011, 45(24): 10454–10462
34. Wang W, Wang X, Xing J, Gong Q, Wang H, Che Z, Ai Y, Wang X. Multi-heteroatom doped graphene-like carbon nanospheres with 3D inverse opal structure: A promising bisphenol-A remediation material. Environmental Science. Nano, 2019, 6(3): 809–819
35. Ai Y, Liu Y, Huo Y, Zhao C, Sun L, Han B, Bao X, Wang X. Insights into the adsorption mechanism and dynamic behavior of tetracycline antibiotics on reduced graphene oxide (RGO) and graphene oxide (GO) materials. Environmental Science. Nano, 2019, 6(11): 3336–3348
36. Wei D, Zhao C, Khan A, Sun L, Ji Y, Ai Y, Wang X. Sorption mechanism and dynamic behavior of graphene oxide as an effective adsorbent for the removal of chlorophenol based environmental-hormonies: A DFT and MD simulation study. Chemical Engineering Journal, 2019, 370: 121964
37. Wang J, Chen Z, Chen B. Adsorption of polycyclic aromatic hydrocarbons by graphene and graphene oxide nanosheets. Environmental Science & Technology, 2014, 48(9): 4817–4825
38. Wang X, Yu S, Jin J, Wang H, Alharbi N S, Alsaedi A, Hayat T, Wang X. Application of graphene oxides and graphene oxide-based nanomaterials in radionuclide removal from aqueous solutions.

Science Bulletin, 2016, 61(20): 1583–1593

39. Wang L, Yuan L, Chen K, Zhang Y, Deng Q, Du Y, Huang Q, Zheng L, Zhang J, Chai Z, Barsoum M W, Wang X, Shi W. Loading actinides in multi-layered structures for nuclear waste treatment: The first case study of uranium capture with vanadium carbide MXene. ACS Applied Materials & Interfaces, 2016, 8(25): 16396–16403
40. Wang L, Song H, Yuan L, Li Z, Zhang P, Gibson J, Zheng L, Wang H, Chai Z, Shi W. Effective removal of anionic Re(VII) by surface-modified Ti_2CT_x MXene nanocomposites: Implications for Tc(II) sequestration. Environmental Science & Technology, 2019, 53(7): 3739–3747
41. Li S, Wang L, Peng J, Zhai M, Shi W. Efficient thorium(IV) removal by two-dimensional Ti_2CT_x MXene from aqueous solution. Chemical Engineering Journal, 2019, 366: 192–199
42. Du Y, Wei L, Wang Y, Zhang X, Ye S. Efficient removal of Pb(II) by $Ti_3C_2T_x$ powder modified with a silane coupling agent. Journal of Materials Science, 2019, 54(20): 13283–13297
43. Liu X, Chen G R, Lee D J, Kawamoto T, Tanaka H, Chen M L, Luo Y K. Adsorption removal of cesium from drinking waters: A mini review on use of biosorbents and other adsorbents. Bioresource Technology, 2014, 160: 142–149
44. Aguila B, Banerjee D, Nie Z, Shin Y, Ma S, Thallapally P K. Selective removal of cesium and strontium using porous frameworks from high level nuclear waste. Chemical Communications (Cambridge), 2016, 52(35): 5940–5942
45. Sheng D, Zhu L, Xu C, Xiao C, Wang Y, Wang Y, Chen L, Diwu J, Chen J, Chai Z, Albrecht-Schmitt T E, Wang S. Efficient and selective uptake of TcO_4^- by a cationic metal-organic framework material with open Ag^+ sites. Environmental Science & Technology, 2017, 51(6): 3471–3479
46. Zhu L, Sheng D, Xu C, Dai X, Silver M A, Li J, Li P, Wang Y, Wang Y, Chen L, et al. Identifying the recognition site for selective trapping of Tc-99 in a hydrolytically stable and radiation resistant cationic metal-organic framework. Journal of the American Chemical Society, 2017, 139(42): 14873–14876
47. Zhu L, Xiao C, Dai X, Li J, Gui D, Sheng D, Chen L, Zhou R, Chai Z, Albrecht-Schmitt T E, Wang S. Exceptional perrhenate/pertechnetate uptake and subsequent immobilization by a low-dimensional cationic coordination polymer: Overcoming the Hofmeister bias selectivity. Environmental Science & Technology Letters, 2017, 4(7): 316–322
48. Li Y, Yang Z, Wang Y, Bai Z, Zheng T, Dai X, Liu S, Gui D, Liu W, Chen M, et al. A mesoporous cationic thorium-organic framework that rapidly traps anionic persistent organic pollutants. Nature Communications, 2017, 8(1): 1354
49. Wang Y, Liu W, Bai Z, Zheng T, Silver M A, Li Y, Wang Y, Wang X, Diwu J, Chai Z, Wang S. Employing an unsaturated Th^{4+} site in a porous thorium-organic framework for Kr/Xe uptake and separation. Angewandte Chemie International Edition, 2018, 57(20): 5783–5787
50. Lv Z, Fan Q, Xie Y, Chen Z, Alsaedi A, Hayat T, Wang X, Chen C. MOFs-derived magnetic chestnut shell-like hollow sphere NiO/Ni@C composites and their removal performance for arsenic(V). Chemical Engineering Journal, 2019, 362: 413–421
51. Wang N C, Wang J, Zhang P, Wang W B, Sun C C, Xiao L, Chen C, Zhao B, Kong Q R, Zhu B K. Metal cation removal by P(VC-r-AA) copolymer ultrafiltration membranes. Frontiers of Chemical Science and Engineering, 2018, 12(2): 262–272
52. Efome J E, Rana D, Matsuura T, Lan C Q. Effects of operating parameters and coexisting ions on the efficiency of heavy metal ions removal by nano-fibrous metal-organic framework membrane filtration process. Science of the Total Environment, 2019, 674: 355–362
53. Efome J E, Rana D, Matsuura T, Lan C Q. Experiment and modeling ofr flus and permeate concentration of heavy metal ion in adsorptive membrane filtration using a metal-organic framework incorporate nanofibrous membrane. Chemical Engineering Journal, 2018, 352: 737–744
54. Zhong X, Liang W, Hu B. Highly efficient enrichment mechanism of U(VI) and Eu(III) by covalent organic frameworks with intramolecular hydrogen-bonding from solutions. Applied Surface Science, 2020, 504: 144403
55. Bai C, Li J, Liu S, Yang X, Yang X, Tian Y, Cao K, Huang Y, Ma L, Li S. *In situ* preparation of nitrogen-rich and functional ultra-microporous carbonaceous COFs by “segregated” microwave irradiation. Microporous and Mesoporous Materials, 2014, 197: 148–155
56. Zhang M, Li Y, Bai C, Guo X, Han J, Hu S, Jiang H, Tan W, Li S, Ma L. Synthesis of microporous covalent phosphazene-based frameworks for selective separation of uranium in highly acidic media based on size-matching effect. ACS Applied Materials & Interfaces, 2018, 10(34): 28936–28947
57. Li B, Sun Q, Zhang Y, Abney C W, Aguila B, Lin W, Ma S. Functionalized porous aromatic framework for efficient uranium adsorption from aqueous solutions. ACS Applied Materials & Interfaces, 2017, 9(14): 12511–12517
58. Wei D, Li J, Chen Z, Liang J, Ma J, Wei M, Ai Y, Wang X. Understanding bisphenol-A adsorption in magnetic modified covalent organic frameworks: Experiments coupled with DFT calculations. Journal of Molecular Liquids, 2020, 301: 112431
59. Xu J, Xu X, Zhao H, Luo G. Microfluidic preparation of chitosan microspheres with enhanced adsorption performance of copper(II). Sensors and Actuators. B, Chemical, 2013, 183: 201–210
60. Wang B, Zhu Y, Bai Z, Luque R, Xuan J. Functionalized chitosan biosorbents with ultra-high performance, mechanical strength and tunable selectivity for heavy metals in wastewater treatment. Chemical Engineering Journal, 2017, 325: 350–359
61. Ngah W S W, Teong L C, Hanafiah M A K M. Adsorption of dyes and heavy metal ions by chitosan composites: A review. Carbohydrate Polymers, 2011, 83(4): 1446–1456
62. Wang L, Song H, Yuan L, Li Z, Zhang Y, Gibson J, Zheng L, Chai Z, Shi W. Efficient U(VI) reduction and sequestration by Ti_2CT_x MXene. Environmental Science & Technology, 2018, 52(18): 10748–10756
63. Wang H, Guo H, Zhang N, Chen Z, Hu B, Wang X. Enhanced Photoreduction of U(VI) on C_3N_4 by Cr(VI) and Bisphenol A: ESR, XPS and EXAFS investigation. Environmental Science & Technology, 2019, 53(11): 6454–6461
64. Yu S, Wang S, Liu Y, Chen Z, Wu Y, Liu Y, Pang H, Song G, Chen J, Wang X. Efficient removal of uranium(VI) by layered double hydroxides supported nanoscale zero-valent iron: A combined experimental and spectroscopic studies. Chemical Engineering

Journal, 2019, 365: 51–59

65. Zhu F, Li L, Ren W, Deng X, Liu T. Effect of pH, temperature, humic acid and coexisting anions on reduction of Cr(VI) in the soil leachate by nZVI/Ni bimetal material. Environmental Pollution, 2017, 227: 444–450
66. Yang S Y, Li Q, Chen Z S, Hu B W, Wang H H, Wang X K. Synergistic removal and reduction of U(VI) and Cr(VI) by Fe_3S_4 micro-crystal. Chemical Engineering Journal, 2020, 385: 123909
67. Sheng G, Alsaedi A, Shammakh W, Monaquel S, Sheng J, Wang X, Li H, Huang Y. Enhanced sequestration of selenite in water by nanoscale zero valent iron immobilization on carbon nanotubes by a combined batch, XPS and XAFS investigation. Carbon, 2016, 99: 123–130
68. Pang H, Wu Y, Huang S, Li S, Wang X, Yu S, Chen Z, Song G, Ding C, Wang X. Macroscopic and microscopic investigation of uranium elimination by Ca-Mg-Al-layered double hydroxide supported nanoscale zero valent iron. Inorganic Chemistry Frontiers, 2018, 5(10): 2657–2665
69. Wang J Q, Pang H W, Tang H, Yu S J, Zhu H T, Wang X X. Recent advances in carbon nitride-based nanomaterials for the removal of heavy metal ions and radionuclides from aqueous solution. Journal of Inorganic Materials, 2020, 35(3): 373–380
70. Shu H, Chang M, Chen C, Chen P. Using resin supported nano zero-valent iron particles for decoloration of acid blue 113 azo dye solution. Journal of Hazardous Materials, 2010, 184(1–3): 499–505
71. Li J H, Yang L X, Li J Q, Yin W H, Tao Y, Wu H Q, Luo F. Anchoring nZVI on metal organic framework for removal of uranium(VI) from aqueous solution. Journal of Solid State Chemistry, 2019, 269: 16–23
72. Guo Z, Zhou J, Zhu L, Sun Z. MXene: A promising photocatalyst for water splitting. Journal of Materials Chemistry. A, Materials for Energy and Sustainability, 2016, 4(29): 11446–11452
73. Iqbal M A, Tariq A, Zaheer A, Gul S, Ali S I, Iqbal M Z, Akinwande D, Rizwan S. Ti_3C_2-MXene/Bismuth ferrite nanohybrids for efficient degradation of organic dyes and colorless pollutants. ACS Omega, 2019, 4(24): 20530–20539
74. Yuan X, Zhou C, Jing Q, Tang Q, Mu Y, Du A K. Facile synthesis of g-C_3N_4 nanosheets/ZnO nanocomposites with enhanced photocatalytic activity in reduction of aqueous chromium(VI) under visible light. Nanomaterials (Basel, Switzerland), 2016, 6(9): 173–185
75. Raziq F, Qu Y, Humayun M, Zada A, Yu H, Jing L. Synthesis of SnO_2/B-P codoped g-C_3N_4 nanocomposites as efficient cocatalyst-free visible-light photocatalysts for CO_2 conversion and pollutant degradation. Applied Catalysis B: Environmental, 2017, 201: 486–494
76. Wang Y, Wang H, Chen F, Cao F, Zhao X, Meng S, Cui Y. Facile synthesis of oxygen doped carbon nitride hollow microsphere for photocatalysis. Applied Catalysis B: Environmental, 2017, 206: 417–425
77. Dutta D P, Dagar D. Efficient selective sorption of cationic organic pollutant from water and its photocatalytic degradation by $AlVO_4$/g-C_3N_4 nanocomposite. Journal of Nanoscience and Nanotechnology, 2020, 20(4): 2179–2194
78. Du X Y, Bai X, Xu L, Yang L, Jin P K. Visible-light activation of persulfate by TiO_2/g-C_3N_4 photocatalyst toward efficient degradation of micropollutants. Chemical Engineering Journal, 2020, 384: 123245
79. Nguyen T B, Huang C P, Doong R A, Chen C W, Dong C D. Visible-light photodegradation of sulfamethoxazole (SMX) over Ag-P-codoped g-C_3N_4 (Ag-P@UCN) photocatalyst in water. Chemical Engineering Journal, 2020, 384: 123383
80. Sridharan K, Jang E, Park T J. Novel visible light active graphitic C_3N_4-TiO_2 composite photocatalyst: Synergistic synthesis, growth and photocatalytic treatment of hazardous pollutants. Applied Catalysis B: Environmental, 2013, 142-143: 718–728
81. Wang H, Chen Z, Zhang S, Li Q, Wang W, Zhao G, Zhuang L, Hu B, Wang X. Visible-light-driven N_2-g-C_3N_4 as a high stable and efficient photocatalyst for bisphenol A and Cr(VI) removal in binary systems. Catalysis Today, 2019, 335: 110–116
82. Zhang S, Song S, Gu P, Ma R, Wei D, Zhao G, Wen T, Jehan R, Hu B, Wang X. Visible-light-driven activation of persulfate over cyano and hydroxyl groups co-modified mesoporous g-C_3N_4 for boosting bisphenol A degradation. Journal of Materials Chemistry. A, Materials for Energy and Sustainability, 2019, 7(10): 5552–5560
83. Wang L, Tao W Q, Yuan L Y, Liu Z R, Huang Q, Chai Z F, Gibson J K, Shi W Q. Rational control of the interlayer space inside two-dimensional titanium carbides for highly efficient uranium removal and imprisonment. Chemical Communications (Cambridge), 2017, 53(89): 12084–12087
84. Fan M, Wang L, Pei C X, Shi W Q. Alkalization intercalation of MXene for electrochemical detection of uranyl ion. Journal of Inorganic Materials, 2019, 34(1): 85–90
85. Zhao C F, Jin J R, Huo Y Z, Sun L, Ai Y J. Adsorpiton of phenolic organic pollutants on graphene oxide: A Molecular dynamics study. Journal of Inorganic Materials, 2020, 35(3): 277–283