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Applications of graphene-based materials in environmental protection and detection

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Many efficient adsorbents and sensors based on graphene and functionalized graphene have been constructed for the removal and detection of environmental pollutants due to its unique physicochemical properties. In this article, recent research achievements are reviewed on the application of graphene-based materials in the environmental protection and detection. For environmental protection, modified graphene can adsorb heavy metal ions in a high efficiency and selectivity, and thus reduces them to metals for recycling. High adsorption capacity of graphene-based materials to kinds of organic pollutants in water was also presented. Several graphene-based sensors with high limit of detection were reported to detect heavy metal ions, toxic gases and organic pollutants in environment. Finally, a perspective on the future challenge of adsorbents and detection devices based on graphene is given.

graphene, environmental protection and detection, adsorbent, sensor

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Environmental pollution especially toxic gases, heavy metal ions and organic pollutants in air and water, caused by industry and agricultural activities, severely threaten ecological balance and human health, and have received extensive attention worldwide. For example, the heavy metal ions in bodies accumulated from the food chains will cause various chronic diseases. Therefore, it is necessary to develop simple, sensitive and inexpensive methods to remove and detect these pollutants. Currently, many efficient adsorbents and sensitive detection devices based on nanomaterials especially graphene have been designed due to their unique chemical, thermal, electronic, and mechanical properties.

Graphene, a two-dimensional (2D) one atom thick nanomaterial consisting of sp^2-hybridized carbon, has attracted great interest among scientists due to its unique properties, including high specific surface area (SSA) of 2600 $m^2 g^{-1}$ [1], excellent thermal conductivities of 5000 W m^{-1} K^{-1} [2], high-speed electron mobility of 200000 $cm^2 V^{-1} s^{-1}$ at room temperature [3], high stiffness and strength with Young's modulus of around 1000 GPa and break strength of 130 GPa [4], extraordinary electrocatalytic activity [5] and optical properties [6]. These outstanding physicochemical properties indicate its potential application in many research fields. For example, considering the high surface area and strong adsorption capacity of graphene, many efficient adsorbents [7] and photocatalysts [8] are developed for the removal and photocatalytic degradation of pollutants. Moreover, based on the excellent electrical conductivity and optical properties of graphene, many sensitive electrochemical [9] and fluorescent [10] sensors are also designed for the detection of pollutants. However, aggregations of graphene decrease its available surface area and further reduce its adsorption capacity. Functionalization of graphene with molecules, which have water-solubility and affinity toward target analytes, will improve the selectivity of adsorbents or detection devices, as well as prevent the aggregation. Based on this

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idea, diverse derivatives of graphene have been reported and applied to environmental protection and detection.

Herein, we review recent research achievements based on graphene and its derivatives for environmental protection and detection. Meanwhile, according to the categories of environment pollutants, such as toxic gases, heavy metal ions and organic pollutants, we describe several selected examples to introduce the application of graphene in the removal and detection of these pollutants.

1 Functionalized graphene for environmental protection

1.1 Adsorption and reduction for heavy metal ions

Heavy metal ions, such as lead (Pb^{2+}), cadmium (Cd^{2+}), chromium (Cr^{3+}, Cr^{6+}), mercury (Hg^{2+}), copper (Cu^{2+}) and arsenic (As^{3+}), have severe risks to environment and human health, and need to be removed from soil and water. Graphene and its derivatives with high surface areas and many functional groups, which benefit to the adsorption or preconcentration of heavy metal ions, are given great attention in the present researches.

Graphene oxide (GO) and reduced graphene oxide (RGO) with many functional groups such as –O–, –OH, and –COOH, which can form complexes with metal ions, are used to remove heavy metal ions. Zheng et al. [11] reported low-temperature exfoliated graphene nanosheets (GNS), which could be used to adsorb Pb^{2+} from aqueous system. The morphology and SSA did not show apparent differences although the adsorption capacity against Pb^{2+} is enhanced obviously after heat treatment, and the enhanced adsorption capacity was ascribed to the increase in the Lewis basicity and electrostatic attraction of graphene. Recently, RGO obtained by a modified Hummers' method has an adsorption capacity of 8.06×10^{-3} g g^{-1} for antimony (III) Sb^{3+} [12]. In order to overcome the hydrophobicity of graphene, which limits the capacity of removing heavy metal ions in wastewater to some extent, a stable and water-dispersible GNS was prepared by a one-step route [13]. In that method, Tea polyphenols was used as a simultaneous reductant and functionalization reagent, and the obtained tea polyphenols-graphene showed superior adsorption efficiency and selectivity for Pb^{2+} in aqueous solution. Compared with graphene, GO with more oxygen-containing groups display a higher adsorption capacity. Mi et al. [14] prepared a GO aerogel with highly oriented porous structure from GO nanosheets by a unidirectional freeze-drying method. The obtained aerogel can act as a good adsorbent of Cu^{2+} in aqueous solutions with fast adsorption rate, which attributed

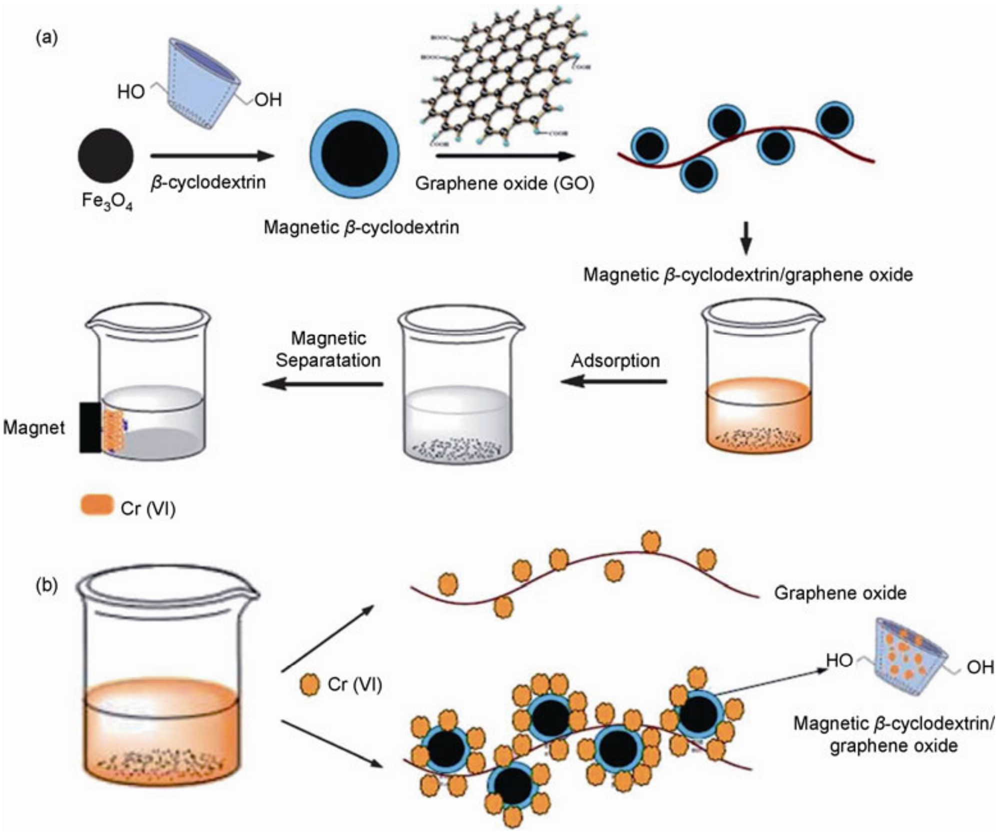

Figure 1 (Color online) (a) The synthesis and application for removing Cr^{6+} of MCGNs. (b) the comparison of adsorption mechanisms on GO and MCGN. Reprinted from ref. [25] with permission from the Royal Society of Chemistry.

to its interconnected pore structure being conducive to the diffusion of Cu^{2+}. According to Zhao's group [15], few-layered GO nanosheets had also a higher adsorption capacity for Cd^{2+} (0.106 g g^{-1}) and Co^{2+} (0.068 g g^{-1}), and it also can be an adsorbent of Uranium (VI) (0.299 g g^{-1}) [16].

Graphene functionalized with metal oxides, such as Fe_3O_4 [17,18], MnO_2 [19,20], Al_2O_3 [21], TiO_2 [22], ZnO [23,24], has also attracted great interest in scientists for the reduction and removal of heavy metal ions. Among these metal oxides, Iron-oxides especially Fe_3O_4 nanoparticles have been investigated widely due to the magnetism in favor of separation. Fan et al. [25] fabricated a magnetic β-cyclodextrin/GO nanocomposite (MCGN) with a large saturation magnetization of 50.13 emu g^{-1} by the amidation of the carboxyl group of GO with the amine group of magnetic NH_2-β-cyclodextrin, which combined the unique properties of magnetic cyclodextrin (e.g. super-paramagnetism, high adsorption capability and strong acid-resistance) and GO (e.g. large surface area and good mechanical properties). This MCGN displayed fast removal of Cr (VI) in wastewater with a high adsorption capability of 0.12 g g^{-1}, and can be reused by treating the Cr (VI)-adsorbed MCGN with NaOH solution. The synthesis and application for the removal and adsorption mechanism of Cr (VI) are shown in Figure 1(a) and (b). In their later experiment, they synthesized water-dispersible magnetic chitosan/GO composites with the similar method [26], and it can be used as a sorbent of Pb (II) with a maximum adsorption capacity of 0.077 g g^{-1} from large volumes of aqueous solutions. For comparison, a method of simultaneous removal of Cr (VI) and Pb (II) with higher adsorption capacities was reported by Cong et al. [27]. They investigated a facile one-step synthesis of three-dimensional (3D) macroscopic graphene/iron oxide hydrogels. The formation mechanism was based on the synergistic effect of the self-assembly of GO sheets and *in situ* simultaneous deposition of metal oxide nanoparticles, such as α-FeOOH nanorods and magnetic Fe_3O_4 nanoparticles on GNS, which were produced by reduction of ferrous under mild conditions (Figure 2(a)). The adsorption behavior of graphene/α-FeOOH hydrogel for Cr (VI) or Pb (II) was investigated (Figure 2(b)), and the maximum adsorption capacities for Cr (VI) and Pb (II) were 0.139 and 0.374 g g^{-1}, respectively, which indicated it could be an ideal adsorbent in industrial water purification. More importantly, other 3D macroscopic graphene/metal oxide hydrogels such as graphene/Mn_2O_3, graphene/CeO_2 could be synthesized in the same way. For the removal of As (III) and As (V), Chandra et al. [28] synthesized water-dispersible magnetite-RGO hybrids via chemical precipitation of Fe^{3+} and Fe^{2+} in the solution of GO, and it showed near completely (over 99.9%) removal of As within 1×10^{-6} g L^{-1}. Compared with it, Bhunia et al. [29] prepared a porous iron-iron oxide matrix dispersed on RGO, which had a higher surface area and adsorption capacity for As (III)(0.044 g g^{-1}).

Photocatalytic degradation, as an effective method, is also applied to the removal of heavy metal ions widely, especially for Cr (VI). Traditional photocatalysts such as TiO_2 and ZnO combined with graphene possess a higher catalytic activity for degradation of Cr^{6+} than pure TiO_2 and ZnO. Jiang et al. [30] synthesized two-dimensional (2D) porous graphene/TiO_2 composites by in situ depositing TiO_2 nanoparticles on GO and calcining at 200°C. The obtained TiO_2-RGO exhibited 5.4 times higher photo-reductive conversion rate than that of P25 for Cr (VI). Meanwhile, ZnO-RGO had a maximum removal rate of 96% under UV light irradiation for Cr (VI) compared with pure ZnO (67%) [23].

In addition, graphene modified with some polymer and organic molecules demonstrates good adsorption to heavy metal ions. For example, polypyrrole-RGO composite can adsorb Hg^{2+} selectively, with the adsorption capacity of 0.98 g g^{-1} [31]. Ethylene diamine tetraacetic acid-GO can remove Pb^{2+} with an adsorption capacity of 0.479 g g^{-1} [32]. Cr (VI) can be also reduced and removed by ethylenediamine-RGO [33].

1.2 Adsorption for organic pollutants

Organic pollutants in wastewater, especially for oils and organic solvents, dyes, phenolic comopunds and pesticides, need to be removed timely because of their severe risks. At present, many methods based on graphene have been presented and will be applied to environmental protection gradually.

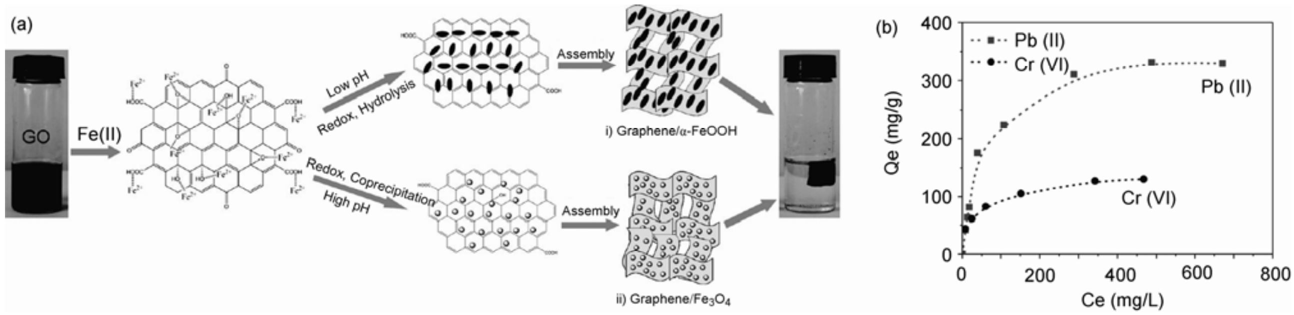

Figure 2 (a) The formation mechanism of graphene/iron oxide hydrogel; (b) the adsorption isotherms of Cr^{6+} and Pb^{2+} on graphene/FeOOH hydrogel at room temperature. Reprinted from ref. [27] with permission from the American chemical Society.

Compared with 2D graphene sheets, 3D graphene sponges or foams have attracted extensive attention due to the high porosity for the practical application of being a high-efficient adsorbent. For example, Sun et al. [34] made ultra-flyweight and multifunctional carbon aerogels by freeze-drying aqueous solution of CNTs and giant graphene oxide sheets, it could be obtained for the desired densities and shapes such as rods, cylinder, and papers (Figure 3(a) and (b)). More importantly, it exhibited super-high adsorption capacity and ultra-fast adsorption rate for oil and organic solvents. Wang et al. [35] fabricated a 3D architectures of graphene, based on the chemical reduction of GO with the assist of natural phenolic acids (gallic acid GA) and *in situ* self-assembly of graphene sheets through π-π interactions. The obtained 3D graphene exhibited super hydrophobicity, low density (10000–20000 g m^{-3}) and high porosity (SSA 100–350 m^2), and was proved to have excellent adsortion capacity and fast adsorption rate towards oils and organic solvents. Their morphology and capacity of adsorption are displayed in Figure 3(c), (d) and (e). Similarly, Zhao et al. [36] prepared spongy graphene (SG) by self-assembly of GO sheets under the assistance of thiourea. This SG had a tunable pore structure, and displayed high adsorption capacity of 129 g g^{-1} to diesel oil, which was mainly related to its SSA of 399 m^2 g^{-1}. Compared with it, a shape-mouldable SG with a higher SSA of 423 m^2 g^{-1} was developed by Bi and co-workers [37]. The acquired SG exhibited highly efficient absorption towards toxic solvents as well as petroleum products and fats, even up to 86 times of its weight. More importantly, it can be reused more than 10 times after removing the adsorbates via heat treatment. It is well known the hydrophobicity can be improved by surface roughness. Based on this idea, superhydrophobic and superoleophilic 3D graphene-carbon nanotubes hybrids were synthesised by Dong's group [38]. It can be employed to remove oils and organic solvents selectively from the surface of water with high adsorption capacity and well recyclability.

Dyes from industries are the major source of water pollution, and many adsorbents based on graphene are reported to removal the pollutants in recent years. For instance, Liu et al. [39] reported that graphene prepared by a modified Hummers' method had the maximum adsorption capacity of 0.153 g g^{-1} to methylene blue. Zhang et al. [40] presented polyethersulfone enwrapped GO, which showed porous structures inside and a dense skin layer, and displayed well-selective adsorbability to cationic dyes such as methylene blue and methyl violet. In order to extract the adsorbents from solution easily and rapidly after adsorbing dyes, Fe_3O_4 is used widely due to its strong superparamagnetism in favor of separation. So far, many composites based on graphene and Fe_3O_4 have been synthesized such as GO-Fe_3O_4 [41], RGO-Fe_3O_4 [42,43], RGO-MFe_2O_4(M=Mn, Zn, Co and Ni) [44] and so on. Xie et al. [41] fabricated GO-Fe_3O_4 hybrids by depositing amino-functionalized Fe_3O_4 on the surface of GO. The hybrids showed the adsorption capacities of 0.167 g g^{-1} for methylene blue and 0.171 g g^{-1} for neutral red, and it can be easily seperated by external magnetic filed after adsorption. Fan et al. [45] synthesized magnetic chitosan/GO (MCGO) composite. The MCGO can be used as a magnetic adsorbent towards methylene blue with higher adsorption capacity (0.18 g g^{-1}), fast adsorption rates, and excellent separation properties. Based on this research, magnetic β-cyclodextrin-chitosan/GO (MCCG) was synthesised in their later research. This adsorbent had good and versatile adsorption capacity to the dyes due to the synergistic effect of the surface property of GO, hydrophobicity of β-cyclodextrin, the abundant amino and hydroxyl functional groups of chitosan and the magnetic property of Fe_3O_4 [46]. More importantly, it can be regenerated easily and rapidly. Liu and co-workers [47] reported that a 3D GO sponge displayed the high adsorption

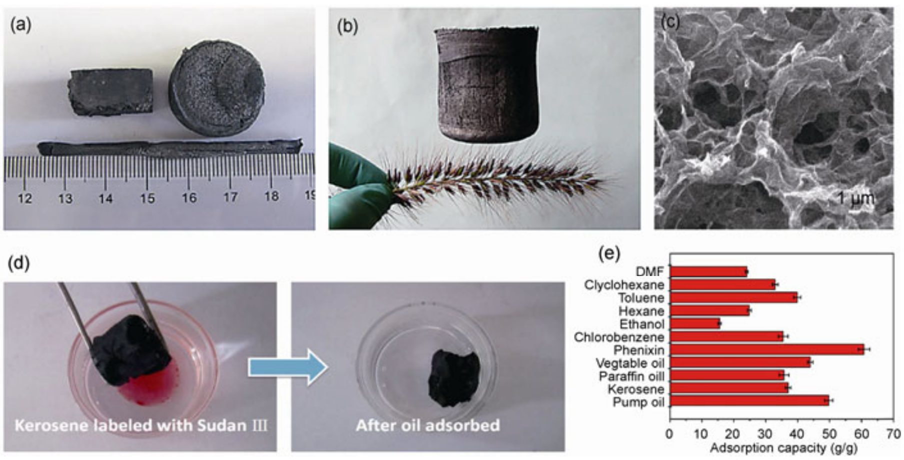

Figure 3 (Color online) (a), (b) Macroscopic structures of ultra-flyweight aerogels with diverse shapes. Reprinted from ref. [34] with permission from the WILEY-VCH Verlag GmbH & Co. kGaA, Weinheim; (c) SEM image; (d) photograph of the kerosene labeled with Sudan III adsorption; (e) adsorption capacities for different oils and organic solvents at saturated state of GaA-GA. Reprinted from ref. [35] with permission from the Royal Society of Chemistry.

capacity of 0.397 g g^{-1} for methylene blue and 0.467 g g^{-1} for methylene violet due to the strong π-π stacking and anion-cation interaction between dyes and 3D GO sponge. For the removal of dyes. another technology used widely is photocatalytic degradation, and many highly efficiency graphene-based photocatalyst such as ZnO/RGO [48–50], CdS/RGO [51,52], TiO_2/RGO [53–55] have been reported. More recently, Khan et al. [56] improved the photocatalytic activity of CdS/ZnO and CdS/Al_2O_3 by combining with GO. The obtained CdS/ZnO/ GO and CdS/Al_2O_3/GO exhibited highly efficient photodegradation toward methyl orange (~99% for CdS/ ZnO/GO while ~90% for CdS/Al_2O_3/GO within 60 min).

In addition, graphene and its derivatives can be applied to the removal of pesticides [57, 58] and phenolic compunds [59,60]. For example, Liu and co-workers [58] presented graphene-coated silica can achieve higher levels of adsorption for eleven organophosphorous pesticides than another five sorbens (graphite carbons, activated carbon, pure graphene, C18 silica, and silica). Graphene can be used as a sorbent of bisphenol A, with the maximum adsorption capacity of 0.182 g g^{-1} [59]. Table 1 shows the preparation and application of different graphene-based materials in the adsorption of metal ions and dyes.

2 Functionalized graphene for environmental detection

2.1 Detection for toxic gases in air

The detection of gas molecules is necessary in many fields especially environmental monitoring due to theirs toxicity and risk. Recently, many gas sensors based on graphene have been devised because of the advantages of graphene such as high electron mobility, large surface-to-volume ratio and low electrical noise, and the sensing mechanism is mainly attributed to the change in the conductance or resistance of graphene caused by the charge transfer between adsorbed gas molecules and graphene sheets.

Wang et al. [61] used partially RGO thin film prepared by thermal treatment (at 500°C in a vacuum) as an active sensing element to develop a hydrogen gas sensor, which exhibited fast response time (~20 s), good sensitivity (~4.5 %) and quick recovery time (~10 s) to 0.16 g g^{-1} of hydrogen gas at room temperature. Based on chemically RGO, Lu et al. [62] fabricated a room temperature gas sensor for detecting low-concentration NO_2 (0.10 g L^{-1}) and NH_3 (1%) in air. Meanwhile, Dua et al. [63] devoloped a chemiresistor to detect chemically aggressive vapors NO_2 and Cl_2 reversibly and selectively. The sensitivity of gas

Table 1 The preparation and application of different graphene-based materials in the adsorption of metal ions and dyes

Graphene-based materials	Analytes	Preparation	References
Graphene nanosheets	Pb^{2+},Cd^{2+},Co^{2+},U^{5+}	Vacuum-promoted low-temperature exfoliation of graphene	[11,15,16]
GO aerogel	Cu^{2+}	Unidirectional freeze-drying of GO suspension	[14]
Magnetic graphene composites	Cu^{2+},Cd^{2+},Pb^{2+}, Co^{2+}	*In situ* coprecipitation of Fe^{3+} and Fe^{2+} in the presence of GO	[17,18,28,29]
Metal oxides/graphene nanosheets	Cu^{2+},Pb^{2+} ,Cr^{6+}	δ-MnO_2 reduction via a microwave-assisted method; UV-assisted photocatalytic reduction of GO by ZnO nanoparticles in ethanol; Fe^{2+} as reducing agent for the reduction of GO; In situ depositing TiO_2 nanoparticles on GO nanosheets	[20,23,25,27,30]
Polypyrrole-reduced GO composite	Hg^{2+}	Reduction by hydrazine hydrate	[31]
Ethylenediaminetetraacetc acid-GO	Pb^{2+}, Cr^{6+}	Silanization reaction of *N*-(trimethoxysilylpropyl) ethylenediamine triacetic acid and GO in ethanol solution	[32,33]
Polyethersulfone/GO	Methylene blue Methyl violet	Liquid-liquid phase separation technique	[39,40]
Fe_3O_4/GO hybrids	Methylene blue Neutral red	Refluxing GO in $SOCl_2$, followed by depositing NH_2-Fe_3O_4 on the surface of GO; One-step solvothermal method	[41,42]
Reduced GO-MFe_2O_4 hybrids	Rhodamine B Methylene blue	One-pot solvothermal method using ethylene glycol as medium with controlled amount of GO, Fe^{3+} and Mn^{2+}, Zn^{2+}, Co^{2+} or Ni^{2+}	[44]
Chitosan/GO composites	Methylene blue	Amidation reaction between GO and magnetic chitosan	[45]
β-cyclodextrin-chitosan/GO	Methylene blue	Mixing and sonicating magnetic β-cyclodextrin-chitosan, GO and glutaraldehyde, followed by stirring the mixture at 65°C	[46]
GO sponge	Methylene blue Methyl violet	Centrifugal vacuum evaporation of GO suspension	[47]
Reduced GO/ZnO nanohybrids	Rhodamine B Methylene blue	Depositing ZnO nanocrystals on reduced GO sheets via microwave-assisted route in diethylene glycol	[48]
Reduced GO/CdS hybrid	Methylene blue	One-step solvothermal method using dimethylsulfoxide as medium with controlled amount of GO and Cd^{2+}	[51,52,56]
Reduced GO-TiO_2 composites	Methyl orange	*In situ* liquid phase depositing TiO_2 on GO, followed by thermal reduction in N_2 atmosphere.	[53]

sensors can be further enhanced by modifying the graphene with catalytic metals such as Pt, Pd and Au, and many platforms of sensing different toxic gases have been reported by this method [64–67]. For instance, Li and co-workers [66] developed a graphene-based device of detecting NO by alternating current dielectrophoresis. This sensor composed of sensing channels of palladium-decorated RGO and the electrodes covered with chemical vapor deposition-grown graphene, and the procedure of fabrication and test is shown in Figure 4(a). Although it had a detection range from 2×10^{-6} to 4.2×10^{-4} g L^{-1} for NO and improved sensitivity and stability, it needed an extremely long recovery time, and was almost irrecoverable. In order to overcome this problem, current annealing was applied to the sensor and a ~1000 s recovery time was obtained at 2×10^{-6} g L^{-1} NO concentration, which is shown in Figure 4(b).

More recently, graphene functionalized with semiconductor metal oxidess, especially TiO_2 [68], SnO_2 [69], ZnO [70], Cu_2O [71,72], and WO_3 [73] spark intense research interest and have been applied to gas-sensing. For example, Mao et al. [69] reported a gas-sensing platform with RGO decorated with tin oxide nanocrystals (RGO-SnO_2), which displayed improved NO_2 but weakened NH_3 sensing compared with the single RGO. An et al. [73] assembled single crystalline WO_3 nanorods on the surface of graphene, and the obtained WO_3/graphene nanocomposites exhibited superor sensitivity and selectivity to NO_2 due to the unique properties of this new material, such as the improved conductivity, specific electron transfer and increased gas adsorption. For the detection of H_2S, Zhou and co-workers [71] designed a sensor using Cu_2O nanocrystals grown on functionalized graphene sheets (Cu_2O/FGS) as a conducting channel. The synthesis of Cu_2O/FGS and the mechanism of sensing H_2S are shown in Figure 4(c) and (d). H_2S can be chemisorbed on the Cu_2O at room temperature when the Cu_2O decorated on the FGS encounters H_2S, which lead to the transfer of electrons from H_2S to Cu_2O and the decrease of hole carrier density causing the increase of resistance. This sensor demonstrated fantastic sensitivity (11%) even at the lower concentration of 5×10^{-6} g L^{-1} (Figure 4(e)), due to the synergistic effect of Cu_2O (higher surface activity) and FGS (greater electron transfer efficiency). In addition, gas sensor based on graphene decorated with polymer have

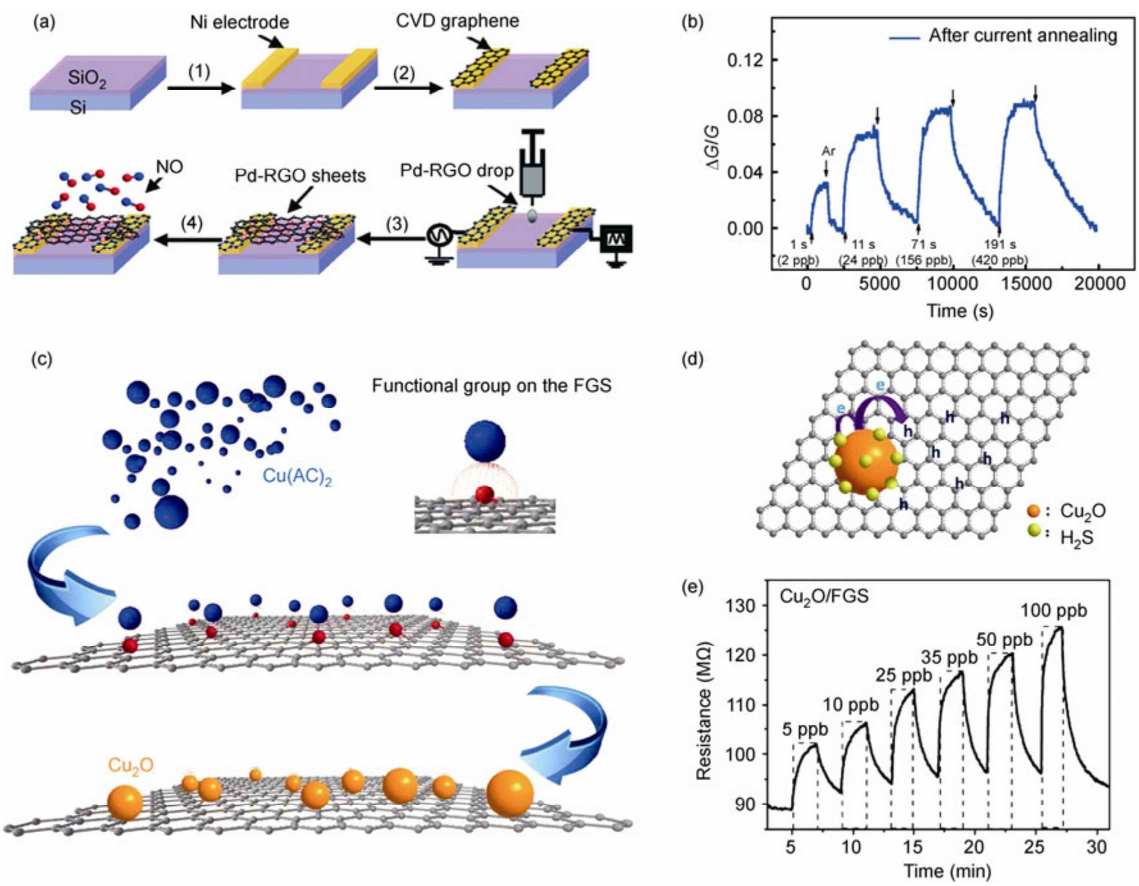

Figure 4 (Color online) (a) Schematics of graphene-Pd-RGO device fabrication and gas sensing test. (b) The response of the sensor to different concentrations of NO. To decrease the recovery time, Ar and current annealing are used. Reprinted from ref. [66] with permission from the American Chemical Society. (c) The schematic illustration of *in situ* synthesis of Cu_2O/FGS. (d) The H_2S sensing mechanism and (e) the dynamic H_2S sensing behaviour of the Cu_2O/FGS-based sensor. Reprinted from ref. [71] with permission from the Elsevier Science Ltd.

been repoted [74,75].

2.2 Detection for heavy metal ions

The maximum contamination level of heavy metal ions in ambience especially in drinking water , are defined clearly by EPA (U.S. Environmental Protection Agency) and WHO (World Health Organization) due to their high toxicity. Therefore, it is urgent to develop highly sensitive and well selective devices for the detection of heavy metal ions. Currently, many platforms based on graphene and its derivatives have been constructed due to the extraordinary optical property and excellent electrical conductivity of graphene.

Fluorescence resonance energy transfer (FRET)-based sensors are explored by a number of research groups, due to the ability of graphene to quench fluorescence. For example, Fu et al. [76] developed a "turn-on" fluorescence sensor based on graphene-gold nanoparticles (AuNPs) to detect Pb^{2+} in aqueous solution，which was attributed to the accelerated leaching rate of AuNPs by adding Pb^{2+}. AuNPs on the surface of graphene would form complexes $Au(S_2O_3)_2^{3-}$ in thiosulfate liquors. Then, the $Au(S_2O_3)_2^{3-}$ was dissolved rapidly to form $Au(2\text{-}ME)_{2-}$ after adding Pb^{2+} and 2-ME, which lead to the rapid leaching of AuNPs from the graphene surfaces (Figure 5(a)). As a result, the fluorescence of graphene quenched by AuNPs would reappear and increase, and the relative fluorescence intensity displayed a good linearity against logarithm concentration of Pb^{2+}, as shown in Figure 5(b). The result revealed that this platform had a higher detection limit of 1.0×10^{-8} mol L^{-1} and more excellent selectivity over common metal ions such as Al^{3+}, Ca^{2+}, Cd^{2+}, K^{+}, Mg^{2+}, Zn^{2+}, Li^{+}, Co^{2+}, Ni^{2+}, Hg^{2+}, Cu^{2+}, Ag^{+}, Mn^{2+}, Cr^{3+}, and Fe^{2+}. It will have a promising application in environmental monitoring. Considering the advantages of the photoluminescence of quantum dots (QDs), such as a high quantum yield, low photobleaching and size-dependent and tunable adsorptions and emissions, Li's group [77] constructed another one "turn-on" fluorescent biosensor based on the energy transfer from CdSe/ZnS QDs to GO. This sensor exhibited a limit of detection as low as 9.0×10^{-11} mol L^{-1} toward Pb^{2+} with excellent selectivity, and it is proved to be applied in river water sample.

Functional nucleic acids have more flexibility as molecular recognition tools, and many fluorescence sensors are designed based on this advantage. Liu et al. [78] presented a

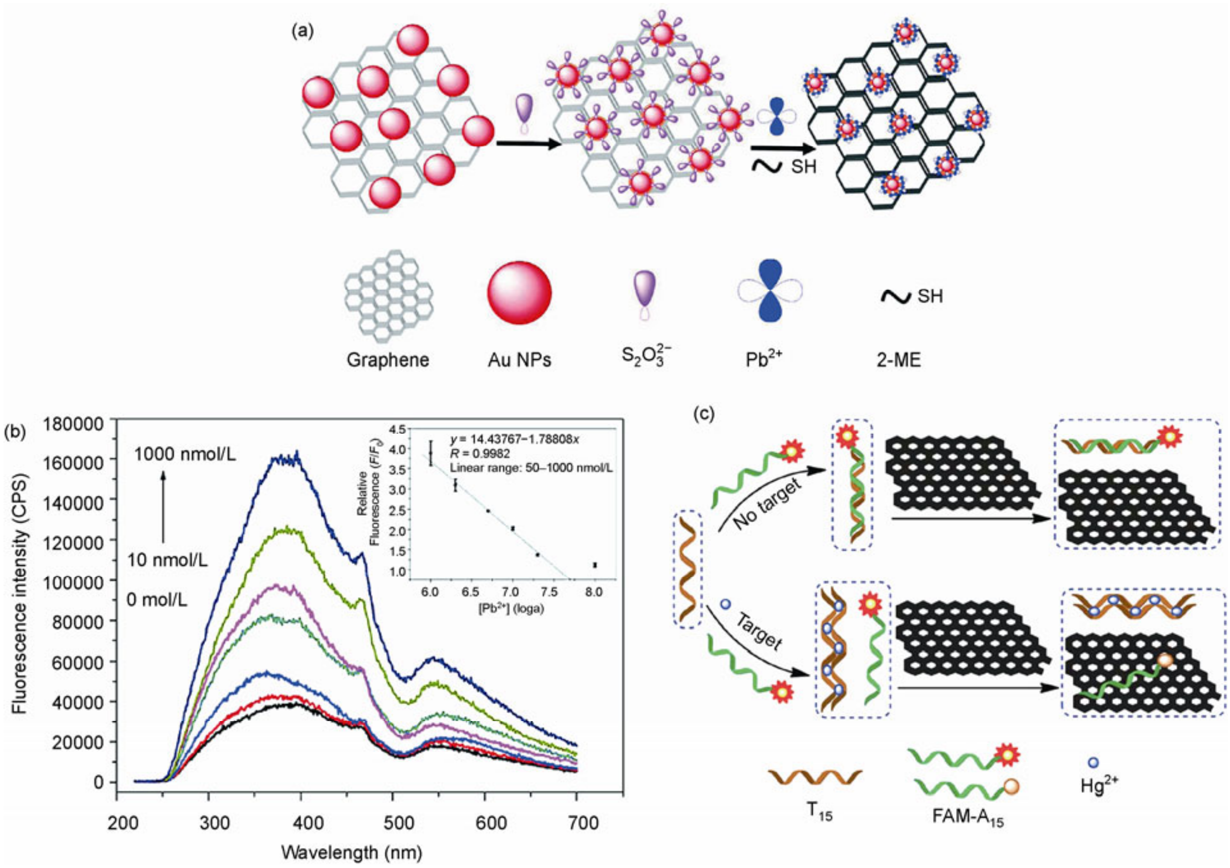

Figure 5 (Color online) (a) The sensing mechanism for Pb^{2+} and (b) the fluorescence spectra of Pb^{2+} ($0–1.0\times10^{-6}$ mol L^{-1}) of G-AuNCs. Reprinted from ref. [76] with permission from the American Chemical Society. (c) The schematic illustrating the fluorescence detection of Hg^{2+} based on DNA duplexes of poly(dT) and GO. Reprinted from ref. [82] with permission from Royal Society of Chemistry.

sensor for the detection of Ag^+. Based on the interactions between the fluorogenic silver-specific cytosine-rich oligonucleotide and GO, Wen et al. [79] designed a fluorescent sensor to detect Ag^+ with a limit of detection of 5.0×10^{-9} mol L^{-1}. In their later research, they used GO and Pb^{2+}-dependent DNAzyme to develop a nanoprobe for fluorescent detection of Pb^{2+} [80]. Meanwhile, A self-assembled DNA-GO-based fluorescent platform was developted to detect Ag^+ and Hg^+ with the lower concentrations of 2.0×10^{-8} and 5.7×10^{-9} mol L^{-1} respectively [81]. More recently, Zhang et al. [82] reported a highly sensitive, selective, and rapid method for fluorescence detection of Hg^{2+} for the first time. It was based on DNA duplexes of poly(dT) and GO, and the mechanism of detecion is shown in Figure 5(c). Withouting Hg^{2+}, the target probe T_{15} would form double-stranded DNA by hybridizing with A_{15} labelled with 6′-carboxy fluorescein (FAM-A_{15}), and the FAM exhibited strong fluorescence. Upon adding Hg^{2+}, FAM-A_{15} wouldl be in a single-stranded state because of the formation of DNA duplexes of poly(dT), and it would result in the fluorescence quenching of FAM by binding GO. Basd on the linearity of the intensity of fluorescence against the concentration of Hg^{2+}, this sensor had a detection limit of 5.0×10^{-10} mol L^{-1}, and could be used in river water samples.

Compared with fluorescence detections, electrochemical methods attract considerable attention for the advantages of fast, portability, high-sensitivity, and low cost in recent years. Among the electrochemical techniques, potentiometry and voltammetry are employed widely.

In potentiometric sensors, filed effect transistor (FET)-based sensors are developed rapidly. For example, Sudibya and co-workers [83] introduced a nanoscale FET sensor, using micropatterned, protein-functionalized RGO films as the sensing channel. This RGO-FETs were able to detect Ca^{2+}, Mg^{2+}, Hg^{2+} and Cd^{2+} via the change of conductance caused by the adding of target metal ions. Considering the relatively complex fabrication procedure of protein-based FET sensors, Chen et al. [84] fabricated a FET based on thermally RGO decorated with thioglycolic acid(TGA) functionalized gold nanoparticles for the detection of Hg^{2+}, and the schematic diagram was displyed in Figure 6(a). The sensor showed a lower detection limit (2.5×10^{-8} mol L^{-1}) and faster responses (less than 10 s) (Figure 6(b)), and it would be a promising detector of Hg^{2+} providing fast, real-time, simple detection with high sesitivity and selectivity.

In the voltammetric techniques, anodic stripping voltammetry is the most frequently used for the detection of heavy metal ions due to the high sensitivity and selectivity. Based on this method, many electrochemical detection devices are constructed using graphene decorated with molecules possessing affinity toward certain heavy metal ions as electrode materials. For instance, the highly selective adsorption of polypyrrole/RGO to Hg^{2+} was reported by Zhao's group [85]. Based on this discovery, they fabricated an electrochemical sensor for the detection of Hg^{2+} with the detection limit of 1.5×10^{-8} mol L^{-1}, and the schematic of selective detection is shown in Figure 7. A more sensitive method for detecting Hg^{2+} was presented by Zhou et al. [86], based on GO decorated with cysteamine and had lower detection limit of 3.0×10^{-9} mol L^{-1}. More importantly, this sensor demonstrated excellent selectivity towards Hg^{2+} in the presence of Cu^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+} and Mn^{2+} with a 200 times higher concentration of Hg^{2+}.

For simultaneous detection of several heavy metal ions, Wei et al. [87] prepared a sensor based on SnO_2/RGO nanocomposite for the simultaneous detection of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} by square wave anodic stripping voltammetry (SWASV). Compared with the bare and other glassy carbon electrodes modified with GO, the electrode modified with SnO_2/RGO exhibited improved selectivity and sensitivity to the four heavy metal ions. Gao et al. [88] developed a platform of simultaneously detecting Pb^{2+} and Cd^{2+}, using AlOOH-RGO nanocomposites as the sensing material. The limit of detection (LOD) is 4.46×10^{-11} mol L^{-1} for Cd^{2+} and 7.60×10^{-11} mol L^{-1} for Pb^{2+} respectively, and this sensor is proved to be highly sensitive and well stable. More recently, Ion and co-workers [89] presented an amino-functionalized exfoliated graphite nanoplatelet-based electrochemical sensor for the detection of Pb^{2+} with a detection limit of 1.0×10^{-9} g L^{-1}, being lower than the

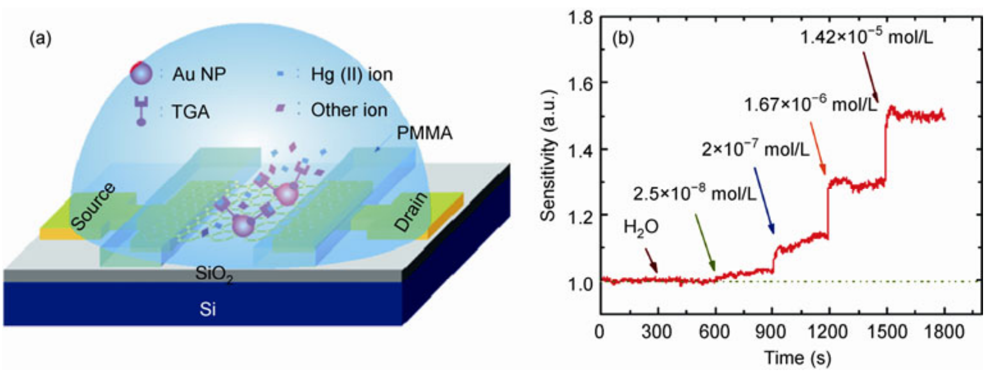

Figure 6 (Color online) (a) The schematic diagram and (b) the dynamic response for Hg^{2+} of the rGO/TGA-AuNP hybrid sensor. Reprinted from ref. [84] with permission from the American Chemical Society.

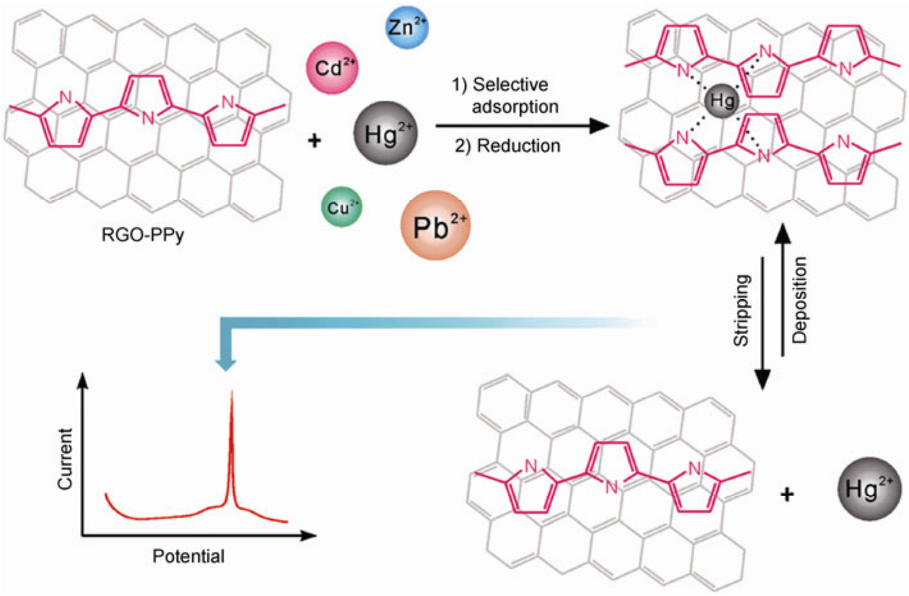

Figure 7 (Color online) A schematic drawing of Hg^{2+} electrochemically selective detection by the PPy-RGO nanocomposite. Reprinted from ref. [85] with permission from the Royal Society of Chemistry.

previous reports.

2.3 Detection for organic pollutants

Among the organic pollutants, phenolic compounds, as raw materials of dyes, cosmetics and pesticides, are used widely in chemical and pharmaceutical industries and the maximum level permitted is defined strictly by the wastewater discharge standard. Furthermore, dyes and pesticides are also limited due to their risk to human health and environment. Therefore, the qualitative and quantitative anaysis of these pollutants are of great importance.

For the detection of phenolic compounds, Li et al. [90] constructed an electrochemical sensor for simultaneous detection of dihydroxybenzene isomers, using thermally RGO as a electrocatalyst. This sensor demonstrated the detection limits of 7.5×10^{-7} mol L^{-1} for hydroquinone, and 8.0×10^{-7} mol L^{-1} for catechol. At present, modification of graphene with functional small molecules having specific interaction with the target analytes is a good approach to enhance the selectivity and sensitivity of electrochemical detection. Cyclodextrin causes great interest in many research groups because of its unique structural properties, which can bind selectively many kinds of inorganic, organic and biological molecules into its cavities. Therfore, many sensors based on graphene and cyclodextrin have been developed rapidly. Recently, our group [91] synthesized hydroxypropyl-β-cyclodextrin modified GNSs (HP-β-CD-RGO) by the esterification of GO carboxyl(-COOH) with the hydroxyl (-OH) of HP-β-CD under microwave irradiation in water medium. This nanocomposite possessed high surface area and excellent supermolecular recognition, and the synthesis procedure and the interaction between host and guest are shown in Figure 8. More important, the HP-β-CD-RGO modified glassy carbon electrode exhibited high electrochemical response to six phenolic organic pollutants, and had a detection limit of 1×10^{-8} mol L^{-1} for nitrophenol. Later, Liu and co-workers [92] used β-CD-RGO to detect simultaneously nitrophenol isomers. Zhu et al. [93] applied β-cyclodextrin-platinum nanoparticles/ graphene nanohybrids to the selective detection of naphthol isomers. More recently, graphene-based electrochemical enzyme biosensors are devised [94,95]. Wu et al. [96] demonstrated a graphene-based tyrosine biosensor for the determination of bisphenol A and it displayed superior analytical performance with sensitivity of 31084 A m^{-2} M^{-1} and detection limit of 3.3×10^{-8} mol L^{-1}. In addition, graphene decorated with copper oxide [97], poly(3,4-ethylenedioxythiophene) [98] and polydopamine [99] also can be applied to the detection of phenolic pollutants.

Concerning the detection of pesticides especially organophosphate pesticides, Wang et al. [100] self-assembled acetylcholinesteraseon on gold nanoparticles/ chemically RGO in the presence of poly(diallyldimethylammonium chloride) stabilizing cholinesterase with high activity and loading efficiency as well as enhancing the dispersion of AuNPs. The obtained composites were utilized as the catalyst to detect paraoxon, and it showed a low detection limit of 1.0×10^{-13} mol L^{-1}. With the similar method, Zhang and co-workers [101] prepared another RGO biosensor. The electrochemical measurements indicated that this sensor had rapid response and high sensitivity for the detection of monocrotophos with lower concentration of 1.0×10^{-7} g L^{-1}. In order to detect methyl parathion, two enzymeless sensors respectively based on GNSs decorated with zirconia nanoparticles [102] and

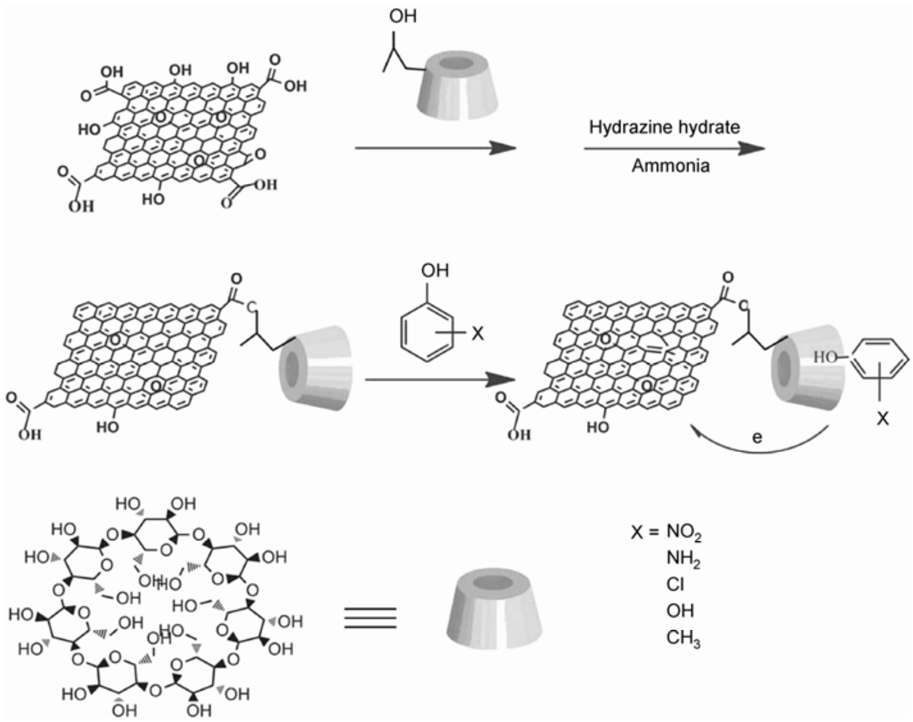

Figure 8 Schematic of the synthesis process of HP-β-CD-RGO composites and the interaction between the guest (*o*-nitrophenol) and the host (cyclodextrin moiety linked up to RGO). Reprinted from ref. [91] with permission from the Royal Society of Chemistry.

Ni/Al layerd double hydroxides [103] were proposed and they had the same detection limit of 6.0×10^{-7} g L^{-1}. Furthermore, graphene-based voltammetric [104] and fluorescent [105] sensor of detecting various dyes and hydrogen peroxide [106] have been reported recently.

3 Conclusions and perspectives

We have summarized the latest studies and progresses on the application of graphene-based materials in the environmental protection and detection. With the unique structure and physicochemical properties, graphene has attracted much attention. Many efficient adsorbents and sensitive detection devices have been mentioned in this review. However, these achievements are still in the stage of laboratory investigation and few of them have been in commercial production for the treatment of large-scale industrial pollutions at present. In order to overcome these challenges, the future works should focus on the following issues. First, low-cost and simple methods for the synthesis of one or few layer graphene are urgently required. Second, more functional molecules, which have specific interaction with certain contaminants should be designed for improving the sensitivity and selectivity of the adsorbents and sensors. Third, more potential applications in environmental protection and detection remain to be discovered and investigated. With more and more efforts, we believe that graphene will have a more widely application prospect.

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