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REVIEW

Recent Analytical and Environmental Approaches on Graphene Based Materials for Toxic Heavy Metals and Dye Pollutants

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ABSTRACT

Recent approaches on synthesis and characterization of graphene based materials are reviewed. Some typical materials include graphene oxide, graphene oxide modified with thiol and amino groups, nanocomposite of graphene-metal oxides and graphene quantum dots. Graphene oxide posses a wide range of impressive properties with numerous studies of dye adsorption. The modified functional graphene oxides have also been applied for removal of some toxic heavy metals in aqueous solution. Regarding thermodynamic and kinetics study, their adsorption isotherms are well-known established according to their multifunctional materials. Some ternary nanocomposite materials with or without magnetic property of specific graphene-metal/metal oxide or biopolymers have been used in both photocatalytic and sonocatalytic degradation of different industrial dye pollutants. In addition, graphene quantum dots as either chemical sensor or biosensor *via* turn-on/turn-off on its fluorescence were mostly applied for highly sensitive and selective detection of inorganic and organic compounds in real samples.

KEYWORDS

Graphene oxide, Graphene quantum dots, Multifunctional groups, Nanocomposite, dye, Heavy metal, Photocatalytic, Sonocatalytic, Chemical sensor.

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INTRODUCTION

Carbon, one of the most abundant elements on the earth, brings us as star materials over and over again. The football-shaped fullerenes and needle-liked carbon nanotubes (CNTs), both as new allotropes of carbon, attract great interests from scientists of chemistry, physics, biology and medical sciences. Graphitic forms include 0D fullerene, 1D CNT and 3D graphite and 2D case comes to graphene, a single layer of carbon atoms formed in honeycomb lattice, which was rewarded with Nobel Prize in Physics in Year 2010 [1]. Graphene, one layer of sp^2 bonded carbon in a honeycomb lattice, or more simply, one single layer of graphite, was discovered by Geim, Novoselov and co-workers (2004) at University of Manchester [2,3]. A wide range of impressive properties has been reported for graphene including the following: high electron mobilities of over 200,000 cm^2 V^{-1} s^{-1} at electron densities of about 2×10^{11} cm^{-2} [4], high thermal conductivity of about 5×10^3 W m^{-1} K^{-1} [5], impermeability to gasses despite being one atom thick [6], ballistic transport of electrons [7,8], absorption of 2 % of the light passing through it [9], high specific surface area (theoretical value of 2630 m^2 g^{-1}) [10], chemical stability and being "the strongest material ever measured" with a Young's modulus of 1100 GPa [11]. The fact that all of these properties are found within a single material has stimulated great interest in graphene [12]. Therefore, its synthesis has been investigated in many different fields with potential applications in biomedicines, reinforced composites, sensors, catalysis, energy conversion and storage devices. Importantly, it could be used in pollutant removal in environmental remediation, which has attracted increasing research in recent years [13-18].

For environmental applications of graphene based materials, graphene oxide (GO) was demonstrated to be a candidate carbon-based adsorbent for toxic metal ions and dyes removal due to having of non-specific functional groups (carbonyl, hydroxyl and epoxide) on its surface, providing anchor sites for both dye and metal ion complexation. The abundance of functional groups on its surface gives graphene oxide adsorption capability for dyes and metal ions such as methylene blue [19], congo red [20], acridine orange [21], methyl orange [22], methyl violet, rhodamine B, orange G [23], Au(III), Pd(II) and Pt(IV) [24]. Moreover, the graphene oxide surface can be modified with several ligands, making it a potential material as a super adsorbent. In previous studies, several ligands for chemically functionalized graphene oxide such as N-(trimethoxysilyl propyl) ethylenediamine triacetic acid [25], cetyltrimethyl-ammonium bromide [26], polyglycerol [27], 9-(4-aminophenyl) acridine [28], ethylenediamine, 1,6-hexane diamine [29] and polyhedral oligomeric silsesquioxane [30] have been reported. From the above statements, it is indicated that graphene based materials can be used as a high potential adsorbent for such toxic metal and dye pollutants.

In addition, the unique properties of two-dimensional structure, great intrinsic carrier, well developed porosity, active surface area, outstanding electronic properties and promising mechanical and thermal stability make graphene as the current support key material in the heterogeneous catalyst system. Accordingly, graphene plays a pivotal role in most heterogeneous catalysts ranging from single to bi-functional, hybrid, oxide and nano systems [31]. This combination also inspires and widens the heterogeneous catalyst application areas, including chemical conversion [32], photocatalyst [33], sensor [34], fuel cell [35], energy storage and others [36-38]. Particularly photocatalyst, during the past few years, graphene-based photocatalysts have been attracting ever-increasing research attention. Various composite photo-catalysts of graphene based materials have been studied, such as Ag/ZnO/graphene oxide [39], Ag/TiO$_2$/graphene [40], Pt/graphene oxide/TiO$_2$ [41], CdS/reduced graphene oxide/TiO$_2$ nanotube [42], ZnO-g-C$_3$N$_4$/graphene oxide [43], graphene/TiO$_2$ nanorod [44], graphene/ZnO and graphene/ZnO/cobalt phthalocyanine [45], indicating graphene based composite can be used as promising photocatalyst materials for dye degradation. However, because these composite materials have some drawbacks such as the need for UV activation and complex preparation procedures, new composite catalysts have recently been developed.

For applications of graphene based materials as a sensor, graphene quantum dots (GQDs) have generated enormous excitement because of their superiority in various advantage properties. It was discovered very recently as a class of zero-dimensional graphitic nanomaterials with lateral dimensions less than 100 nm in single layer, double layers and a few layers (3 to < 10) [46-48]. The graphene quantum dots exhibit new phenomena due to quantum confinement and edge effects, which are similar to carbon dots [49]. Compared with organic dyes and semiconductive quantum dots (QDs), graphene quantum dots are superior in terms of their excellent properties, such as high photostability against photobleaching and blinking, biocompatibility and low toxicity [50]. Moreover, similar to graphene, graphene quantum dots have excellent characteristics of large surface area, large diameter, fine surface grafting using the π-π conjugated network or surface groups and other special physical properties [51,52]. Furthermore, the carboxyl and hydroxyl groups at their edge enable them to display excellent water solubility and suitability for successive functionalization with various organic, inorganic, polymeric or biological species [53,54]. For these reasons, graphene quantum dots have attracted significant attention from researchers. Nowadays, graphene quantum dots have been applied as sensor for detection of various target analytes in numerous kinds of real samples such as free chlorine in drinking water [55], graphene oxide in water samples [56], 2,4,6-trinitrotoluene (TNT) in solution [57], ATP level in cell lysates and human blood serum [58], Fe^{3+} in water [59], H$_2$O$_2$ changes in biological systems [60], monosaccharides in aqueous solution [61], glucose in human serum [62], Ag$^+$ and biothiols [63], Hg^{2+} and biothiols in complex matrices [64], indicating graphene quantum dots can be used as a promising sensor for detection of not only metal ions but also non-metal ions in various samples. However, application of graphene quantum dots usually involves tedious processes for dual detection of target analytes. Thus, dual detection of graphene quantum dots sensors are in high demand for the trace analysis of cations, anions, molecules and biomacromolecules [65,66].

Graphene based materials for removal of dye pollutants: Currently in many industries including paper production, textiles, leather tanning, plastics, hair colouring and food technology, synthetic dyes have been used to colour their final products. Particularly, malachite green and alizarin red S are two types of the most commonly used dyes for cotton, leather, silk, paper and printing inks [67]. Especially, malachite green can also be used as an anti-parasitic and antifungal agent in aquariums [68]. However, malachite green and its major metabolite, leucomalachite green, both have mutagenic, carcinogenic, genotoxic and teratogenic effects [69,70]. Whenever environmental contamination occurs, they bioaccumulate in aquatic life such as fish, crab, shrimp, mollusk and other animals [71,72] and cause detrimental effects in liver, gall, kidney, intestine, gonad and pituitary gonadotrophic cells [73]. Ultimately, human being has been affected in food chain risk becoming sick. Therefore, it is necessary to remove these dye contaminants from wastewater before release into the environment to protect both the environment and humans.

Recently, graphene oxide was demonstrated to be a candidate carbon-based adsorbent due to having of non-specific functional groups (carbonyl, hydroxyl and epoxide) on its surface, providing anchor sites for both dye and metal ion complexation. The abundance of functional groups on its surface gives graphene oxide adsorption capability for various dye pollutants. A series of graphene oxides with different oxidation degrees (OD) for removal of methylene blue from aqueous solutions was reported [74]. The graphene oxide series show an overall fast and pH-independent methylene blue adsorption, which is even capable of removing trace levels of dye completely from very dilute solutions. Moreover, they reported that the binding features of the methylene blue loaded graphene oxide gradually change from methylene blue molecule parallel stacking on graphite plane through hydrophobic π-π interaction to vertical standing *via* electrostatic interaction with increasing oxidation degrees, resulting in a significant improvement of methylene blue uptakes.

The performance of graphene oxide for the removal of congo red dye from aqueous solution was also evaluated [75]. Batch sorption studies were carried out to determine the effect of pH, contact time, initial concentration of congo red and temperature on the adsorption of congo red onto graphene oxide. Circum neutral pH was found to be favourable for the adsorption of congo red onto graphene oxide. The equilibrium data fitted well with the Redlich-Peterson model and characterized by a Langmuir type isotherm. The kinetic parameters obtained from the kinetic studies suggested that the adsorption process is film-diffusion-controlled. The results obtained from thermodynamic studies revealed that the adsorption process is endothermic in nature as well as the feasibility and spontaneity of congo red adsorption onto graphene oxide. The low value of ΔH° (< 40 kJ/mol) indicated that adsorption process occurs mainly through a physical means.

For influence of immobilized graphene oxide on host structures, it was incorporated into calcium alginate and macroporous alginic beads and acridine orange was used as a typical dye pollutant to eliminate [76]. Characterizations demonstrated that graphene oxide was well encapsulated and had promoted both beads more porous yet to a varying extent. Kinetics studies exhibited the addition of graphene oxide resulted in adsorption with shorter equilibrium time and faster initial adsorption rate and the adsorbents with higher equilibrium capacities. Isotherm studies indicated the hybrid absorbents following Langmuir-type adsorptive behaviour which had highly maximum adsorption capacity.

Magnetic hybrid nanomaterials could be prepared by calcining graphene oxide (GO)/layered double hydroxide (LDH) hybrid in nitrogen atmosphere [77]. This nanomaterial exhibits excellent adsorption ability toward methyl orange in aqueous solution. The removal process of methyl orange is found to obey the Redlich-Peterson isotherm model and its kinetics follows pseudo-second-order rate equation. In addition, the magnetic hybrid also exhibits good recycle ability for removal of methyl orange. This novel nanomaterial derived from the GO/LDH hybrid demonstrates great potential in the applications of water treatment.

Regarding the applications of exfoliated graphene oxide (EGO) and reduced graphene oxide (rGO) for the adsorption of various charged dyes, such as methylene blue, methyl violet, rhodamine B and orange G from aqueous solutions [78], the large negative charge density available in aqueous solutions helps in the effective adsorption of cationic dyes on exfoliated graphene oxide while its adsorption is negligible for anionic dyes. On the other hand, reduced graphene oxide that has high surface area does not possess as a high negative charge and is found to be very good adsorbent for anionic dyes. From these literatures, it can be seen that the synthesized graphene based materials can be used as a highly effective adsorbent for dye removal from wastewater.

Graphene based materials for removal of toxic heavy metals: Graphene based materilas have been proposed as the ‘‘next generation material’’ owing to its remarkable electronic, optical and thermal properties, chemical and mechanical stability and large surface area [79]. Chemical structure of graphene oxide is reported as an oxidized graphene, decorated with various oxygenated functionalities such as hydroxy, epoxy on the basal plane and carbonyl, carboxylic acid at the edges. There are some recent reports demonstrating high adsorption ability of graphene oxide for Cd(II) [80], Pb(II) [81], Cu(II) [82] and Cr(VI) [83]. Moreover, the modification of graphene oxide surface can be made the graphene oxide more versatile in application oriented research. Several ligands for chemically functionalized graphene oxide have previously been reported.

A new type of triethylenetetramine-magnetite reduced graphene oxide (TET-MRGO) was prepared and applied to remove Cu(II) [84]. It exhibits strong saturation magnetization and can be easily separated from aqueous solution by an external magnetic field. A series of batch adsorption experiments were systematically conducted to study their adsorption property. The high adsorption capacity, excellent selectivity and effective adsorption-desorption results indicated the as-prepared TET-MRGO could be an effective adsorbent for removing Cu(II) from aqueous solution.

The modified magnetic graphene oxide with ethylenediamine-tetraacetic acid (EDTA-mGO) was also prepared [85]. It exhibited a good adsorbent for Pb(II), Hg(II) and Cu(II). The adsorption of these metal ions mainly depends on the metal chelation of EDTA and the electrostatic attractions of abundant functional groups on graphene oxide surface. Besides, good magnetic performance of EDTA-mGO makes it easy to achieve the solid-liquid separation. The adsorption kinetic data describe well with the pseudo-second-order model and the equilibrium data are fitted well to Freundlich and Temkin isotherms. Thermodynamic studies imply an endothermic and spontaneous adsorption process in nature. Furthermore, the excellent reproducibility indicates that EDTA-mGO has a promising application in water treatment.

The magnetic polyaniline/graphene oxide (MPANI/GO) adsorbent was prepared by using aniline in the presence of graphene oxide [86]. The sorption of Cu(II) on the MPANI/GO was studied as a function of pH, contact time, ionic strength, foreign cation and anions and the results showed that Cu(II) sorption was strongly dependent on pH and independent of ionic strength. The sorption of Cu(II) was mainly dominated by outer-sphere surface complexation at low pH and by inner-sphere surface complexation at high pH. The thermodynamic parameters calculated from temperature-dependent sorption isotherms indicated that the sorption process was spontaneously endothermic. The adsorbents were effective materials for the removal of Cu(II) from large volumes of aqueous solution and could be separated by using magnetic separation method in practical applications.

Chitosan functionalized graphene oxide as an efficient adsorbent to remove arsenic from aqueous solution was also applicable [87]. The chitosan functionalized graphene oxide adsorbent acts as a good host of welcoming the incoming guest, arsenic oxyanion and several interesting interactions such as cation-π interaction, (RNH^{3+}–aromatic π moiety), electrostatic interactions ($H_2AsO_4^-$, $HAsO_4^{2-}$–$^+NH_3R$), intra and intermolecular hydrogen bonding as well as anion-π interaction ($RCOO^-$–aromatic π moiety), (RO^-–aromatic π moiety), could be conceptualized in this process. The abundant oxygen-containing functional groups on the adsorbent surfaces play an important role on As(V)/As(III) adsorption. The applicability of this method is demonstrated economical and practical applications for efficient adsorption of arsenic from aqueous solution.

Glycine functionalized graphene oxide (GO-G) as an adsobent for removal of Ni(II) was reported [88]. Amino group was used to be a functionalizing agent for the surface modification of graphene oxide to GO-G. The effect of numerous influential parameters such as contact time, temperature and initial concentration of Ni(II) in the aqueous solution was well illustrated and optimized using batch adsorption study. Adsorption isotherm for the adsorption process was carried out using four types of the Langmuir and Freundlich isotherm models. Results clearly depict that adsorption of Ni(II) on to the graphene oxide adsorbent surface was well fitted and found to be in good agreement with the type (II) Langmuir isotherm as the obtained regression constant value (R_2) is found to be 0.999 while the adsorption of Ni^{2+} on GO-G surface was found to be in good agreement with the Freundlich isotherm, since the regression constant value (R_2) is 0.999.

Chitosan/sulfydryl-functionalized graphene oxide composite (CS/GO-SH) was synthesized *via* covalent modification and electrostatic self-assembly [89]. The obtained CS/GO-SH was used as an adsorbent material for removal of Cu(II), Pb(II) and Cd(II) in single- and multi-metal ions systems. This composite has potential applications for adsorptive materials due to its superiority of the chemical characteristic and the specific surface area.

Cysteine functionalized magnetic graphene oxide nanosheets was used to adsorb cadmium [90]. The cysteine has more affinity to coordinate with cadmium, therefore, the modified graphene oxide nanosheets were used as a selective sorbent for solid-phase extraction and determination of trace cadmium in different food samples (rice, wheat, milk and shrimp). Satisfactory recoveries were obtained. The results showed good adsorption capacities of the adsorbent with high selectivity toward Cd(II). The process was relatively fast and the equilibrium state was established within 5 min and its kinetics was followed the pseudo-second order mechanism. The best interpretation for the equilibrium data was given by Langmuir isotherm and the thermodynamic parameters showed that the adsorption process was spontaneously endothermic in nature.

In another studies, the phosphate-functionalized graphene oxide (PGO) was prepared by grafting triethyl phosphite onto the surface of graphene oxide and applied to remove U(VI) from aqueous solution [91]. The adsorption mechanism was proceeded *via* a chemical adsorption of U(VI) on PGO surface. Moreover, the results gave a better removal efficiency toward U(VI) than other heavy metal ions at acidic solution, indicating the selective extraction of U(VI) from environmental pollutants.

Thiol functionalized graphene oxide (GO-SH) was prepared with various cocentrations of cysteamine, which worked as the functionalizing agent for conversion of graphene oxide to thiol functionalized graphene oxide [92]. These adsorbents were applied to remove Pb(II). The optimized values for adsorbent dose, initial concentration of Pb(II), contact time and solution pH were found to be 20 mg, 25 mg/L, 60 min and 6, respectively at 298 K. The kinetic experimental data for GO-SH1, GO-SH2 and GO-SH3 were in good agreement with pseudo first-order model, pseudo-second-order model and pseudo-second-order model, respec-tively. Results revealed that the adsorption capacity of Pb(II) on to the developed adsorbent increased with the increase in temperature, hence this process was spontaneously endo-thermic.

From the above literatures, it can be seen that several ligands can be modified on the surface of graphene based materials. Especially, both amino and thiol groups are very popular ligand. However, uses of these ligands are not only rather time-consuming but also tedious sample preparation processes. Therefore, new functionalized adsorbents have recently been developed.

Graphene based materials as a photocatalytic degradation of dye pollutants: Since the discovery of photocatalytic splitting of water on TiO_2 electrodes was found, a significant progress has been made in the area of highly active oxide semiconductor photocatalysts because of their applicability in solar energy conversion and environmental protection [93]. Some semiconductors (*e.g.*, ZnO, WO_3, CdS, Bi_2WO_4 and TiO_2, *etc.*) can act as photocatalysts for light-induced chemical transformations due to their unique electronic structure composed of a filled valence band (VB) and an empty conduction band (CB). When a photon with energy of hν matches or exceeds the band gap energy (E_g) of the semiconductor, an electron in the valence band is excited into the conduction band, leaving a positive hole in the valence band. The photogenerated holes and electrons play a very important role in pollutant degradation and photocatalytic disinfection and solar energy conversion including hydrogen production and solar photovoltaics, respectively. However, the photogenerated electrons and holes in the excited states are unstable and can easily be recombined, dissipating the input energy as heat, which results in low efficiency of photocatalysis [94-97].

During the past decade, a variety of strategies have been employed to improve the photocatalytic performance of semiconductor photocatalysts, for instance, *via* suitable textural design [98-103], doping [104-107], noble metal loading [108-110] and forming semi-conductor composites [111,112]. In particular, numerous attempts have been made to combine graphene with semiconductor photocatalysts to enhance their photocatalytic performance [113-118]. In addition, recently researchers are more interested in the preparation of graphene based ternary composite, several ternary composite systems of graphene have been reported in efforts to obtain a composite with superior photocatalytic performance.

TiO_2-Fe_3O_4/graphene (RGO) composite was prepared by a facile hydrothermal method with RGO and magnetic TiO_2 as starting materials in ethanol-water solvent [119]. The results showed that the TiO_2 coated Fe_3O_4 nanoparticles with a strong response to external magnetic fields were dispersed uniformly on the surface of RGO nanosheets. The composite catalysts can cause an obvious red shift of UV-visible spectrum compared with pure TiO_2. The adsorption and photocatalytic activity of the composite catalysts were evaluated by using methylene blue as organic pollutants. The photocatalytic degradation of methylene blue by TiO_2-Fe_3O_4/RGO composites under visible light irradiation exhibited high performance for the photocatalytic degradation of methylene blue.

A ternary composite of Cu_2O/graphene/rutile TiO_2 nanorod (CGT) was synthesized *via* a chemical bath deposition process [120]. The red shift of light absorption edge and more absorption in the visible light region were observed for the resulted ternary samples compared with TiO_2 and graphene/TiO_2 composites. The photocatalytic activity was evaluated by the photodegradation of methylene blue under visible light irradiation, which gave 2.8 times corresponding enhancement of the degradation efficiency for the ternary composites compared with TiO_2.

The nanocomposite of Ag/ZnO-TiO_2 under cetyltrimethylammonium bromide (CTAB) was synthesized [121]. The obtained Ag/ZnO-TiO_2 not only showed the improved morphology with an enlarged varying degree of BET specific surface area and pore volume, but also had a stronger response in the visible area. Moreover, photocatalytic properties of the as-nanocomposites Ag/ZnO-TiO_2 were tested by different modes of radiation including ultraviolet, visible light, simulated sunlight and microwave-assisted irradiation photocatalytic degradation of rhodamine B. The results showed that the photocatalytic activities of the product Ag/ZnO-TiO_2 were much higher than that of P25, ZnO and other samples. In addition, the as-nanocomposite Ag/ZnO-TiO_2 showed good degradation for different structure dyes including crystal violet, methylene blue and methyl orange under UV light irradiation. Furthermore, the Ag/ZnO-TiO_2 still has certain stability under ultraviolet light after three cycles of the experiment.

The ternary composite material for Ag/ZnO/graphene oxide (GO) was prepared [122]. The obtained composite was found to exhibit remarkably enhanced light-harvesting ability ranging from 200 to 800 nm. Moreover, the Ag/ZnO/GO composite presented the improvement of efficient removal toward a representative dye, rhodamine B, by synergistic adsorption-degradation effects derived from the specific Ag/ZnO/GO heterostructure. It is suggested that the heterostructure promotes electron-hole separation and charge transfer in the interface under UV light irradiation, whereas, under visible light illumination, only electrons from sensitized rhodamine B move to the conduction band of ZnO and finally transfer to Ag or graphene oxide. Subsequently, reactive oxygen species (ROS) generated in the photocatalytic reactions are responsible for the enhanced photocatalytic degradation activity. Therefore, it is suggested that obtained Ag/ZnO/GO nanocomposite will be a promising material for the elimination of organic pollutants in environment. In addition, the applications of ternary graphene based materials for photocatalytic degradation of various dye pollutants are summarized in Table-1.

From these literatures, it can be shown that graphene based ternary composites can be used as promising photocatalyst materials for dye degradation. However, various photocatalysts have some drawbacks in either limiting by its UV activation requirement or complexity of preparation process, thus new photocatalysts have recently been developed.

Graphene based materials as new fluorescent sensors: It is well known that graphene has found widespread applications in many diverse fields in physics, chemistry, material science and biology. It has been shown that when a graphene sheet is small enough, its properties can vary significantly [145]. At a size less than 100 nm, a new kind of materials called graphene quantum dots (GQDs) is produced [146]. Graphene quantum dots usually contain one or two layers of graphene with a size distribution mainly in the range of 3-20 nm [147]. Graphene quantum dots are highly luminescent as a result of the quantum confinement and edge effects [148]. The amounts of oxygen-containing groups, structural defects and doping elements also contribute considerably to their luminescence properties [149]. They have higher surface area, larger diameter and better surface grafting properties compared with the conventional quantum dots (QDs) and carbon dots (CDs) [150]. In addition, graphene quantum dots show excellent water solubility, low toxicity, high stability and good biocompatibility. They are considered to be a promising material to replace the commonly used semiconductor nanocrystals for a number of biosensing and bioimaging related applications [151].

Wu *et al.* [152] developed a facile method for the highly sensitive and selective sensing of biothiols based on graphene quantum dots (GQDs). They reported that graphene quantum dots emitted strong blue fluorescence in an aqueous buffer solution. It was observed that Hg(II) could efficiently bind with graphene quantum dots and quench its fluorescence intensity. When the biothiol compounds (glutathione, cysteine, or homocysteine) were added to the assay mixture of graphene quantum dots and Hg(II), it bound with Hg(II). Hg^{2+}–graphene quantum dot complex dissociated and the fluorescence turn-on signal was detected. The emission intensity changes in the graphene quantum dots could be directly related to the amount of biothiol added to the assay solution. This assay is highly sensitive; the limits of detection (LOD) for GSH, Cys and Hcy were 5, 2.5 and 5 nM, respectively. The assay is also highly selective, while a number of amino acids and proteins were tested and only little interference was observed.

Zhou *et al.* [153] reported that an effective approach to produce graphene quantum dots (GQDs) has been developed, which based on the cutting of graphene oxide powder into smaller pieces and being reduced by a green approach, using sodium polystyrene sulfonate as a dispersant and L-ascorbic acid as the reducing agent, which is environmentally friendly. Then, the as-prepared graphene quantum dots were further used for the detection of heavy metal ions, Pb(II). This kind of graphene quantum dots has greater solubility in water and is more biocompatible than graphene oxide that has been reduced by hydrazine hydrate. The few-layers of graphene quantum dots with defects and residual OH groups were shown to be particularly well suited for the determination of metal ions in the liquid phase using an electrochemical method, in which a remarkably low detection limit of 7×10^{-9} M for Pb(II) was achieved.

Wang *et al*. [154] prepared graphene quantum dots *via* the hydrothermal method using reoxidized graphene oxide. Based on the quenching of the as-prepared graphene quantum dots fluorescence by Cu(II) in water, a facile and direct fluorescence sensor for the detection of Cu^{2+} ion has been studied. They reported that it exhibits an extraordinarily high sensitivity and selectivity to Cu(II) compared to other metal ions in aqueous solution. The fluorescence intensity is inversely proportional to the concentration of Cu(II) and calibration curve displays a linear region over the range of 0-15 µM, with a detection limit of 0.226 µM. These results indicate that graphene quantum dots, as a fluorescent sensing platform, could meet the selective requirements for biomedical and environmental application and be sensitive enough to detect Cu(II) in environmental water samples, even in drinking water, which has a limit of 20 µM as defined by U.S. EPA drinking standards.

TABLE-1
APPLICATIONS OF TERNARY GRAPHENE BASED MATERIALS FOR PHOTOCATALYTIC DEGRADATION

Photocatalyst	Target pollutant	Ref.
Cu_2O/graphene/rutile TiO_2	Methylene blue	[120]
Reduced graphene oxide/*meso*-TiO_2/AuNPs	Methyl blue	[123]
Graphene oxide/magnetite/cerium-doped titania	Tetracycline	[124]
CuAu–ZnO–graphene	Methyl orange, Methylene blue, Indigotin, Sunset yellow, Tartrazine	[125]
Reduced graphene-oxide/TiO_2/ZnO	Methylene blue	[126]
Cu–P25–graphene	Methylene blue	[127]
Ag/TiO_2/graphene	Methylene blue	[128]
Graphene-Ag/ZnO	Methylene blue, Rhodamine B, Methyl orange	[129]
Reducing graphene/polyaniline/cuprous oxide	Congo red	[130]
Graphene oxide/Ag_3PO_4/g-C_3N_4	Rhodamine B	[131]
Fe(III)/graphene/g-C_3N_4	Methylene orange	[132]
Graphene nanosheets/$K{=}PW_{12}O_{40}$	Methylene orange	[133]
Ag/AgBr graphene oxide	Methyl orange	[134]
Magnetic reduced graphene oxide–$ZnFe_2O_4$	Rhodamine B	[135]
Ag_3PO_4/TiO_2/rGO	Methylene blue	[136]
CdS//TiO_2/reduced graphene oxide	Rhodamine B, Crystal violet	[137]
ZnO–RGO/RuO_2	Methylene blue	[138]
AgBr/ZnO/RGO	Methylene orange	[139]
MoS_2/P25/graphene aerogel	Methylene orange	[140]
Reduced-graphene-oxide/Bi_2MoO_6/Au	Rhodamine B	[141]
Ag/TiO_2/γ-Fe_2O_3@r-GO	Crystal violet	[142]
Mn-doped ZnO/Graphene	Methylene blue	[143]
Graphene–carbon nanotubes (CNTs)–TiO_2	Methylene blue, Cr(VI)	[144]

TABLE-2
APPLICATIONS OF GRAPHENE QUANTUM DOTS AS A SENSOR FOR VARIOUS TARGET ANALYTES

Sensor system	Target analyte	Ref.
Nitrogen-doped graphene quantum dot–mercury(II) system	Cysteine	[157]
Graphene quantum dots/polystyrenic anion-exchange resin (GQDs/PS-AER)	Fe(III)	[158]
Graphene quantum dots (GQDs)	Fe(III), pH value	[159]
GQDs/α-Fe_2O_3	Trimethylamine	[160]
Ligninsulfonate/graphene quantum dots (SL/GQDs)	Fe(III)	[161]
Nitrogen-doped graphene quantum dots (Ag NPs-N-GQDs)	Glutathione	[162]
Graphene quantum dots co-doped with N and S (N-S/GQDs)	Pyrophosphate ions	[163]
Creatinine/N-GQDs-chitosan	Picric acid	[164]
Graphene quantum dots (GQDs)	Dopamine	[165]
Glucose-derived GQDs (g-GQDs)	Au(III)	[166]
L-Cysteine-capped core/shell/shell quantum dot-graphene oxide (L-Cysteine-CdSeTe/ZnSe/ZnS QDs-GO)	Polycyclic aromatic hydrocarbons (PAHs)	[167]
Polydopamine/graphene quantum dots (pDA/GQDs)	Dopamine	[168]
S and N co-doped graphene quantum dots/polyaniline hybrid (S, N: GQDs/PANI hybrid)	Ammonia	[169]
Graphene quantum dots	Hg(II)	[170]
Pristine graphene quantum dots	Cu(II)	[171]
N-doped graphene quantum dots (N-GQDs)	Cr(VI)	[172]

Hosseini *et al*. [155] reported that graphene quantum dots (GQDs) have successfully been utilized as an efficient nanosized fluorescence chemosensor to detect selectively glutamate (Glu) in *tris*-HCl buffer solution (pH 9). The fluorescence emission spectrum of graphene quantum dots was maximized at about 430 nm. The sensor showed high selectivity toward glutamate in comparison with other amino acids.

Benítez-Martínez and Valcárcel [156] reported a new method for the determination of the phenol fraction of olive oil. An optical nanosensor based on graphene quantum dots, obtained by pyrolysis of citric acid, was specifically developed for this purpose. The ensuring fluorescence sensing method, which is simple and highly sensitive and reproducible, was used here to determine gallic acid and oleuropein as model analytes commonly found in olive oils, as well as the phenolic concentration of olive oil in real samples. The detection limits were lower than 0.12 mg/L and the precision, expressed as relative standard deviation was lower than 1.7 %.

From these literatures, it can be seen that graphene quantum dots can be used a promising sensors for detection of various targets as summarized in Table-2. However, an application of graphene quantum dots usually involves tedious processes for dual detection of target analytes. Thus, dual detection of graphene quantum dots sensors are in high demand for the trace analysis of cations, anions, molecules and biomacromolecules.

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