Preparation of Modified Graphene Oxide Nanomaterials for Water and Wastewater Treatment

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Abstract. Because of the population explosion, industrialization and environmental disruption which cause big water crisis to all human beings, the development of high-efficient water treatment technologies is highly desirable. Recently, graphene oxide (GO) has drawn wide attention from the scientific community. the two-dimensional GO nanosheets possess high specific surface area and high surface activity, which make GO-based nanomaterials have great potential in various fields. In this paper, recent methods on modification of graphene oxide nanomaterials are introduced and compared. The prospects of GO-based nanomaterials applied in water treatment from three aspects of absorbent, catalysis and membrane separation are further analysed.

1. Introduction

Since water is the origin of all life on the earth, natural world and human being cannot live without clean and safe water. However, with the development of human civilization, the explosive growth of world population, industrialization and urbanization, water resource were polluted by different kinds of dye, heavy metal and pharmaceuticals globally [1]. Numerous pollutants seriously threaten living beings, and water resource crisis has emerged as a worldwide big issue. The development of high-efficient strategies for the purification of polluted water is of paramount importance.

In last few decades, various technologies such as chemical precipitation, advanced oxidation, photocatalysis, evaporation, adsorption, membrane filtration, ion-exchange and electrochemical methods have been developed to purify water and wastewater. Among these technologies, adsorption, photocatalysis and membrane filtration are most considerable techniques for their easy operation and environmentally friendly. In pursuit of higher operation efficiency and economic effectiveness, there are different kinds of new materials applied in adsorption, photocatalysis and membrane filtration, such as zeolites, metal-organic frameworks (MOFs), metal oxides, carbon nanotubes (CNT) and graphene oxides (GO) [2-9].

On the basis of unique two-dimensional (2D) nanostructure and highly oxide surface, GO nanosheets possess high surface area and surface activity, which are the essential in designing adsorbents, catalysts and membranes. Herein, we summarized the recent developed modification of
GO from the aspect of composite materials and we present the potential applications of GO-based nanomaterials in water and wastewater treatment from three aspect of application including adsorption, catalysis and membrane separation.

2. Modification of graphene oxide

Compared to graphene, GO is more economical available owing to the development of mass-production techniques, such as Hummers method. Moreover, GO is more chemical active because the oxidation process makes the surface of GO a mass of carboxyl, hydroxyl and epoxy group. These functional groups take new potential applications in the field of water and wastewater treatment. Besides, the decrease of electrical properties comes with the functional group, limiting the application of GO in electrical catalytic degradation of pollutant in contaminated water. In order to take full advantage of GO, researches are now focusing on the surface modification of GO (mGO). In general, due to the synergistic effect between GO and other materials, mGO-based nanocomposites are endowed with specific properties, such as magnetism, preferential adsorption and photochemical properties. Typically, there are mainly three kinds of materials used to modify the GO, including micromolecules, inorganic nanoparticles and polymers [10].

2.1. Micromolecule modified graphene oxide

So far, GO nanosheets can be modified with micromolecules via two approaches. The first one is to connect the micromolecule to graphene oxide with π–π staking, hydrogen bond and electrostatic adsorption, as shown in Figure 1. In particular, molecules with extended π bond are commonly used to modify graphene oxide by π–π staking. The other way is covalent grafting by chemical reaction, including Diels-Aider reaction, diazotization reaction, radical reaction and the reaction between the surface oxygenic groups and other active groups. For example, rhamnolipid-functionalized GO (RL-GO) was synthesized by a facile one pot esterification reaction. The prepared RL-GO showed great adsorption property to methylene blue (MB), with the maximum adsorption capacity of 529.10g, 568.18g and 581.40g at 298K, 308K and 318K, respectively.

![Figure 1. Noncovalent modification of graphene oxide by micromolecules.](image)

2.2. Inorganic nanoparticles modified graphene oxide

There are many inorganic materials introduced to composite with GO including carbon nanotubes (CNT), metal nanoparticles, metal oxide nanoparticles, metal sulfide nanoparticles and metal-organic frameworks (MOFs). These inorganic materials can be mixed with GO or in situ synthesized on the
surface of GO. For example, Song et al. fabricated a high conductive CNT/GO hybrid membrane by mixing the CNT and GO. Han Yan et al. synthesized magnetic Fe₃O₄@GO by simple in situ synthesis, in which the magnetic Fe₃O₄@GO could rapidly adsorb iron (II) and Manganese (II) from polluted water.[11] In our previous work, MOF-encapsulated GO yolk–shell superstructures were fabricated by a facile spray-drying method. The fabricated MOF-GO composite showed great potential in preferential adsorption and sustained release of small molecule [12].

2.3. Organic polymers modified graphene oxide
Similar to micromolecule and inorganic nanoparticles, organic polymer can be composited with GO by two main ways - non-covalent connection and covalent connection. Moreover, non-covalent connection can be divided into solution-mixing and melt mixing. Covalent connection also can be divided into covalent grafting and in situ polymerization. Covalent grafting is mainly used to connect polymers and GO by the chemical reaction between functional groups on the surface of polymers and GO (Figure 2). While in the process of in situ polymerization, GO is firstly modified with functional groups which is reactive to polymer monomers, and then polymerized with polymer monomers in certain conditions.

Figure 2. Synthetic route of polystyrene graft graphene oxide through hydroxy modification.

3. Application of modified graphene oxide in water treatment
High specific surface area and high surface activity make GO as an excellent candidate in coordinating with other materials or molecules, and it offers great possibilities in the application of water and wastewater treatment. Recent works have shown that GO can perform multiple roles in water and wastewater treatment including adsorbents, photocatalysts and membrane filtration [13].

Figure 3. Synthesis of metal oxide/reduced graphene oxide composites.

3.1. Micromolecule modified graphene oxide
GO have been explored as adsorbents for many pollutants, including dye and heavy metal ions. Yang [14] reported that GO showed tunable adsorption property to methylene blue (MB) in wide range of
pH, and the maximum absorption capacity was up to 714mg/g. Kumar and coworkers synthesized trioctylamine modified mGO, and the prepared surface functional mGO can adsorb 99.4% of Cr VI (chromium VI) in water within 60 minutes [15]. In addition, the GO composites usually show higher capacity than GO. Recently, Fe₃O₄@GO nanocomposite has been paid much attention for its great adsorption capacity and magnetism. Sun et al. synthesized Fe₃O₄@GO nanocomposite by one-pot hydrothermal method [16]. The synthesized Fe₃O₄@GO nanocomposite could efficiently remove rhodamine B and MG in water, with a removal rate over 90%. Chandra et al. [17] removed arsenic ions from polluted water by a magnetite reduced GO, and also found the positive effect of pH to the adsorption ability of the nanocomposite.

3.2. Photocatalysts
Owning to the high surface area and activity of GO, the application of graphene/metal oxide nanocomposites as photocatalysts for water purification is growing up. Various active metal oxides nanoparticles, such as TiO₂, ZnO, Cu₂O and iron oxides, have been loaded on GO surface by in situ synthesis (Figure 3) [13]. Bahnemann et al degraded methylene blue by TiO₂ loaded TiO₂-GO, the photocatalytic degradation rates of MB by TiO₂-GO were 3 times faster than that by P25 [18]. In our previous study [19], we fabricated Fe₂O₃ nanoparticles well-distributed hollow reduced graphene oxide microspheres via a spray-drying methodology, the prepared Fe-rGOS exhibited a remarkable photocatalytic activity to methylene blue (MB) in a wide pH range. In addition, metal oxide loaded GO also can be applied to the reduction of hypertoxic heavy metal ions and some micro-molecular organics. For example, Cr VI (chromium VI) can be reduced to low toxic trivalent chromium Cr (III) by ZnO-TiO₂/RGO nanocomposite. The work of phenol degraded by titanate/graphene composite was also reported.

3.3. Membrane filtration
As one of the most promising two-dimensional nanomaterial, GO have demonstrated excellent performance in the application of ion and molecular sieving. As shown in Figure 4, water molecules can quickly flow through the pores between GO layers, while ions selectively permeate through the GO layers. Therefore, GO and its derivatives can be widely used in membrane filtration, including ultrafiltration, nanofiltration, reverse osmosis, forward osmosis and pervaporation. The addition of GO derivatives not only enhances the retention rate, but also improves the hydrophilicity and erosion resistance. Qiu et al. prepared the modified graphene nanofiltration membrane, which was prone to fold in aqueous solution. and the degree of interlayer folding can be controlled by heat treatment [20]. The flux of nanofiltration membrane was 400 L/(m²·h·MPa), while the retention rate of azo dye DY was 67%. Lu and coworkers fabricated GO/polyamide-polyulfone mixed matrix reverse osmosis membrane, the water flux rate was up to 63 L/h with the retention rate of 98%. The as prepared membrane had good resistance to chlorine. Liang et al. used PAN ultrafiltration membrane as the basement membrane, and fabricated GO/PAN pervaporation membrane by vacuum extraction. When the operating temperature was 90°C, the water flux was 65.1 L/h and the salt retention reached as high as 99.8%.
4. Conclusion
In summary, the functional GO have shown great properties in the fields of adsorption, photocatalysis and membrane filtration. More importantly, the combination of GO and various kinds of materials, including micromolecule, inorganic materials and polymers, are found to be more efficient in water and wastewater treatment. The specific preferential adsorption, magnetism and photocatalytic performance make GO-based nanocomposites one of the most promising candidates in solving the world’s severe water crisis.

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