DEVELOPMENT OF GRAPHENE OXIDE FROM GRAPHITE: A REVIEW ON SYNTHESIS, CHARACTERIZATION AND ITS APPLICATION IN WASTEWATER TREATMENT

Hamidreza Sadegh

Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

Abstract. Graphene oxide (GO) have built broad interest in most areas of science and engineering because of their extraordinary physical, mechanical, thermal and optical properties. Graphene is a two dimensional one-atom-thick planar sheet of sp^2-bonded carbon atoms. This review presents and discusses the past and current advancement of synthesis and characterization of GO from graphite. Herein, we critically discuss the synthesis and characterization of graphene, the specific advantages that graphene-based adsorbents can provide over other materials in wastewater treatment research and their related chemical and physical properties. Furthermore, we describe the latest developments in the use of these materials for wastewater treatment, including removal of heavy metal ions and dyes.

1. INTRODUCTION

Within a decade, graphene has emerged as one of the most promising nanomaterials incontemporary nanotechnology. The unique structure and remarkable properties of graphene have boosted its use in various domains of science and technology such as nanoelectronics, catalysis, sensing, energy storage and environmental [1-4].

Graphene materials vary in layer number, lateral dimension, surface chemistry, defect density or purity which give rise to various related forms of graphenes, such as, few-layer-graphene (FLG), ultrathin graphite, graphene oxide (GO), reduced graphene oxide (rGO), graphene nanoplatelets (GNP) etc. [5-7].

Graphene oxide (GO) has high aspect ratio and large μ-electronic surface provide strong intermolecular forces among these layers and adsorbates [8]. Due to the opened-up layer structure, GO would exhibit markedly fast adsorption kinetics [9,10]. Experimentally, a comparison between pristine graphene and GO with coal base AC, single and multi-walled carbon nanotubes (SWCNTs, MWCNTs), Graphene exhibites better adsorption capacities for two synthetic organic compounds (SOCs; phenanthrene and biphenyl) in aqueous solutions [11]. More importantly, graphene is much cheaper than SWCNTs [12]. Graphene has been used as adsorbent for the removal of cationic red X-GRL [13], methylene blue [14,15], methyl orange [16], congo red [17] basic red 12 [18], basic red 46 [19] and other organic materials from aqueous solutions. GO and graphene were unprecedented substrates for these adsorption technologies [20-22]. In this review, we highlight the past and present attempts for using graphen materials as adsorbents for the removal of heavy metal ions and dyes from wastewater.

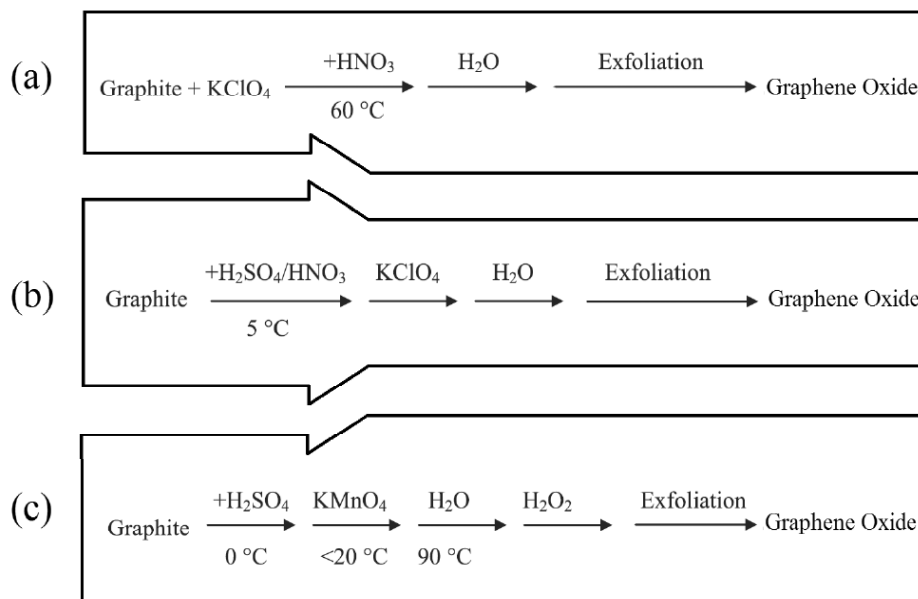Corresponding author: Hamidreza Sadegh, e-mail: hamidreza.sadegh@srbiau.ac.ir and h.sadegh@chemist.com

Fig.1. Synthesis processes of graphene oxide by (a) Brodie, (b) Staudenmaier, and (c) Hummers-Offerman method.

2. SYNTHESIS OF GRAPHENE OXIDE

In the past a few years, most grapene oxide (GO) is synthesized by chemical oxidation and exfoliation of pristine graphite using either the Brodie, Staudenmaier, or Hummers method, or some variations of these methods. Brodie first found that the oxidizing mixture ($KClO_4$ + fuming HNO_3) could form GO only with graphitizable carbons that contain regions of graphitic structure [23]. Staudenmaier then reported the formation of GO when graphite was heated with H_2SO_4, HNO_3, and $KClO_4$ [24]. Later, Hummers and Offeman introduced a convenient method to prepare GO using H_2SO_4 and $KMnO_4$ [25]. Fig. 1 shows the preparation processes of the above three methods.

Exfoliation is an important step in GO synthesis and is usually achieved in liquid solution using ultrasonic method with different solvents [26,27]. The typical procedures involve exposure of graphite or graphite oxide powders to particular solvents, and then exposing these solutions to sonication. Recently, other methods were also developed for simultaneously exfoliation and reduction of GO to obtain graphene nanosheets (GNs), such as thermal treatment [28], chemical method [29], plasma [30], and microwave [31].

GO usually has several oxygen-containing groups, such as carboxylic, hydroxyl, and epoxide functional groups on carbon surface. It is believed that GO is a nonstoichiometric compound with a variety of compositions depending on the synthesis conditions. In spite of extensive scientific investigations, the exact composition and structure of chemically synthesized GO are still questionable. Different structural models, which correspond to an ideal formula of $C_8O_2(OH)_2$, have been advanced. Its models are based either on a wrinkled carbon sheet composed of trans-linked cyclohexane chairs with oxygenated surface groups (Ruess model), on Lerf's epoxide-containing GO structure or on the keto/enol structure proposed by Scholz and Boehm [32]. Szabo et al. [33] proposed a new model based on several techniques. Fig. 1 shows the different GO structural models proposed by some researchers. It is generally believed that the important properties of GO are its layered structure and negatively charged surface, which can provide a wide applications in adsorption [34].

3. CHARACTERIZATION OF GRAPHENE OXIDE

The characterizations of GO such as as XRD and TEM have also been reviewed in detail.

3.1. XRD

XRD can be one of the tools but not perfect for the determination of single-layer graphene. Pristine
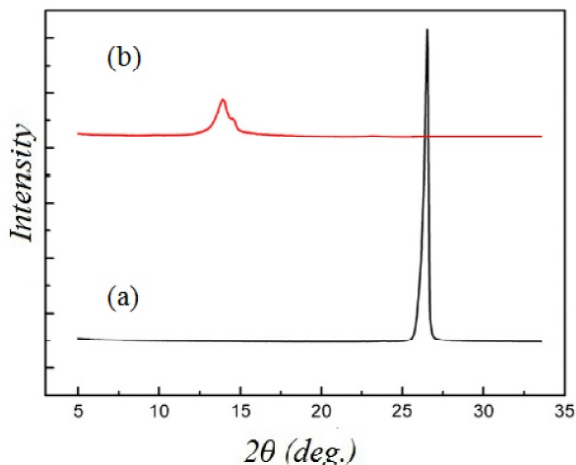
Fig.2. XRD patterns of graphite (a), graphene oxide (b).

graphite shows a basal reflection (002) peak at $2\theta = 26.6°$ in the XRD pattern. After pristine graphite was oxidized, the 002 peak shift to a lower angle at $2\theta = 13.9°$ which is due to the existence of oxygen functionalized group and water molecules in between the layer of graphite. After GO was thermal exfoliated completely, there was no apparent diffraction peak detected which means the GO structure was removed and graphene nanosheets were formed (Fig. 2) [35]

3.2. TEM

The thickness of graphene can be determined accurately by TEM analysis as reported by Hernandez et al. by observing a large number of TEM images
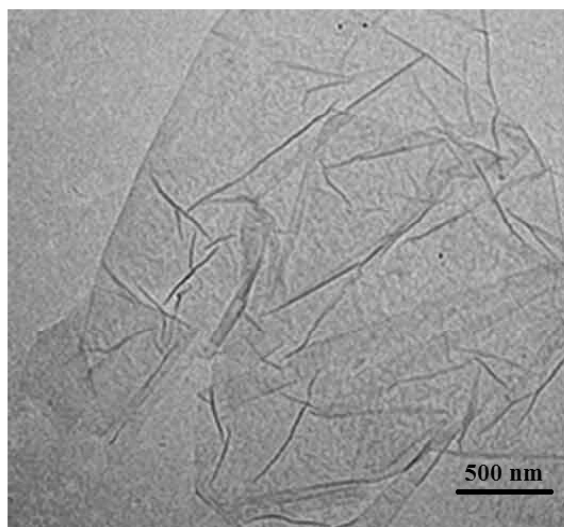

Fig. 3. TEM image for graphene oxide.

to generate a series of thickness statistics [36]. Single-layer graphene can be observed as transparent sheets by TEM analysis. When graphene sheets were fold back, cross-sectional can be viewed and the number of layers can be measured using TEM at several locations [37]. Monolayer and bilayer folded graphene can be observed as one and two dark lines, respectively when the folded graphene sheet are placed parallel to the electron beam [38]. A more accurate identification way of number of graphene layer can be determined by nanoarea electron diffraction patterns by changing incidence angles between the electron beam and the graphene sheet [36,39]. Fig. 3 shows the TEM images of graphene oxide.

4. APPLICATION OF GRAPHENE OXIDE TO WASTEWATER TREATMENT

Graphene, which can be used as nanosorbents, is typically made of one and/or several atomics layered carbon atoms, and possesses special two-dimensional structure and good mechanical, thermal and electrical properties [40,41]. Using van der Waals' forces and p – p stacking interactions, the adsorption of dyes on few-layered graphene oxide nanosheets (GONSs) could be realized. To modify the chemical and physical properties and improve the processability of graphene nanosheets/graphene oxide nanosheets (GNSs/GONSs), GNSs/GONSs could first be incorporated into composite materials. Whether, a GNSs layer or a single GONSs layer, the high aspect ratio and large ð-electronic surface provide strong intermolecular forces among these layers and adsorbates [42] . Due to the opened-up layer structure, GNSs would exhibit markedly faster adsorption kinetics than CNTs [43,44].

Experimentally, a comparison between pristine GNSs and GONSs with coal base AC (HD4000), SWCNTs and MWCNTs, GNSs and GONSs, the former exhibited better adsorption capacities for two synthetic organic compounds (SOCs; phenanthrene and biphenyl) in aqueous solutions [45] . More importantly, GNSs are much cheaper than SWCNTs [46] . GNSs have already been used as adsorbents for the removal of cationic red X-GRL [47], MB [48,49] , methyl orange (MO) [50] , Congo red (CR) [51], and other organic materials from aqueous solutions. The maximum adsorption capacities of p-toluenesulfonic acid (p-TA), 1-naphthalenesulfonic acid (1-NA) and MB on GNS reach up to 1430

mg·g^{-1}, 1460 mg·g^{-1} and 1520 mg·g^{-1} at 303K, respectively, which are the highest among all of the current nanomaterials [52]. The observed adsorption capacities for the adsorption of three types of pesticides, chlorpyrifos (CP), endosulfan (ES), and malathion (ML), onto GONSs and GNSs from water are as high as 1200, 1100, and 800 mg·g^{-1}, respectively, and GONSs and GNSs were unprecedented substrates for these adsorption technologies [53].

The few-layered GONSs through the modified Hummers' method have been synthesized [54]. These GNSs can be used as sorbents for the removal of Cd(II) and Co(II) ions from aqueous solution [54]. It was reported that heavy metal ions sorption on nanosheets is dependent on pH, ionic strength [54]. The abundant oxygen-containing functional groups on the surfaces of graphene oxide nanosheets were reported to play an important role on sorption [[54].

Magnetite-graphene composite adsorbents with a particle size of ~10 nm was reported to give a high binding capacity for As(III) and As(V) [55]. The high binding capacity was resulted due to the increased adsorption sites in the graphene composite [55]. The strong functional groups on graphene oxide (GO) surface, makes it a potential adsorbent for metal ion complexation through both electrostatic and coordinate approaches. Generally, GO showed high adsorption capacity on cationic metals. GNSs can be used for adsorption of both cationic and anionic metals. After modification of GO with organics or metal oxides, its composites can also be used for anionic metal removal due to functionalization. Cu(II)-GO interaction in aqueous solution showed that Cu(II) causes GO sheets to be folded and form large aggregates [56]. The coordination between Cu(II) and oxygen atoms on GO was the primary driving force. GO has a Cu(II) adsorption capacity of 46.6 mg·g^{-1}, higher than that of CNTs (28.5 mg·g^{-1}) and AC (4-5 mg·g^{-1}) [56] .

The removal of Cd(II) [54,57], Co(II) [54], Pb(II) [57,58], and U(VI) [59] ions from aqueous solutions have been studied using few-layered GONSs. It was found that the abundant oxygen-containing functional groups on GONSs surfaces play an important role in metal sorption which was in agreement with the results of Zhao et al., [54]. It was also reported that Cd(II) and Co(II) sorption on GONSs is strongly dependent on pH and weakly dependent on ionic strength. The presence of humic acid reduced Cd(II) and Co(II) sorption on GONSs at pH < 8. The maximum sorption capacities of Cd(II) and Co(II) on GONSs at pH 6.0 and 303K were about 106.3 and 68.2 mg·g^{-1}, respectively. For Pb(II), the maximum

adsorption capacities were about 842, 1150, and 1850 mg·g^{-1} at 293, 313, and 333K, respectively [58], but sorption capacity of U(VI) at pH 5.0, 293K was 97.5 mg·g^{-1} [59].

Modification of GO with organic materials can change the surface functional groups for better adsorption of various metal ion species. A modified GO with thiol (SH) groups by diazonium chemistry was reported to adsorb 6-fold higher concentration of Hg(II) ions than GO and AC [60]. When N-(trimethoxysilylpropyl) ethylenediamine triacetic acid (EDTA-silane) was used to obtain a chelating GO for Pb(II) removal, the adsorption was fast and completed within 20 min, with an adsorption capacity of 479 mg·g^{-1} at pH 6.8 [61]. Compared to AC and CNTs, GO and GNs present stronger adsorption for many water pollutants.

5. CONCLUSIONS

In this study we summarize present and discusses the past and current advancement of synthesis and characterization of GO from graphite. Graphen based nanomaterials have advantages over conventional materials in various environmental applications. The development of cost-effective and highly efficient manufacturing routes may find the entry point to integrate graphene into traditional water treatment processes. In brief, the following conclusions can be drawn based on the above discussions: (1) GO can act as more effective adsorbent than CNTs and activated carbon in terms of larger adsorption capacity, superior adsorption selectivity, shorter equilibrium time and easier regeneration. The adsorption potential of GO can be predicted using molecular simulations. (2) GO can serve as efficient catalyst support owing to their high electrical conductivity, high strength and adsorption capacity.

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