Facile synthesis of soluble functional graphene by reduction of graphene oxide via acetylacetone and its adsorption of heavy metal ions
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Abstract

The synthesis of graphene (GR) from graphene oxide (GO) typically involves harmful chemical reducing agents that are undesirable for most practical applications. Here we report a green and facile synthesis method for the synthesis of GR that is soluble in water and organic solvents and that includes the additional benefit of adsorption of heavy metal ions. Acetylacetone, as both a reducing agent and a stabilizer, was used to prepare soluble GR from GO. Transmission electron microscopy and atomic force microscopy provide clear evidence for the formation of few-layer GR. The results from Fourier transform infrared spectroscopy and ultraviolet-visible spectroscopy show that reduction of GO to GR has occurred. Raman spectroscopy and X-ray photoelectron spectroscopy also indicate the removal of oxygen-containing functional groups from GO, resulting in the formation of GR. The results of dispersion experiments show that GR can be highly dispersed in water and N,N-Dimethylformamide. The reaction mechanism for acetylacetone reduction of exfoliated GO was also proposed. This method is a facile and environmentally friendly approach to the synthesis of GR and opens up new possibilities for preparing GR and GR-based nanomaterials for large-scale applications. Of even greater interest is that inductively coupled plasma atomic emission spectroscopy suggests that synthesized GR may be applied in the absorption of Cd$^{2+}$ and Co$^{2+}$ due to the strong coordination capacity of acetylacetone on the surfaces and edges of GR and the large surface area of GR in aqueous solutions. The maximum adsorptions are 49.28 mg g$^{-1}$ for Cd$^{2+}$, which is 4.5 times higher than that of carbon nanotubes, and 27.78 mg g$^{-1}$ for Co$^{2+}$, which is 3.6 times higher than that of titania beans.

Keywords: graphene, acetylacetone, graphene oxide, adsorption

1. Introduction

Ever since graphene (GR) was discovered in 2004, it has been one of the most sought-after materials in the scientific community because of its unique chemical and physical properties, such as large surface area (theoretical surface area as high as 2630 m$^2$ g$^{-1}$) and high electrical conductivity (calculated to be about 6400 S cm$^{-1}$) [1, 2]. It can be applied in dye-sensitized solar cells [3], catalysis of Knoevenagel condensation [4], fuel cells [5], analytical sensors [6], and so on. In recent research, the aforementioned analytical sensors have mostly been used in the detection of metal ions [7] and other molecules such as H$_2$O$_2$ [8] by using the electrochemical or fluorescent properties of the functional groups in GR [9, 10]. GR can act as an electrode or as macromolecules, directly detecting trace amounts of metal ions or target molecules. However, there is little research regarding adsorption of metal...
ions by means of the coordination capacity of the reducing agent.

Common synthetic methods for GR have been documented in numerous articles; these methods include exfoliation [11], chemical vapor deposition (CVD) [12], arc discharge [13], and reduction [14]. Common reduction methods include, among others, electrochemical reduction [15], photocatalytic reduction [16], thermal reduction [17], and chemical reduction [18]. Moreover, the normal chemical reduction method is used to prepare GR, that is, by the reduction of graphene oxide (GO) using reducing agents such as hydrazine, dimethylhydrazine, and sodium borohydride [19]. However, these reducing agents are highly toxic, so trace amounts of these poisonous agents can have a detrimental effect, especially in biomedical applications. Therefore, environmentally friendly chemical reduction methods urgently need to be developed. In addition, a common mechanism for chemical reduction is that the reducing agents lose electrons, whereas GO sheets act as electron-accepting monomers [20]. Chemical reduction is a large-scale and economical way to prepare GR. There are various functional groups or reducing agents on the surfaces or edges of the obtained GR sheets. The molecules that bind to GR with unique properties, such as fluorescence or coordination, can be used to absorb or detect metal ions.

In this paper, acetylacetone (Hacac), whose pKa is about 8 – 9 [21, 22], is used to reduce GO to GR in an alkaline environment for the first time. This method has many advantages. For example, Hacac is cheap and safe, no hazardous waste is generated, the process does not require a tedious procedure, and the colloidal route is currently considered the most attractive option for many other prospective applications of GR. Hacac is used as a coordination agent to form coordination complexes that can be used as precursors to prepare nanoparticles [23] and detect heavy metal ions [24]. In addition, Hacac possesses strong coordination capacity with respect to most inorganic metal ions—especially heavy metal ions—so Hacac functionalized on the surfaces and edges of GR may be used to absorb the heavy metal ions Cd$^{2+}$ and Co$^{2+}$. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is used to measure the adsorption amounts of Cd$^{2+}$ and Co$^{2+}$. A schematic diagram of reduction of GO using Hacac and its ion adsorption is shown in figure 1.

![Figure 1. Schematic diagram of reduction of GO using Hacac and its ion adsorption.](image)

2. Experiment details

2.1. Materials

High-purity natural graphite (99.99%, 500 mesh) was obtained from Qingdao Tianyuan Graphite Co., Ltd (Shandong, China). All chemicals were of analytical-reagent grade and were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), without further purification. Deionized water with a resistivity of 18.1 MΩ cm was used for all experiments.

2.2. Preparation of GR with Hacac

GO was prepared using a modified Hummers method [25, 26], which was similar to our previous work [27, 28]. The typical procedure was as follows: 2 g of graphite and 50 mL of concentrated sulfuric acid were added into a 250 mL flask. The mixture was stirred vigorously for 30 min. Next, 5 g of NaNO$_3$ were added, followed by cooling of the mixture to 0 °C using an ice water bath. After continuous stirring for 2 h, 7.3 g of KMnO$_4$ were added in small portions over the course of 1 h. Subsequently, the system temperature was increased to 35 °C. The reaction was allowed to take place for 2 h and was then quenched by adding 0.2 L of ice water and 7.0 mL of H$_2$O$_2$ (30%). The resultant GO was filtered and washed with plenty of aqueous HCl (3%) until no precipitation of BaSO$_4$ occurred in the presence of the aqueous BaCl$_2$ solution. Further washing with water was carried out until the chloride test with AgNO$_3$ was negative. The resultant products were dried at 40 °C for 24 h in a vacuum oven.

GR was reduced from GO by using Hacac as the reducing agent. Typically, 0.10 g GO was sonicated in 250 mL...
deionized water. 2 mL Hacac were added into this solution, and then the pH of the solution was adjusted to 10 using ammonia aqueous solution. Subsequently, the solution was continuously stirred at 80 °C for 24 h. Next as-prepared GR was washed with water, acetone, and ethanol several times and finally dried in air at 50 °C overnight.

2.3. Adsorption of heavy metal ions

2.3.1. Single metal ion equilibrium adsorption. 50 mg GR were individually added to a series of 100 mL Cd^{2+} and Co^{2+} aqueous solutions with different concentrations from 0.2 to 40 mg L\(^{-1}\) for Cd^{2+} and 0.2 to 50 mg L\(^{-1}\) for Co^{2+}. The pH value of the solutions was adjusted to 6.0. The suspension was allowed to remain magnetically stirred for 4 h. Then the solution was filtered with a 0.22 \(\mu\)m filter membrane. The concentrations of Cd^{2+} and Co^{2+} in the filtrate were detected by ICP-AES.

2.4. Effect of pH on adsorption

The concentrations of Cd^{2+} and Co^{2+} were maintained at 40 mg L\(^{-1}\) and 30 mg L\(^{-1}\), respectively. 50 mg GR were individually added to this solution by adjusting the pH values from 3.0 to 9.0. Then the solution was magnetically stirred for 4 h and filtered with a 0.22 \(\mu\)m filter membrane. The concentrations of Cd^{2+} and Co^{2+} in the filtrate were detected by ICP-AES. The aforementioned adsorption experiments were carried out at room temperature.

2.5. Characterization

The morphology of GR was analyzed by field emission scanning electron microscope (SEM, Carl Zeiss Ultra 55, Germany) at 5 kV, transmission electron microscopy (TEM, JEM-2100, Japan), and atomic force microscopy (AFM, E-Sweep, SEIKO, Japan). GR was dispersed in water and then deposited on mica substrate for AFM measurement. For TEM observation, GR was dispersed in water and then deposited on 300 mesh carbon-coated Cu grids. Raman spectra were obtained by dispersive Raman microscope (Senterra R200-L, Bruker Optics, Germany) with an excitation wavelength at 532 nm. The functional groups in GR were analyzed by Fourier transform infrared spectrometer (FT-IR, VERTEX 70, Bruker Optics, Germany), with a detection range of 4000 to 400 cm\(^{-1}\). Ultraviolet-visible spectra (UV–vis, Lambda 500, PerkinElmer, USA) characterizations were carried out in the region from 250 to 800 nm. Thermogravimetric analysis (TGA, Pyris 1 TGA, PerkinElmer, USA) characterizations were used to analyze the thermal stability of graphite, GO, and GR in a nitrogen atmosphere under heat treatment from 30 to 900 °C. The heating rates of graphite, GO, and GR are 10, 1, and 10 °C min\(^{-1}\), respectively. ICP-AES (iCAP 6000 Radial, Thermo Fisher Scientific Inc., USA) was used to detect the concentrations of Cd^{2+} and Co^{3+}. X-ray photoelectron spectroscopy (XPS, PH1500C, Japan) was used to detect surface elements of GO and GR.

3. Results and discussion

Reduction of GO under different control conditions was carried out. GO aqueous solutions were added separately with Hacac, ammonia, and Hacac and ammonia at room temperature, 40 °C, 60 °C, and 80 °C for 24 h. It was found that the solution obviously turned black after the addition of Hacac and ammonia into the GO aqueous solutions at 80 °C for 24 h. At other temperatures and conditions, the color of the solution either did not change or changed slightly. Moreover, the reason for choosing 10.0 as the pH value of the solution was that Hacac can be transferred easily from keto to enol under alkaline conditions. We took UV–vis measurements to monitor the degree of reduction in the control experiments. As shown in figure 2, as the reduction progressed, the intensity of the UV–vis absorption peak was centered at 300 nm (this was caused by the GO), decayed gradually with the increase in reaction time, and disappeared after 24 h. Meanwhile, the absorption peak shown around 231 nm was redshifted with the increase in reduction time.

The dispersion of 0.7 mg mL\(^{-1}\) GR in different solvents is shown in figure 3. The solubility of Hacac-reduced GR in water is the best among all solvents. In nonpolar solvents such as acetone, the solubility is poorer, which is probably attributable to the interactions of nonpolar solvent molecules and...
the functional groups (such as Hacac) of GR. The homogeneous colloidal suspensions of GR are easily obtained in water and can be stable for several months.

The morphologies of GR were investigated by SEM, AFM, and TEM. The SEM image of solid GR in figure 4(a) shows that two or more layers are overlapped and wrinkled to display a silklke appearance and that a large number of grooves are formed by extrusion in order to reduce the surface energy of the GR. The size of the surface area of the GR is several tens of micrometers in length.

The thickness as measured by AFM is shown in figure 4(b), which illustrates that the thickness of the GR is about 0.7 nm as measured from the height profile. Although the interlayer spacing of graphite is 0.34 nm in theory, practical AFM measurements of a single GR layer on substrate always lead to high values due to the weak sample/substrate interactions and the presence of ambient species (nitrogen, oxygen, argon, or water) between the substrate and the GR [29]. Thus, based on GR thicknesses reported in other works [25, 30], as-prepared GR is considered to be monolayer.
TEM images and the selected area electron diffraction (SAED) pattern shown in figures 4(c) and (d) illustrate that the structural feature of as-prepared GR is that of a sheet. The low-magnification TEM image shown in figure 4(c) displays the wrinkled morphology of the GR, which may be attributable to the interaction between GR sheets. The size of an as-prepared GR sheet is several micrometers. The high-resolution TEM image in figure 4(d) shows that GR sheets tend to be stacked together. The SAED pattern of GR shows that the diffraction pattern is relatively diffused, which may be due to the fact that GR nanosheets are not perpendicular to the electron beam [31] or that chemically reduced GR has a few defects and the reducing agent molecules are functionalized on its surfaces and edges.

The structural changes of GR and GO were characterized by Raman spectra as shown in figure 5(a). Two typical feature peaks of GR are exhibited in the Raman spectra. The peak at 1344 cm$^{-1}$ is the D mode of GR, which arises from the breathing mode of the $A_{1g}$ symmetry. The peak at 1596 cm$^{-1}$ is G mode, arising from first-order scattering of the $E_{2g}$ photon of $sp^2$ C atoms. Change in the relative intensity between the D and G bands ($I_D/I_G$) indicates the change in the diffraction pattern is relatively diffused, which may be due to the fact that GR nanosheets are not perpendicular to the electron beam [31] or that chemically reduced GR has a few defects and the reducing agent molecules are functionalized on its surfaces and edges.

Functional groups of GO and GR can be corroborated and deduced from FT-IR spectra in figure 5(b). The peaks of GO are situated at 3447 and 1633 cm$^{-1}$, corresponding to hydroxyl groups on the surface of GO and aromatic C=C bonds, respectively. The peak at 997 cm$^{-1}$ is ascribed to the $=$C-H out-of-plane wagging vibration. The IR spectrum of GR at 3500 $\sim$ 3240 cm$^{-1}$ and 1580 cm$^{-1}$, corresponding to associated hydroxyls and the stretching vibration of C=O, which is blueshifted due to C=C conjugated to C=O. It is verified that Hacac acts as functional groups of as-prepared GR. The intensities of the bands associated with oxygen functional groups greatly decrease relative to those of unreduced GO.

UV–vis spectra are shown in figure 5(c). The maximum absorption peak of GO, which is situated at 300 nm, is attributable to $\pi-\pi^*$ electron transition of C=O bonds. The characteristic absorption peak of Hacac located at 274 nm is attributable to conjugated C=C and $\pi-\pi^*$, or n-$\pi^*$ electron transition. The absorption peak of as-prepared GR is blue-shifted, attributable to Hacac functionalized on the surfaces and edges of GR.

The thermal stability of pristine graphite, GO, and GR was analyzed by TGA in a nitrogen atmosphere. As shown in figure 5(d), the weight of the graphite starts to decrease at 617 °C due to the decomposition of the carbon skeleton. It can be seen that the curve of GO has three drops. The weight losses at 137 and 207 °C are ascribed to the decomposition of labile oxygen functional groups of as-prepared GO, yielding CO, CO$_2$, and H$_2$O [35]. The weight loss curve of GO starting at 538 °C is lower than that of GR, which demonstrates that
there are more functional groups in GO than in GR. Moreover, the first drop in the GR curve at 178 °C is attributed to the hydroxyl groups on the basal plane of the GR. It exhibits only a little loss at 254 °C, which is much lower than for GO, indicating a significant decrease in oxygenated functional groups. The later steep drop at 594 °C is caused by the pyrolysis of the remaining oxygen-containing groups as well as the burning of the carbon skeleton. The decomposition temperature of GR (594 °C) is higher than that of GO (538 °C), indicating the removal of the thermally labile oxygen functional groups by chemical reduction, which leads to the enhanced thermal stability of GR.

Figure 6 shows the C1s XPS spectra of GO and GR. Before reduction, four different peaks shown in figure 6(a) centered at 284.8, 286.9, 287.8, and 289.1 eV, corresponding to C=C/C-C in aromatic rings, C-O (epoxy and alkoxy), C=O, and COOH groups, respectively, are detected. After the reduction with Hacac and ammonia for 24 h, as shown in figure 6(b), the intensities of all C1s peaks of the carbon binding to oxygen, especially the peak of C-O (epoxy and alkoxy), decreased dramatically, revealing that oxygen-containing functional groups are removed after reduction [25]. In addition, a new peak at 285.5 eV, corresponding to the C-N group, appears due to the collaborative reduction of Hacac and ammonia [36].

The formation mechanism of GR by reduction of GO via Hacac is shown in figure 7. Epoxy groups of GR are changed into the double bonds, leaving Hacac molecules to increase the stability of GR [32].

3.1. Adsorption of heavy metal ions

Single metal ion equilibrium adsorption studies were conducted to investigate the maximum metal adsorption capacities of carbon nanotubes. The adsorption isotherm of Cd^{2+} and Co^{2+} by obtained GR is shown in figure 8(a). It is observed that the amount of adsorbed Cd^{2+} and Co^{2+} increases significantly in the range of low equilibrium concentration; it then increases gradually and reaches 51 mg g^{-1} for Cd^{2+} and 26 mg g^{-1} for Co^{2+} at an equilibrium concentration of 15 mg L^{-1}. 
A linear Langmuir adsorption isotherm model is used to calculate the maximum adsorption amount of Cd$^{2+}$ and Co$^{2+}$. The Langmuir absorption equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$

where $C_e$ stands for the equilibrium concentration of Cd$^{2+}$ or Co$^{2+}$ (mg/L), $q_e$ is the adsorption amount (mg/g), $q_m$ stands for the maximum adsorption capacity corresponding to complete monolayer coverage (mg/g), and $b$ represents the Langmuir constant indirectly related to the energy of adsorption (L/mg). The Langmuir parameters of GR adsorption of Cd$^{2+}$ and Co$^{2+}$ are calculated and summarized in table 1. The correlation coefficients, $r^2$, are high and close to 1, suggesting that the experimental data can be represented by the Langmuir adsorption and that the adsorbed metal ions form monolayer coverage on the surfaces of the GR.

The effect of pH on the adsorption of Cd$^{2+}$ and Co$^{2+}$ in GR is shown in figure 8(b). When the pH value is lower than 5.0, the adsorption capacity increases with the increase in pH, which leads mainly to the conclusion that the enol form of Hacac occurs prior to the forming of the coordination complex with Cd$^{2+}$ and Co$^{2+}$ in GR. However, the adsorption amount remains almost unchanged as pH values increase from 5.0 to 6.0. Therefore, the pH value 6.0 is chosen as the optimum condition. As the pH values increase from 6.0 to 9.0, the adsorption capacity increases gradually; this may be due to the combined role of adsorption and precipitation.

The adsorption capacities of Cd$^{2+}$ and Co$^{2+}$ by GR were compared with those of other adsorbents (table 2, with the data collected under different conditions). The Cd$^{2+}$ adsorption capacity of Fe$_3$O$_4$/MnO$_2$ nanocomposite [40] and the Co$^{2+}$ adsorption capacity of copolymer 2-hydroxyethyl methacrylate with monomer methyl methacrylate [41] are higher than that of our GR. The metal removal capacities of the other adsorbents such as carbon nanotubes, biosorbent [39], granular

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Table 1. Langmuir parameters of single adsorption isotherm models for Cd$^{2+}$ and Co$^{2+}$ in GR.

<table>
<thead>
<tr>
<th>Types of ions</th>
<th>$q_m$ (mg g$^{-1}$)</th>
<th>b (L mg$^{-1}$)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$^{2+}$</td>
<td>49.28</td>
<td>7.8</td>
<td>0.99902</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>27.78</td>
<td>3.1</td>
<td>0.99578</td>
</tr>
</tbody>
</table>

Figure 8. (a) The adsorption isotherm of GR for Cd$^{2+}$ and Co$^{2+}$ at pH 6.0 and (b) the effect of pH on the adsorption of Co$^{2+}$ and Cd$^{2+}$ by GR.

Table 2. Comparison of individual Cd$^{2+}$ and Co$^{2+}$ adsorption capacities of different adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Cd$^{2+}$ (mg g$^{-1}$)</th>
<th>Co$^{2+}$ (mg g$^{-1}$)</th>
<th>Conditions</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>49.28</td>
<td>27.78</td>
<td>pH 6.0; RT$^1$</td>
<td>our data</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>10.86</td>
<td>—</td>
<td>pH 5.0; RT 37</td>
<td>37</td>
</tr>
<tr>
<td>Biosorbent</td>
<td>24.3</td>
<td>—</td>
<td>pH 4.7; 293 K</td>
<td>39</td>
</tr>
<tr>
<td>Granular AC$^2$</td>
<td>3.37</td>
<td>—</td>
<td>pH 5.0; 303 K</td>
<td>39</td>
</tr>
<tr>
<td>Powdered AC</td>
<td>3.37</td>
<td>—</td>
<td>pH 5.0; 303 K</td>
<td>39</td>
</tr>
<tr>
<td>Titania beans</td>
<td>8.94</td>
<td>7.62</td>
<td>pH 5.9; RT 38</td>
<td></td>
</tr>
<tr>
<td>Fe$_3$O$_4$/MnO$_2$</td>
<td>53.2</td>
<td>—</td>
<td>PH 6.3; RT 40</td>
<td></td>
</tr>
<tr>
<td>Nanocomposite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PHEMA$^3$</td>
<td>—</td>
<td>0.74</td>
<td>pH 6; 303 K</td>
<td>41</td>
</tr>
<tr>
<td>P(MMA-HEMA)$^4$</td>
<td>—</td>
<td>28.84</td>
<td>pH 6; 303 K</td>
<td>41</td>
</tr>
</tbody>
</table>

1 RT stands for room temperature.  
2 AC stands for activated carbon.  
3 PHEMA stands for poly 2-hydroxyethyl methacrylate.  
4 P(MMA-HEMA) stands for copolymer 2-hydroxyethyl methacrylate with monomer methyl methacrylate.

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activated carbon (AC), powdered AC, titania beans, and poly 2-hydroxyethyl methacrylate are lower than those of our GR. The comparison suggests that GR has great potential for use in heavy metal ion adsorbents in wastewater treatment.

4. Conclusions

In summary, a green and facile approach to preparing soluble GR has been developed via a new reducing agent, Hacac, which acts as both reducing agent and stabilizer during the formation of GR. Moreover, Hacac is an excellent coordination agent that can coordinate with most metal ions. The maximum adsorption of obtained GR is 49.28 mg g⁻¹ for Cd²⁺, which is 4.5 times higher than that of carbon nanotubes, and 27.78 mg g⁻¹ for Co²⁺, which is 3.6 times higher than that of titania beans. The greater capacity of GR to adsorb Cd²⁺ and Co²⁺ may be attributed to the strong coordination capacity of Hacac on the surfaces and edges of GR and the large surface area of GR in aqueous solutions. Therefore, we expect that our findings will further the preparation of high-quality GR and GR-based nanocomposites and significantly facilitate the application of GR in water pollution treatment and environmental protection.

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