Investigation on the Room-temperature preparation of Cobalt hybrid/Graphene Nanocomposite and application in wastewater purification: Highly Efficient Removal of Congo Red

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Abstract. Here, we are going to report a simple, low-cost and environmental friendly process to prepare the cobalt hybrid/graphene (Co/G) nanocomposite at room temperature. NaBH₄ was used as the reducing agent. Such an approach can be extended to grow some other metal/G nanocomposites, for example, Ni/G, Co/G nanocomposite possesses narrow size-distribution and good dispersion. Because of the special appearance with large surface area, and the special synthesis process of the productions, adsorption experiments for Congo Red were carried out in synthetic wastewater. The CR removal ability of Co/G nanocomposite can reach 263.2 mg/g.

1. Introduction

As an excellent two-dimensional material, graphene (G) has unusual features excellent thermal property and fracture strength, high specific surface area and charming spin transport. In composite G chip also can be used as electrical conduction channel, so as to improve the conductivity of the material and greatly reducing ohmic losses [1-5]. In addition, graphene has the G slice of its unique structure and excellent softness can not only provide enough space volume change, reduce buffer volume change brought about by the pressure, can also prevent Co particles gathered in circulation process, reduce the electrode degradation [6-7]. Rich electronic Co atoms, of course, the electrostatic attraction between the surface of Co can be firmly fixed G, combined with stability of the composites. The most important of all, the performance of the G can also with Co nanoparticles modified further strengthened. Because of the π - π interaction between adjacent slices, G in use process usually serious phenomenon of reunion. Co nanoparticles exists between G, effectively prevent G piece together, to maintain their highly active surface area, to improve G lithium storage capacity of composite materials [8-10]. Recently, Co₃O₄/grapheme [11], Co(OH)₃/graphene and Co/G composites have been synthesized and applied to lithium ion batteries [12-14]. Preparation of cobalt/graphene(CoG) composite is rare at room temperature.

Will G and Co nanoparticles composite is a suitable method, will compound used as a lithium-ion battery anode active material with high reversible lithium storage capacity and coulomb efficiency. This kind of Co/G nanocomposite provides a unique performance, to improve the prospect of application and extension provides greater.
In addition to as lithium ion battery anode material, the Co/G nanocomposite ability to remove dyes from aqueous solution are also studied. Co/G nanocomposite material has high magnetic, provides efficient separation after removing Congo red (CR) possible suspension. Nanocomposites are large specific surface area is conducive to the adsorption CR in the solution.

In this article, through the simple a pot of hydrothermal synthesis method of synthesis of Co/G nanocomposite, this method can be extended to other metal/G the synthesis of nanocomposites. In this method, sodium borohydride as reducing agent, the oxidation of graphene (GO) and CoCl$_2$ in the process of hydrothermal reduction at the same time. Co nanoparticles dispersed homogeneously in G nanocomposite structure is beneficial to inhibit gathered, thus provide higher available surface area and enhanced the lithium storage capacity and adsorption.

2. Experimental section

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2.1. Sample Preparation

The graphite oxide (GO) was synthesized from natural graphite powder based on a modified Hummers method [15], specific preparation method is as follows: natural graphite powder weighing 1.0 g and 6.0 g KMnO$_4$ into the mixture of concentrated of 9:1 H$_2$SO$_4$/H$_3$PO$_4$ (120:13.3mL) in the mixed acid, heated to 50 °C, the mechanical stirring 12 h. Reaction after cooling to room temperature, add about 400 mL ice, drip into the 3 mL30 % H$_2$O$_2$. Centrifugal separation after 20 min (10000 RPM), clean with 5% HCl solution, and then use distilled water cleaning and centrifugal separation for many times, make pH neutral. Finally, the synthesis of uniform GO solution, after the vacuum drying for characterization and further chemical reactions.

Preparation Cobalt/graphene nanocomposite (Co/G): use of NaBH$_4$ as a reducing agent by hydrothermal synthesis of Co/G nanocomposites. First of all, 15 mg GO dissolved in 15 ml of distilled water, using ultrasonic stirring 30 min to exfoliate oxidized graphite particles to GO sheets. Then 0.1 g of CoCl$_2$·6H$_2$O dissolved in 5 ml of distilled water, and add to GO solution, ultrasonic stirring for 1 hour. Then 0.1 g NaBH$_4$ dissolved in 5 ml of distilled water, one drop to join the GO and CoCl$_2$ solution, and continue to ultrasound for 30 min at room temperature. The reaction is responsive quickly. A black material formed in the bottom of the beaker and followed along with the generating gases. After the reaction of hydrogen generation was completed, the black material was magnetically attracted to the bottom of the beaker by a magnet, removed the upper solution and washed twice with deionized water and ethanol. Black Co/G nanocomposites were prepared.

2.2. Materials Characterizations

The phases were identified by means of X-ray diffraction (XRD) with a Rigaku D/max 2500pc X-ray diffractometer with Cu Kα radiation ($\lambda$) 1.54156 (Å) at a scan rate of 0.02°/1(sec), morphologies were characterized by a JEOL JSM-6700F field emission scanning electron microscopy (FESEM) operated at an acceleration voltage of 8.0 kV. The hysteresis loops were measured on a VSM-7300 vibrating sample magnetometer (VSM) (Lakeshore, USA) in room temperature. An Agilent Cary 50 UV–vis spectrophotometer was used for determination of CR concentration in the solutions.

2.3. Batch adsorption experiments

Stock solution preparation: Congo red is the chemical name of diphenyl - 4, 4 ' - (azo - 2 -) 2-1 - amino naphthalene - 4 - sodium sulfonate, molecular formula is C$_{32}$H$_{27}$N$_2$Na$_2$O$_4$S$_2$ [16], structured as shown in figure 1 [17]. Accurate weighing Congo red dissolved in distilled water, using volumetric flask configuration 1 g·L$^{-1}$ mother liquor as a stock solution.
Figure 1. Structure of Congo red molecule.

Using UV–vis spectrophotometer at lambda max = 497 nm (maximum absorbance value of CR) test known absorbance value of different concentration of CR, determine the standard curve. Determination of adsorption quantity: according to take a certain amount of magnetic powder (W), added to the known concentration (C₀) of a certain volume (V) of Congo red solution, using mechanical mixing device, every once in a certain time interval (t) using the magnet to absorb magnetic powder, will pour into the upper Congo red solution than color plate, using UV–vis spectrophotometer to measure the concentration of a solution of CR (Cₜ). After measuring, recording, the colorimetric dish fell back to the original beaker of solution, continue to stir, measurement, until adsorption reached equilibrium. The adsorption of CR (qₜ) used to calculate the following formula:

$$ qₜ = \frac{(C₀ - Cₜ)V}{W} $$

where qₜ is per gram of adsorbent adsorption ability in time t time, mg·g⁻¹; C₀ is the initial concentration of Congo red solution, mg·dm⁻³; Cₜ is t moment of Congo red solution concentration, mg·dm⁻³; V is the volume of a solution, dm³; W is the quality of magnetic powder, g.

Standard solution with initial concentrations of 150 mg/L was prepared. Then, 10 mg of Co/G nanocomposite was added to 50 mL of above solution under stirring. After a specified time, the solid and liquid were separated by a magnet.

3. Results and discussion

3.1. Structural and Morphological Characterization

Briefly, the Co/G nanocomposite was prepared using a very facile reduced method at room temperature. The crystal structure was further investigated by XRD technique. Figure 2a and 2b is graphite, GO and Co/G nanocomposite of XRD diagrams. Graphite in 26.4° and 54.6° diffraction peak corresponding is graphite (002) and (110) crystal plane (figure 2a). After oxidation treatment, graphite (002) diffraction peak disappear, a GO at 2θ = 11.4° (figure 2a). Figure 2b compared with pure Co nanoparticles XRD figure, was found at 2θ=26.0° added a weak and wide (002) diffraction peak, it is caused by G nano of accumulation [18]. Nevertheless, the broad nature of the reflection indicates poor ordering of the nanosheets along the stacking direction, implying that the sample is composed of mostly few layers of G nanosheets [19, 20]. The diffraction peaks for the as-formed sample at 2θ =41.63, 44.57, 47.51, and 75.97°, which match the reflection planes of (100), (002), (101), and (110), respectively, could be indexed to a pure hcp-Co (JCPDS 05-0727).

Figure 2. (a) XRD patterns of Graphite and GO; (b) XRD pattern Co/G nanocomposite.
The Co nanoparticles with a mean diameter of about 20-100 nm are closely and homogeneously anchored on the surface of G nanosheets (figure 3). A folding nature of G is clearly visible from figure 3, the relatively light area is due to the stacking of several G nanosheets.

**Figure 3.** SEM image of Co/G nanocomposite.

3.2. Magnetic Properties
By using VSM magnetic performance of Co/G nanocomposite was measured. From figure 4 room temperature measuring hysteresis loop can be determined, Co/G nanocomposite of saturation magnetization (Ms) is 57.5 emu·g$^{-1}$, coercive force (Hc) is 667.6 Oe. Ms value of Co/G is lower than Co nanoparticles, and the Hc value is higher than Co nanoparticles. Ms value is lower due to the complex of nonmagnetic material graphene. The Hc value increased significantly, it is because of constraints in G wafer Co nanoparticles of the influence of the rotation of the magnetic vibrator. The result is need to change the alignment of the direction of magnetization of the dipole energy increase the intensity of magnetic field (or higher). Therefore, Co/G nanocomposite exhibited higher Hc [21, 22].

**Figure 4.** Magnetization curve measured at room temperature of Co/G nanocomposite.

3.3. Evaluation of CR Removal Ability
Because of the Co/G nanocomposite material with high specific surface area and magnetic, would be an ideal adsorbent for sewage treatment. Herein, the Co/G nanocomposite was used to remove CR from aqueous solution. The CR removal abilities of Co/G nanocomposite were shown in figure 5. Aqueous solutions with initial CR concentration 150 mg/L was used for the experiment at neutral pH=7, adsorption different time from 0 to 150 minutes, and T = 15 °C. The final CR removal ability of
Co/G nanocomposite is 263.2 mg/g. The maximum adsorption capacity (q_{max}) of Co/G nanocomposite for CR is listed in Table 1 with literature values of q_{max} of other magnetic materials for CR adsorption [23-26]. The adsorption efficiency is far higher than the values as reported in the literatures. In addition, Co/G nanocomposite loaded with CR can be quickly separated by a magnet, and then leaves a clear and colorless solution (Insets of Figure 5).

![Figure 5](Inserts of Figure 5).

**Figure 5.** Removal ability for CR on Co/G nanocomposite. Insets: photos of initial CR solution, with Co/G nanocomposite treatment and magnetic separation.

| Adsorbent (nanoscale)         | q_{max} [mg g^{-1}] | Reference   |
|-------------------------------|----------------------|-------------|
| Co/G nanocomposite            | 263.2                | This study  |
| Fe_{3}O_{4}                   | 208.3                | [23]        |
| Magnetic core–MnO shell       | 42.0                 | [24]        |
| Fe_{2.97}La_{0.03}O_{4}        | 107.6                | [25]        |
| CoFe_{2}O_{4}                 | 244.5                | [26]        |
| Fe_{3}O_{4}                   | 149.7                | [26]        |
| NiFe_{2}O_{4}                 | 97.1                 | [26]        |
| MnFe_{2}O_{4}                 | 92.4                 | [26]        |

**Table 1.** Adsorption capacities of CR dye on various adsorbents.

4. Conclusions
We have presented a facile one-pot method for the synthesis of Co/G nanocomposite based on a simple reduction process using NaBH₄ as reducing agent at room temperature. Uniform Co nanoparticles embedded in G matrix of Co/G nanocomposite are excellent magnetic properties. Furthermore, the regular magnetic properties and high specific surface area of Co/G nanocomposite also make it have a potential application in the field of water treatment.

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