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Synthesis and characterization of graphene oxide composite with Fe_3O_4

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In the paper, a magnetic composite of graphene oxide (MGO) has been successfully synthesized through decomposition of iron (III) acetylacetonate in the mixture solution of triethylene glycol and graphene oxide (GO). Atomic force microscopy (AFM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and superconducting quantum interference device were used to characterize the material. The results show that the magnetic Fe_3O_4 nanoparticles modified graphene oxide composite with superparamagnetic properties, and magnetization saturation of 16.4 emu/g has been obtained. The MGO has a good sustained-release performance, and in vitro cytotoxicity confirming its secure use as a potential drug carrier.

Keywords: *graphene oxide; composite; magnetic* Fe_3O_4

1. Introduction

Nanomaterial-based drug carriers have been known as a bridge linking nanotechnology and advanced drug delivery systems because they can allow and realize efficient loading, targeted delivery, and controlled release of drugs [1–4]. Many drugs, especially cancer-therapy drugs, have toxic side effects. Loading these drugs in magnetic carriers could reduce their side effects, because they can make cancer-therapy drugs accumulation in cancer cells at the external magnetic field, thus, reducing the harm to normal cells.

GO has a large specific surface area, and its two hydrophobic polyaromatic basal planes make it possible to adsorb aromatic compounds, making GO an ideal host for drug delivery [4–7]. Recently, graphene oxide modified with iron nanoparticles has attracted much attention due to its promising applications in target drug delivery. Manjunatha et al. [8] firstly coated GO with sodium polystyrene sulfonate, and then obtained magnetic graphene oxide by high temperature decomposition of iron (III) acetylacetonate, and also studied the applications of magnetic resonance imaging. Chen et al. [9] prepared graphene-Fe_3O_4 nanocomposites under hydrothermal conditions, and studied the application of high-performance lithium ion batteries. Yang et al. [10] obtained graphene oxide – Fe_3O_4 nanoparticles by chemical precipitation method, loaded doxorubicin hydrochloride on it and studied targeted behavior under an influence of an external magnetic field. Herein, we report a facile method to prepare MGO by in-situ reduction of iron (III) acetylacetonate in the mixture solution of triethylene glycol and GO. The process was very simple, and GO did not need any modification. The toxicity of MGO to HeLa cells was also investigated.

2. Experimental

2.1. Materials

Native graphite flakes (48 μm, 99 %) were purchased from Changchun Graphite Limited Company. Iron (III) acetylacetonate ($Fe(acac)_3$, 99 %) was purchased from Sigma. Triethylene glycol (TREG, 99 %) was obtained from Aldrich. All other reagents used were of analytical grade.

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2.2. Synthesis of MGO nanoparticles

Graphene oxide was synthesized from native graphite flakes by a modified Hummers method [11, 12]. Different amounts of the iron precursor $Fe(acac)_3$ were dissolved in 25 mL TRGE, and then 100 mg of GO was added. After being sonicated for 10 min, the resulting mixture was then heated to 284 °C at a rate of 10 °C min^{-1} under vigorous stirring and argon protection, and the reaction was conducted for 30 min. After cooling to room temperature, 30 mL ethyl acetate was added to dilute the solution. Then the obtained composite was separated and washed with ethanol several times and dried in vacuum.

2.3. Characterization

AFM images were obtained using a Veeco Multimode Pico atomic force microscope in a tapping mode. Transmission electron microscopy (TEM) was performed with a JEOL-2100EX. XRD patterns were obtained using a powder X-ray diffractometer (Rigaku D/MAX-2500/PC). Magnetic properties were investigated by an atomic force microscope (SQUID, MPM-LX).

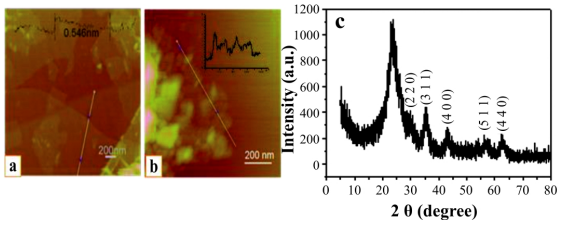

Fig. 1. AFM images of GO (a) and MGO (b), XRD pattern of MGO (c).

3. Results and discussion

Fig. 1 shows the AFM images of GO before (a) and after (b) modifying by Fe_3O_4. It is found that the obtained graphene oxide has an obvious lamellar structure, with an average height of 0.546 nm. Fig. 1b shows lots of nanoparticles attached on the lamellar structure of GO. Fig. 1c is the XRD pattern of MGO. The diffraction peak at 26° could be attributed to a native graphite flake. All the other diffraction peaks belong to the cubic inverse spinel Fe_3O_4 – the peaks match well with the (220), (311), (400), (422), (511), and (440) of Fe_3O_4.

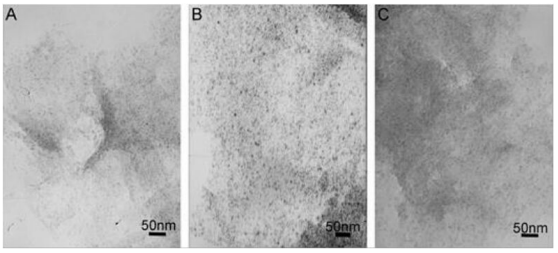

Fig. 2. TEM images of MGO with different quality of iron (III) acetylacetonate: (A) 100 mg (B) 150 mg (C) 200 mg.

The TEM images of MGO are presented in Fig. 2. It is clearly shown that nanoscale Fe_3O_4 particles are modified on the GO, and when the quantity of Iron (III) acetylacetonate increases, more Fe_3O_4 nanopartilces are attached on GO surface.

After acid oxidation, graphene oxide surface has many oxygen-containing functional groups, such as OH, C=O, C–OH. The hydrophilic property and static electricity of these groups make GO dispersed in water well. On the other hand, oxygen-containing functional groups are charged with negative electricity, while iron (III) acetylacetonate has a positive charge. So, Fe^{3+} ions are adsorbed on the surface of GO through electrostatic attraction, and then are restored to Fe_3O_4.

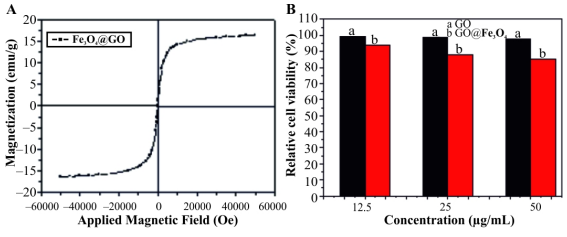

Fig. 3. (A) The room-temperature magnetization curves of MGO, (B) Relative cell viability of GO (a) and MGO (b) at different concentrations.

Magnetic properties of the MGO were investigated with a superconducting quantum interference device (MPM-LX). Fig. 3A shows room temperature magnetization of the MGO. It clearly indicates that the MGO has superparamagnetic properties

with the saturation magnetization of 16.4 emu/g, which indicates that the material has potential application in magnetic targeting drug delivery systems. MTT assays were performed to evaluate the cytotoxicity of GO and MGO at different concentrations. Fig. 3B shows relative cell viability of GO and MGO at different concentrations. The results reveal that the cytotoxicity of GO can almost be ignored. The cytotoxicity of MGO is slightly higher than that of GO, but as the concentration of MGO increases up to 50 μg/mL, cell viability is substantially constant at 88 %. Therefore, MGO can be considered as nontoxic.

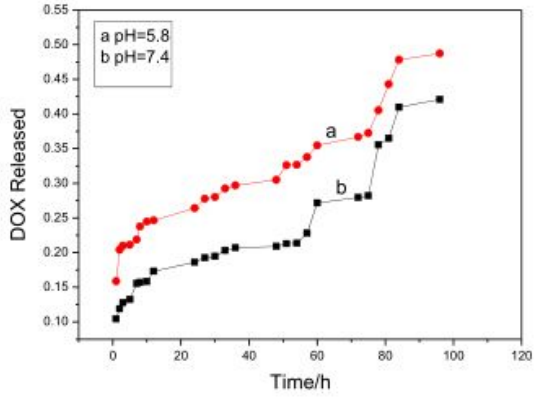

Fig. 4. The release of DOX from MGO at different pH conditions.

The release behavior of DOX from MGO is shown in Fig. 4. It shows that the MGO has a good sustained-release performance and strong pH dependence. After 96 h, the cumulative release rate is 48.73 % and 42.11 % at the pH of 5.8 and 7.4, respectively. This may be due to the stronger hydrogen-bonding interaction between MGO and DOX under basic conditions than that under acid conditions. This effect can be utilized to speed up the drug release inside cancer cells, since the microenvionments in extracellular tissues of tumors and intracellular lysosomes and endosomes are acidic [13].

4. Conclusions

In summary, MGO has been successfully prepared through decomposition of iron acetylacetonate in the mixture solution of triethylene glycol and GO. The obtained product showed a superparamagnetic properties with a saturation magnetization value of 16.4 emu/g. In vitro cytotoxicity confirmed that GO and MGO had no cytotoxicity to HeLa cells. The MGO has a great potential application in magnetic targeting drug-delivery technology.

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