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Synthesis of Fe_3O_4 nanoparticles on the surface of graphene

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The preparation of a new nanocomposite material consisting of magnetite nanoparticles on the surface of graphene using supercritical isopropanol as a reducing agent for graphene oxide was developed.

Nanoparticles (NPs) are of interest because of their unique size-dependent chemical and physical properties and potential applications.[1–3] Magnetite (Fe_3O_4) has a cubic inverse spinel structure with oxygen forming a face-centered cubic close packing and Fe cations occupying the tetrahedral and octahedral interstitial sites. Magnetite NPs are used in catalysis, data storage and bioapplications including magnetic resonance imaging, tissue repair, bioseparation, hyperthermia and targeted drug delivery.[4–6] Dispersions of magnetic NPs are known as ferrofluids. The magnetic properties of materials based on magnetite or other magnetic NPs can be controlled by varying the size, shape, composition and structure of NPs using different matrices.

On the other hand, graphene and graphene-based nanomaterials possess outstanding mechanical, electrical, thermal and optical properties and high specific surface areas.[7–9] Graphene and graphene oxide can serve as a matrix or ligand for various NPs,[10–12] including those of magnetite. The preparation of hybrid Fe_3O_4–graphene oxide and Fe_3O_4–graphene structures has been described.[13–18] However, the described methods include the decoration of magnetic NPs on reduced graphene oxide or involve rigid and toxic reducing agents, such as N_2H_4[17] and $NaBH_4$.[18]

Here, we report the new facile synthesis of Fe_3O_4 NPs/graphene hybrid structures. Previously, we found that the NPs of noble metals were retained on the graphene surface after reduction transformation,[19] and we observed the same phenomenon during the preparation of magnetite NPs on the graphene surface.[†]

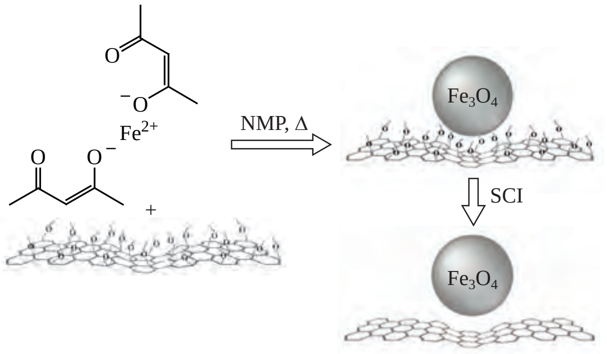

Figure 1 Magnetite NPs obtained on the surface of graphene.

The thermal decomposition of iron(II) acetylacetonate in the presence of graphene oxide dispersed in a solvent leads to the formation of magnetite NPs on the surface of graphene oxide (Figure 1). At the same time, functional oxygen-containing groups act as ligands to the formed NPs. To remove oxygen groups and to reduce graphene oxide to graphene, we used supercritical isopropanol (SCI), which can release atomic hydrogen and recover C–O bonds.[21] According to elemental analysis data, the initial graphene oxide contained about 39 wt% oxygen, and reduction by SCI led to a decrease of the O content of graphene to ⩽ 6 wt%.[22] We did not observe any effect of SCI on the NPs of Fe_3O_4, which remained on the surface of graphene. The powders of Fe_3O_4–graphene oxide and Fe_3O_4–graphene hybrids exhibited magnetic properties after the application of an external magnetic field (Figure 2).

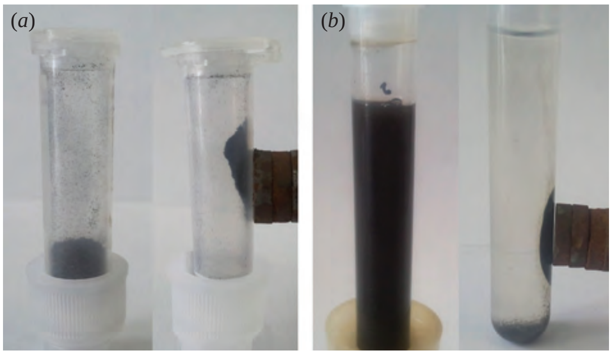

Figure 2 Effect of a magnetic field on the (*a*) Fe_3O_4–graphene oxide and (*b*) Fe_3O_4–graphene nanocomposites.

Figure 3 shows the X-ray diffraction patterns of Fe_3O_4 on graphene oxide and graphene surfaces.[‡] It is obvious that the diffraction peak of graphene oxide appears at 10.9° (002) since the AB stacking order is still observed in graphite oxide with the *d*-spacing being 0.813 nm.[23,24] Six characteristic peaks ($2\theta =$ $= 30.3°, 35.7°, 43.3°, 54.1°, 57.4°$ and $62.9°$) in the range from

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[†] Graphene oxide was synthesized by the oxidation of graphite powder using P_2O_5, $(NH_4)_2S_2O_8$, H_2SO_4 and $KMnO_4$ according to the Hummers method.[20] A portion of graphite oxide powder (100 mg) was dispersed in 30 ml of *N*-methyl-2-pyrrolidone (NMP) by sonication for 1 h to form stable graphene oxide colloid. The reaction mixture was heated to 190 °C in an argon atmosphere with vigorous stirring and then kept at that temperature for 40 min. Then, iron(II) acetylacetonate (431 mg) dispersed in 20 ml of *N*-methyl-2-pyrrolidone was added to the reaction mixture. After refluxing for 4 h, the solution was cooled to room temperature, and a black precipitate was obtained upon adding excess ethanol and centrifuging. Finally, the product was dried at 80 °C in a vacuum oven for 6 h.

A 100 mg of graphene oxide with NPs was dispersed in 5 ml of isopropanol by sonication for 30 min; the dispersion was put in a steel autoclave and kept at ~300 °C for 24 h. Then, the black precipitate was washed with acetone and isopropanol and dried at 80 °C in a vacuum oven.

[‡] The X-ray diffraction analysis was performed at 25 °C on a Bruker D8 Advance diffractometer with CuKα radiation (λ = 1.54056 Å). The diffraction data were recorded for 2θ angles up to 80°. The morphology analysis of the samples was carried out on a JEOL JEM-1011 transmission electron microscope (TEM).

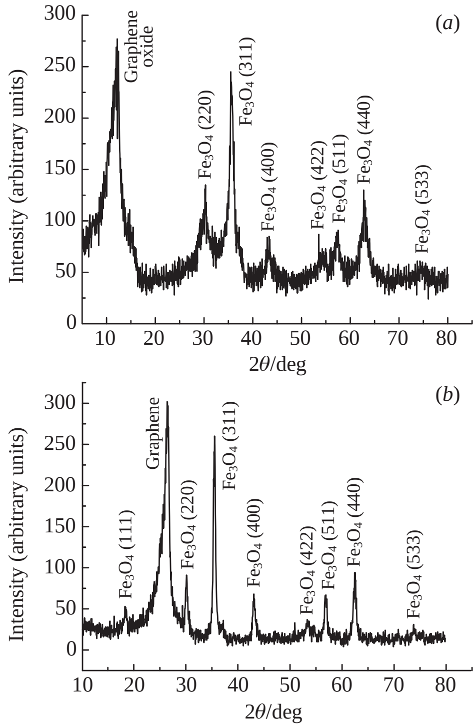

Figure 3 Diffraction patterns of the (*a*) Fe_3O_4–graphene oxide and (*b*) Fe_3O_4–graphene hybrids.

25° to 70° can be seen. All these diffraction peaks are indexed to the magnetic cubic structure of Fe_3O_4 (JCPDS 19-0629) corresponding to the (220), (311), (400), (422), (511) and (440) lattice planes, respectively, indicating that the Fe_3O_4 NPs were obtained on the surface of graphene oxide. The diffraction peaks of Fe_3O_4 can also be observed in the nanocomposite after reduction by SCI, suggesting the presence of Fe_3O_4 as a magnetic phase in the nanocomposite. Moreover, no diffraction peaks of graphene oxide were detected because of its full reduction to graphene by SCI.

Figure 4 shows the TEM images of Fe_3O_4 NPs distributed on the (*a*) graphene oxide and (*b*) graphene surfaces; their size in the first sample is 10–20 nm, and it increases to 40 nm after reduction by SCI. High-resolution (HR) TEM images of the nanocomposite are shown in Figure 4(*c*),(*d*). Well-crystallized Fe_3O_4 NPs were tightly anchored on the graphene. As expected, Fe_3O_4 NPs are chemically deposited on graphene oxide with the aid of the COOH, OH and C=O groups on the graphene oxide surface. Note that the Fe_3O_4 NPs tended to form nanoscale aggregates on the graphene oxide surfaces because of the magnetic dipolar interaction among the magnetite NPs.[25] Graphene has a large number of defects and reaction centers on its surface, which can serve as active sites for attaching metal NPs.[26] The disappearance of functional oxygen-containing groups and the free movement of magnetite particles along the graphene layer can explain the increase in the size of the Fe_3O_4 NPs.

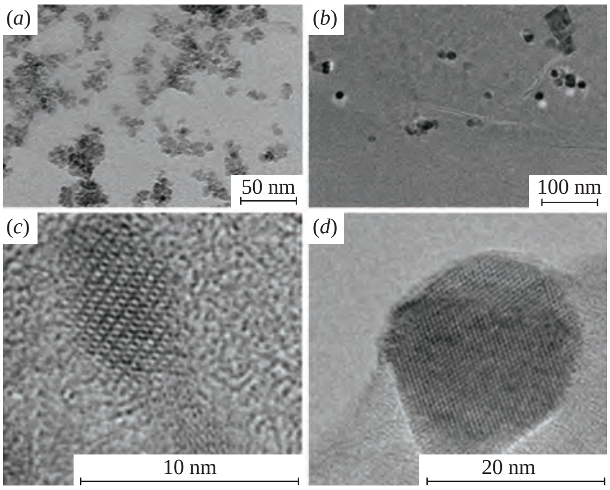

Figure 4 TEM micrographs of the (*a*) Fe_3O_4–graphene oxide, (*b*) Fe_3O_4–graphene hybrids; HR TEM of (*c*) Fe_3O_4–graphene oxide and (*d*) Fe_3O_4–graphene.

In summary, a new method of chemical reduction of graphene oxide with Fe_3O_4 NPs on its surface to graphene by supercritical isopropanol can produce new hybrid materials based on graphene and magnetic NPs of various compositions, providing their different further applications.

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