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# Sol–Gel Autocombustion Synthesis of Graphene/Cobalt Magnetic Nanocomposites

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Here we describe a versatile new strategy for producing graphene/cobalt magnetic nanocomposites by combining the sol-gel method and autocombustion. We used graphene oxide (GO), cobalt nitrate and citric acid as starting materials and prepared a dry gel of them through a routine sol-gel approach. After the autocombustion was activated at 300 °C in a tube furnace under an argon atmosphere, reducing agents such as H<sub>2</sub> and CH<sub>4</sub> were produced and then *in situ* reduced GO and cobalt nitrate to get graphene/cobalt magnetic nanocomposites. X-ray photoelectron spectroscopic and X-ray powder diffraction analysis showed that the nanoparticles loaded on graphene are cobalt but not cobalt oxide. Transmission electron microscopy and scanning electron microscopy revealed that cobalt nanoparticles, with an average diameter of ~10 nm, were homogeniously deposited on the surface of graphene. Further more, other metal nanoparticles such as Ni, Cu, Ag and Bi can also be loaded on graphene using the same method.

Keywords: Graphene, Cobalt, Sol-Gel Method, Citric Acid, In Situ Synthesis.

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## 1. INTRODUCTION

Graphene, a single-atom-thick sheet composed of sp<sup>2</sup>hybridized carbon, has attracted tremendous attention owing to its strictly two-dimensional structure and outstanding electronic,1 thermal2-3 and mechanical properties.<sup>4-7</sup> Metal nanoparticles (NPs) such as cobalt, nickle and siliver nanoparticles has also been studied a lot for their unique magnetic, catalytic and electronic properties.<sup>8–9</sup> However, the practical applications of graphene are holden by its irreversible agglomeration, and the production of small metal NPs are also challenged due to their self-assembling during the growth period. Therefore, the design and synthesis of graphene/metal nanocomposites are very popular recently for the following reasons: (1) Metal nanoparticles (NPs) can be introduced to separate graphene sheets, which will significantly increase the effectiveness of graphene;<sup>10</sup> (2) Graphene sheets, as the loader for the controlled synthesis of metal NPs, can prevent the self-assembling of small metal NPs during the growth period. (3) Extremely good properties of both graphene and metal NPs can be simultaneously obtained in this graphene/metal nanocomposites.

Nowadays, graphene/metal nanocomposites have mainly been prepared by chemical or electrochemical reduction of the mixtures of graphene (or GO) and metallic precursors.<sup>11</sup> These methods are mostly not environmental friendly and multiple reaction steps are required. Herein, we describe a versatile new strategy for producing graphene/ cobalt magnetic nanocomposites by combining the sol–gel method and autocombustion. Using this simple method, cobalt nanoparticles, with an average diameter of  $\sim 10$  nm, can be homogeniously deposited on the surface of graphene. Further more, other metal nanoparticles such as Ni, Cu, Ag and Bi can also be loaded on graphene using the same method.

#### 2. EXPERIMENTAL DETAILS

Graphene oxide (GO) was prepared using modified Hummers method as mentioned in the previous Ref. [12]. Graphene/metal nanocomposites were prepared through a routine sol–gel approach.<sup>13</sup> After the cobalt nitrate, citric acid and proper amount of GO were homogenously dispersed in the water, the pH value was adjusted to 7 by ammonia. Then the resultant solution was heated at 95 °C to develop a dried gel. Under the protection of argon, the dried gel was heated to 300 °C to activate combustion. After cooling to room temperature, black loose powders with good conductivity and magnetic property were obtained.

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Typical tapping mode atomic force microscopy (AFM) measurements were performed using Multimode SPM from Digital Instruments with Nanoscope IIIa Controller. X-ray differential (XRD) measurements were carried out on a Rigaku D/Max-2500 diffractometer with Cu-K $\alpha$  radiation. Thermal gravimetric analysis (TGA) was carried out using a NETZSCH STA 409PC. The heating rate is 5 °C min<sup>-1</sup> from room temperature to 800 °C in  $N_2$  atmosphere. Raman spectra were measured with a Renishaw inVia Raman spectrometer using laser excitation at 514.5 nm.

### 3. RESULTS AND DISCUSSION

XRD patterns of as-prepared nanocomposites were shown in Figure 1. The diffraction peaks at  $2\theta = 44.2^{\circ}$ , 51.5° and 75.9° were attributed to (111), (200) and (222) diffractions of cobalt respectively, but not cobalt oxide. What's more, a weak diffraction peak was located at  $2\theta = 26.4^{\circ}$  (d = 0.34 nm) and no diffraction peak was observed at  $2\theta =$  $\sim 12.1^{\circ}$  (d =  $\sim 0.8$  nm), indicating GO was completely turned into graphene during the reduction process.

XPS analysis, which was shown in Figure 2, also improved that the nanopartilces in the as-prepared nanocomposites were indeed cobalt (2P1: the peak at 793.7 eV and  $2P^3$ : the peak at 778.3 eV), but not cobalt oxide (the peak at 780.2 eV and 778.3 eV). Furthermore, the main peak at 284.8 eV supplied that most of the carbon was sp<sup>2</sup> bond-o: Institute of Molecular ing, which was in good agreement with the XRD results. Ved, 13

Since both XRD and XPS analysis revealed that most Scien nanoparticles in the as-prepared nanocomposites were cobalt but not cobalt oxide. A great deal of TEM and SEM tests were performed to obtain the structural information of graphene/cobalt nanocomposites. As shown in Figures 3(a) and (b), cobalt NPs, with an average diameter of  $\sim 10$  nm, were homogeniously deposited on the surface of graphene.

Figure 4 showed the magnetization curve of graphene/ cobalt nanocomposite and pure cobalt NPs. The specific saturation magnetization,  $M_s$  of the graphene/cobalt nanocomposite, is 108 emu/g. This value is a little smaller than



Fig. 1. XRD patterns of graphene/cobalt nanocomposite and pure cobalt NPs.



Fig. 2. XPS patterns of graphene/cobalt nanocomposite.



Fig. 3. TEM (left) and SEM (right) image of graphene/cobalt nanocomposite

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Fig. 4. Magnetic hysteresis loop of the graphene/cobalt nanocomposite and pure cobalt NPs samples measured at room temperature.



**Fig. 5.** (a) TGA curve of GO/cobalt nitrate gel with a heating rate of 5 K/min under an argon atmosphere. The abrupt drop in the TG curve represents the violent combustion of the gel.

the value of pure cobalt NPs of 120 emu/g. The reduction in the value of  $M_s$  could be attributed to the rather smaller size of the cobalt nanoparticles and the relatively low amount of cobalt nanoparticles in the nanocomposite, which is estimated as 78 wt% calculated from the content of Co by atomic absorption spectrum.<sup>14</sup>

TGA was used to investigate the nanocomposites and give a good understanding of the sol-gel autocombustion process in the synthesis of graphene/metal nanocomposites (Fig. 5). The experiments were carried out from room temperature to 900 °C at a heating rate of 5 K/min under an argon atmosphere. Figure 5 shows that an abrupt weight loss happened around 250 °C, which indicates the combustion of the gel. Previous study has shown that  $H_2$ ,  $H_2O$ ,  $CH_4$ , NO,  $CO_2$ ,  $NH_3$  and  $NO_2$  species were identified near the combustion temperature. Among these  $H_2$  and  $CH_4$  are reducing agents that can be used in the redox reaction for synthesizing metals from oxides.<sup>13</sup> In the meanwhile,

GO could also be reduced into graphene by both thermal reduction and reducing agents like  $H_2$  and  $CH_4$ . As a result, metal NPs can be *in-situ* loaded on the surface of graphene and graphene/metal nanocomposites were obtained by this method.

## 4. CONCLUSIONS

In summary, we demonstrated a versatile new strategy for producing graphene/cobalt magnetic nanocomposites by combining the sol–gel method and autocombustion. Cobalt nanoparticles, with an average diameter of  $\sim 10$  nm, were homogeniously deposited on the surface of graphene. Further more, other metal nanoparticles such as Ni, Cu, Ag and Bi can also be loaded on graphene using this simple method. The special magnetic and electrical properties will endow the graphene/metal nanocomposites with promising applications in electrochemistry, magnetic separation, magnetic head materials and so on.

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