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Distribution-dependent capacitive and magnetic properties of Mn_3O_4 nanoparticles on reduced graphene oxide

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ABSTRACT

The composition of nanoparticles (NPs) and graphene has aroused tremendous attention because it can synergistically combine the advantages of NPs and graphene. However, manipulating the distribution of NPs and identifying the effect of the distribution of NPs on the properties of the composites remain challenges. Here, we used graphene oxide (GO) of different oxidation degrees as the platform to prepare the Mn_3O_4/reduce GO composites. We found that the distribution of Mn_3O_4 NPs could be manipulated by adjusting the oxygen content of GO. Then we investigated the effect of Mn_3O_4 distribution on the capacitive and magnetic properties of the composites. The results showed that the distribution of Mn_3O_4 NPs could change the active sites, charge transfer, uncompensated spins, and spin coupling of the composites, resulting in the distribution-dependent capacitive and magnetic properties. Especially, with discrete Mn_3O_4 distribution, the composites exhibited the high specific capacitance of 1626.0 F g^{-1} and mass magnetization of ca. 85.3 emu g^{-1} normalized to the portion of Mn_3O_4. This work will help in understanding the interaction of NPs and graphene for fundamental research, and push the way for potential capacitive and magnetic applications of graphene-based composites.

1. Introduction

Combining nanoparticle (NPs) and graphene create a new class of multifunctional materials known as NPs/graphene composites, which have aroused tremendous attention in various areas, e.g. capacitive (such as electrical vehicles, portable electronic devices, backup power, etc.) and magnetic applications (such as spintronics, high density magnetic storage, magnetic separation, etc.) [1–15]. In principle, developments of the composites highly depend on the unique properties of NPs (mainly the numerous active sites and uncompensated spins on the surface) and graphene (especially its outstanding electrical conductivity and surface/volume ratio) [3,4]. Experimentally, various factors have been proposed that can influence the unique properties of graphene (including the integrity, size, thickness, etc.) or NPs (including the constitution, portion, size, etc.) [3–11,16,17]. Despite the significant efforts in these reports, we found that the distribution of NPs was usually heterogeneous, accompanying with the different capacitive, magnetic or catalytic performances [3–11]. These results reported hinted that the distribution of NPs may also be an important factor in influencing the properties of the composites. Also theoretically, the unique properties of graphene or NPs are affected by the relative positions between them. In short, for graphene, the charge-transfer compounds between NPs and graphene may be considered as an analog of semiconductor doping [18,19]. Given that the spin density or charge distribution usually changes with the position of dopants [20,21], manipulating the distribution of NPs would modify the properties of graphene. Besides, for NPs, the charge carrier transfer pathway and spin coupling efficiency between adatoms are related to the relative positions. Thus manipulating the distribution may tune the net active sites and magnetic moments of NPs [11,18,22–25]. Namely, manipulating the distribution of NPs on graphene for identifying the effect of the distribution of NPs on the properties of the composites, is of significance to widen the potential applications in the capacitive or magnetic areas.

However, the distribution-dependent properties of the composites are scarcely investigated because there still remains a challenge to manipulate the distribution of NPs. Shortly, due to the delocalized π binding network of graphene [24], the atoms are weakly attracted by graphene and have a low migration barrier [26–28]. Consequently, NPs usually suffer from the tendency of aggregation and distribute heterogeneously [1–3]. Accordingly, to hinder the migration and manipulate the distribution of NPs, it needs to tune the attraction between NPs and graphene. Functionalization of graphene with suitable polar molecules, by them interacting with NPs via non-covalent forces such as

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hydrophilic and ionic interactions, may be an effective way to tune the attraction [29,30]. Among the numerous functionalized graphene, graphene oxide (GO) which has been readily synthesized in a large scale [31,32], is considered to be an excellent candidate. Basically, GO is an amphiphilic copolymer system because of the presence of hydrophilic oxygen containing groups and hydrophobic aromatic frameworks [33,34]. This unique structure enables to adsorb the atoms [30], leading to a wide diffusion barrier for the NPs [32]. Besides, the oxidation degrees of GO can be facilely adjusted, which enables to tune the attraction between NPs and GO. Namely, it is expected to optimize the distribution of NPs by adjusting the oxidation degrees of GO, which facilitate to clarify the effect of the distribution of NPs on the properties of the composites.

Here, we took Mn_3O_4 NPs (with the advantages of high theoretical pseudo-capacitance and surface spins) as an example to investigate the distribution-dependent properties of NPs on reduced GO (rGO) [35,36]. We prepared Mn_3O_4/rGO composites by using GO of different oxidation degrees. We found that Mn_3O_4 distribution could be manipulated by adjusting the oxidation degrees of GO, and the composites with discrete Mn_3O_4 NPs could be achieved from highly oxidized GO. After that, the capacitive and magnetic properties were measured and the results showed that they were dependent on Mn_3O_4 distribution. Especially, with discrete Mn_3O_4 distribution, the composites exhibited the high specific capacitance (C_s) of 1626.0 F g^{-1} and saturated mass magnetization (M_s) of ca. 85.3 emu g^{-1} normalized to the portion of Mn_3O_4. We suggested that the distribution-dependent performances were attributed to the modified active sites, charge transfer, uncompensated spins, and spin coupling of the composites.

2. Experimental

2.1. Synthesis of the Mn_3O_4/rGO composites

GO sheets were prepared by the modified Hummer's method [37]. The GO samples of different oxidation degrees (GO-51.58, GO-36.48, and GO-19.09, numerical numbers denoted the O content which was defined as O/C × 100 at%) were prepared using different mass ratios of graphite to $KMnO_4$ (1:6, 1:4, and 1:2). The Mn_3O_4/rGO composites (Mn_3O_4/rGO-51.58, Mn_3O_4/rGO-36.48, and Mn_3O_4/rGO-19.09, which were prepared from GO-51.58, GO-36.48, and GO-19.09, respectively) were obtained by freeze-drying followed by thermal annealing method. In short, 0.01 mol manganese(II) acetate ($Mn(AC)_2$) and 0.03 mol 3,5-dinitrobenzoic acid (DNBA) were dissolved in 100 mL of absolute ethanol as the starting mixture. Then 100 μL of the mixture was added to the GO aqueous solutions (30 mL of GO-51.58, 25 mL of GO-36.48, and 20 mL of GO-19.09) with concentrations of 2 mg/mL. After that, the obtained solutions were ultrasonicated accompanying by being stirred for 30 min. Finally, the solution was freeze-dried and then annealed at 600 °C for 20 min in Ar atmosphere, and the Mn_3O_4/rGO composites were obtained. For the comparison, 1 mL of the starting mixture was added in 30 mL of GO-51.58, and then Mn_3O_4/rGO-51.58′ was prepared in the similar procedure. In addition, the rGO samples (rGO-51.58, rGO-36.48, and rGO-19.09) were prepared by annealing the corresponding GO samples at 600 °C for 20 min in Ar atmosphere, and pure Mn_3O_4 NPs were prepared by thermal decomposition of Mn $(acac)_2$ in oleylamine without the GO solution [38].

2.2. Microstructure characterization

X-ray photoelectron spectroscopy (XPS) was performed using 200 W monochromatic Al Kα radiation. A 500 μm X-ray spot was used for XPS analysis. The XPS peak fitting program XPSPEAK 4.1 was used for the spectra processing. The thermogravimetry/derivative thermogravimetry (TG/DTG) measurement was performed from 30 to 700 °C at a heating rate of 10 °C/min in air (Pyris 1 DSC, USA). The distribution of Mn_3O_4 NPs in the composites was analyzed by transmission electron microscope (TEM, model JEM-2100, Japan) and atomic force microscope (AFM, model Dimension V, USA).

2.3. Electrochemical measurements

The capacitive properties of the as-obtained products were investigated using a three-electrode cell configuration at room temperature. The working electrodes were fabricated by mixing the prepared composites with 15 wt% acetylene black and 15 wt% polytetrafluorene-ethylene binder. A small amount of *N*-methyl-2-pyrrolidone was added to the mixture to produce a homogeneous paste. Then the mixture (ca. 4–5 mg) was pressed onto nickel foam current-collectors (1.0 cm × 1.0 cm) to make electrodes. Platinum foil and Ag/AgCl were used as the counter and reference electrodes, respectively. 6 M KOH or 1 M KCl aqueous solution were used as the electrolyte. Before the electrochemical test, the prepared electrodes were soaked overnight in the electrolyte. Galvanostatic charge-discharge (GCD), cyclic voltammetry (CV), and electrochemical impedance spectra (EIS) measurements were conducted on an electrochemical workstation (CHI 660D, CH Instrument, China). From the GCD curve, the C_s can be calculated from

$$C_s = \frac{i \times \Delta t}{m \times \Delta V} \tag{1}$$

where i is the discharge current, Δt is the total discharge time, m is the mass of active material and ΔV is the potential difference in the discharge process [39]. From the CV curves, the corresponding C_s can be calculated based on the following equation:

$$C_s = \frac{\int idv}{2 \times m \times \Delta V \times S} \tag{2}$$

where $\int idv$ is the integrated area under the CV curve, m is the mass of the electrode active material in grams, ΔV is the scanned potential window in volts, and S is the scan rate in volts per second.

2.4. Magnetic measurements

The magnetic properties of the powdered samples (ca. 10 mg) were measured using a superconducting quantum interference device (SQUID) magnetometer with a sensitivity better than 10^{-8} emu (Quantum Design MPMS–XL, USA), and all the measured mass magnetization (M) were corrected by subtracting the corresponding linear diamagnetic background of the capsules. The concentrations of magnetic impurity elements (such as Fe, Co, or Ni) of all the samples are below 30 ppm (Table S1) measured by ICP spectrometry (Jarrell–Ash, USA). The total magnetization (M_{total}) at 5 K is mainly composed of two parts: paramagnetization (M_{para}) and ferromagnetization (M_{ferro}), viz. $M_{total} = M_{para} + M_{ferro}$. Considering that M_{ferro} can saturate at a high applied field (H), approximately, one can fit the M_{para} at the high H. The M_{para} is fitted to Brillouin function:

$$M_{para} = NgJ\mu_B\left[\frac{2J+1}{2J}\mathrm{Coth}\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\mathrm{Coth}\left(\frac{x}{2J}\right)\right] \tag{3}$$

where $x = gJ\mu_B H/(k_B T)$, N the number of magnetic moments present, g the Landau factor, J the angular momentum number, μ_B the Bohr magneton, and k_B the Boltzmann constant. By subtracting the M_{para} from the observed data, one can obtain the remaining M_{ferro}. From the saturated M_{para} added to the saturated M_{ferro}, the M_s of the sample can be calculated.

3. Results and discussion

After preparation of the composites, the oxidation degree of GO is usually reduced, and the NPs have various possible constitution [5,39]. Considering that the oxidation degree and the constitution are two important factors in the properties of the composites [2], these two