

Short Communication

Synthesis and Electrochemical Performances of Co₃O₄/graphene as Supercapacitor Material

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In this paper, the Co₃O₄/graphene composition has been successfully prepared by a facile low-temperature oxidation route using Co(NO₃)₂·6H₂O and general type graphene (GGR) as raw materials. The structure and morphology of as-prepared composite is investigated by X-ray diffractometer (XRD) and scanning electron microscopy (SEM), and the results reveal that the sphere-like Co₃O₄ with the diameter the 300-500 nm uniformly loads on the surface of 2D graphene nanosheet. As the supercapacitor material, the Co₃O₄/GR composite displays a specific capacitance of 362.6 F/g at a current density of 0.72 A/g, and a capacity retention rate of 108.1% can be reached after 500 cycles. While the bare Co₃O₄ only delivers a low discharge specific capacitance of 161.6 F/g.

Keywords: Co₃O₄/graphene; low-temperature oxidation; supercapacitor; electrochemical performances.

1. INTRODUCTION

As a new type of energy storage device, the supercapacitor starts to be wildly used in the field of electronic product and electric vehicle. Because it has a higher discharge specific capacitance/energy density than traditional capacitor, and higher power density/longer cycling life than battery (e.g., lithium ion battery)[1-5]. It is well known that, the electrochemical performances of supercapacitor are dependent upon the electrode materials. In comparison with common-used active carbon material, the metal oxides based on redox reaction mechanism can deliver a higher capacitance [2-6].

Among these metal oxides, Co₃O₄ has been considered as one of the most promising electrode material due to its ultra-high theoretical discharge capacitance of 3560 F/g [7-14]. However, some

problems still exist to be overcome for the further development of Co_3O_4 -base electrode materials. Firstly, the low conductivity and specific surface area of Co_3O_4 inhibit the interfacial charge transfer, resulting in low discharge capacitance and poor rate capability. Secondly, the continuous insertion/extraction of electrolyte ions during cycling will lead to severe volume change of Co_3O_4 , and this change is unfavorable to the cycling stability of electrode materials [7-14]. In order to alleviate these problems, design of high specific surface Co_3O_4 and/or construction of Co_3O_4 /carbon (e.g. Co_3O_4 /graphene, Co_3O_4 /carbon nanotube, Co_3O_4 /carbon nanofiber...) have become main tools [8-14].

Graphene, the unique 2D sheet-like structure provides it excellent electronic conductivity, and the kinematic velocity of electron within graphene matrix can reach as high as 1/30 of light speed. Furthermore, the low density ($\sim 0.77 \text{ mg/m}^3$) and high specific surface area ($\sim 2600 \text{ m}^2/\text{g}$) of graphene can provide numerous reaction sites for electron storage, and it is suitable as charge storage and transport medium [15-17]. Thus, the synthesis and application of graphene related materials have attracted more and more attention, especially, the synthesis of metal oxide/graphene composites and their use in the field of energy storage area [11-14, 18-20]. In this paper, a facile low-temperature oxidation route has been developed to prepare the Co_3O_4 /graphene composition. In the composite, the Co_3O_4 nanospheres uniformly load on the surface of 2D graphene, and the existence of 2D graphene may improve the electrochemical conductivity and buffer the volume change during cycling for the composite. As supercapacitor electrode materials, the electrochemical performances of bare Co_3O_4 and Co_3O_4 /graphene are comparably studied, as shown in the text.

2. EXPERIMENTAL

2.1 Synthesis of Co_3O_4 /graphene composite

All of the reagents are A.R. grade, and used without further purification. The Co_3O_4 /graphene composite are prepared by a low-temperature oxidation route as follow: 0.15 g general type graphene powder (Ningbo Morsh) is added into 50 mL distilled water, and then sonification for 2 h to obtain uniform dispersion solution. A 50 mL distilled water and 50 mL ammonia solution (28~30wt% in water) is mixed with dispersion solution under stirring at 90°C . After pumping air into above solution for 10 min at a rate of $30 \text{ cm}^3/\text{min}$, a 20 mL $\text{Co}(\text{NO}_3)_2$ solution with 2 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is slowly added under stirring. After keeping at 90°C for 10 h, the resulting gray precipitate is filtered, washed with distilled water, and dried at 70°C for 12 h. For comparison, the control sample (bare Co_3O_4) is prepared using the same procedure without addition of graphene.

2.2 Materials characterization

The crystalline phases of each sample (bare Co_3O_4 or Co_3O_4 /graphene) were characterized by X-ray diffractometer (DX-2007 LiaoNing DanDong) at a scanning rate of $0.030/\text{s}$ within 2θ degree of $10\text{-}80^\circ$. SEM images were performed using an S-3400N field emission scanning electron microscope (HITACHI, Japan).

2.3 Electrochemical characterization

The working electrode is prepared as follow: 80 wt% active material (i.e., bare Co_3O_4 or $\text{Co}_3\text{O}_4/\text{graphene}$), 10 wt% acetylene black (AB), and 10 wt% Poly-tetra-fluoro-ethylene (PTFE) were well mixed, then was cut into a thin flake with area of 1 cm^2 , pressed onto a nickel foam which served as a current collector. After that, the working electrodes were dried in a vacuum oven at 60°C for 12 h. Electrochemical measurements were performed in a solution of 2 M KOH aqueous electrolyte using a three-electrode cell. Platinum foil and Hg/HgO electrodes were used as counter and reference electrodes, Cyclic voltammetry (CV) are carried out using an electrochemical working station (CHI660D, Shanghai, China) at a scanning rate 100, 50, 20, 10 or 5 mV/s within 0.0-0.62 V ($\text{Co}_3\text{O}_4/\text{graphene}$) and 0.0-0.5 V (bare Co_3O_4). Galvanostatic cycling tests are carried out using a high-precision battery testing system (NEWARE BTS, Shenzhen, China) at room temperature.

3. RESULTS AND DISCUSSION

3.1. Structures and morphologies analysis

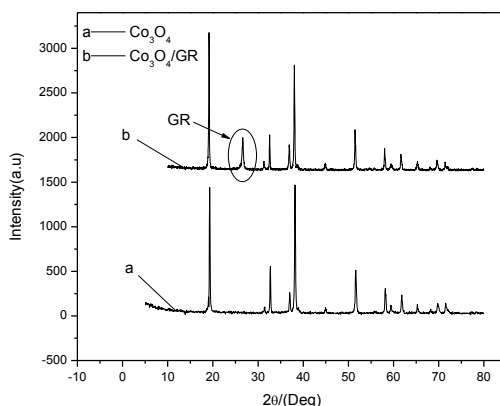


Figure 1. XRD patterns of as-prepared (a) bare Co_3O_4 and (b) $\text{Co}_3\text{O}_4/\text{graphene}$

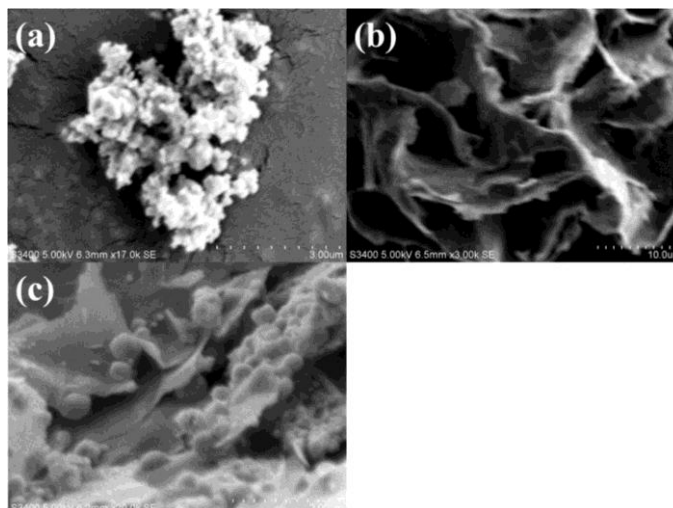
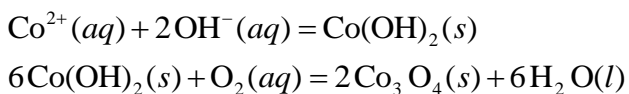


Figure 2. SEM images of as-prepared (a) Co_3O_4 , (b) graphene and (c) $\text{Co}_3\text{O}_4/\text{graphene}$

Fig. 1 shows the XRD patterns of as-prepared bare Co_3O_4 and $\text{Co}_3\text{O}_4/\text{graphene}$. All of diffraction peaks in Fig. 1a can be ascribed to standard data of spinel Co_3O_4 (JCPDS: 43-1003) [7-14], and without any impurities can be detected. This indicates the low temperature oxidation can be used to prepare Co_3O_4 , and the total reaction can be summarized as follow:

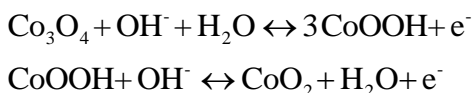


Using an *in situ* composition route, the Co_3O_4 is loaded on the surface of layered graphene. XRD pattern of as-prepared sample is revealed in Fig. 1b. The diffraction peaks of $\text{Co}_3\text{O}_4/\text{graphene}$ are consistent with bare Co_3O_4 (Fig. 1a) except a weak peak nearby 26.6° , and this peak should be the characteristic of graphene, indicating the co-existence of graphene in the composition. Furthermore, according to the $\text{FWHM}_{(111)}$ (full width at half maximum of (111) crystal face) value and Scherrer equation ($D = K\lambda/B\cos\theta$), the estimated particle size of Co_3O_4 component can be calculated as 46.3 nm.

Besides the XRD investigation, the morphologies, sizes and surface microstructures of as-prepared samples are studied by SEM, as shown in Fig. 2. The bare Co_3O_4 in Fig. 2a is composed of some spherical or polyhedral nanoparticles, and the nanoparticles have a uniform size distribution of several hundred nanometers. The commercial graphene in Fig. 2b shows typical 2D sheet-like structure, and the edge of each graphene nanosheet has a little flection due to overlapping of several layers [17-19]. Interestingly, the uniform Co_3O_4 nanospheres are successfully loaded on surface of the graphene (Fig. 2b). In comparison with original graphene in Fig. 2b, the as-prepared composition has single layer structure, which may be attributed to that the insertion of Co_3O_4 destroys the interaction of graphene nanosheet. The size of Co_3O_4 also has been obviously reduced after the addition of graphene, because the graphene can inhibit the crystal growth of Co_3O_4 [15, 16].

3.2. Electrochemical performances

As supercapacitor electrode materials, the graphene can provide high electron conductivity and good structural stability, and the Co_3O_4 has high faradic pseudo-capacitance. Thus, the electrode performances of $\text{Co}_3\text{O}_4/\text{graphene}$ composition deserve to be expected [11-14]. Fig. 3 shows the CV curves of bare Co_3O_4 and $\text{Co}_3\text{O}_4/\text{graphene}$ at different scanning rates. The existed redox peaks of each sample can be attributed to the electrochemical reaction at 2 M KOH solution, described as follow [7-10]:



It can be obviously observed that the peak current increases with enlarged scanning rate. However, the increased scanning rate won't change the general morphologies of curve and redox peaks, indicating each sample (i.e., Co_3O_4 or $\text{Co}_3\text{O}_4/\text{graphene}$) has good structural/electrochemical stability at the 2 M KOH solution.

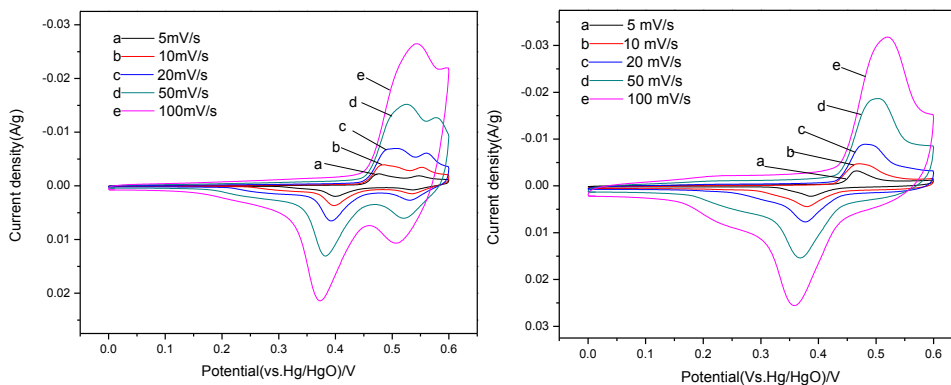


Figure 3. CV curves of (left) bare Co₃O₄ and (right) Co₃O₄/graphene recorded at different scanning rates

For a comparison purpose, the CV curves of bare Co₃O₄ and Co₃O₄/graphene recorded at a same scanning rate are revealed, as shown in Fig. 3e. The scanning area of Co₃O₄/graphene is larger than that of bare Co₃O₄, suggesting the Co₃O₄/graphene has a higher discharge capacitance. The introduction of graphene should be the reason why the Co₃O₄/graphene has better electrochemical performances.

As we know, the discharge capacity and corresponding cycling stability are essential for supercapacitor materials. In this study, these parameters are studied by Galvanostatic cycling tests and following formula:

$$C_s = \frac{I \Delta t}{m \Delta V}$$

Fig. 4 shows the typical charge-discharge curve of Co₃O₄ and Co₃O₄/graphene. It can be clearly seen that, the Co₃O₄/graphene has an obvious voltage plateau nearby 0.4 V, which should be attributed to effective oxidation-reduction of Co₃O₄.

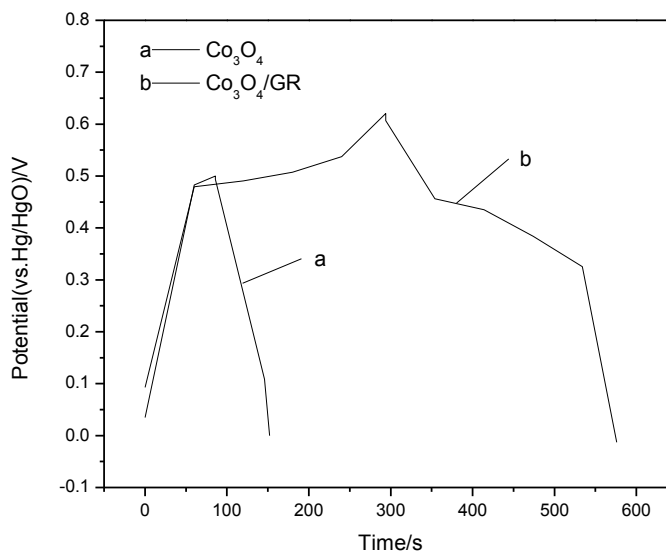


Figure 4. Typical charge-discharge curve of Co₃O₄ and Co₃O₄/graphene recorded at 1.6 A/g, 0-0.5 V and 0.72 A/g, 0-0.62 V, respectively

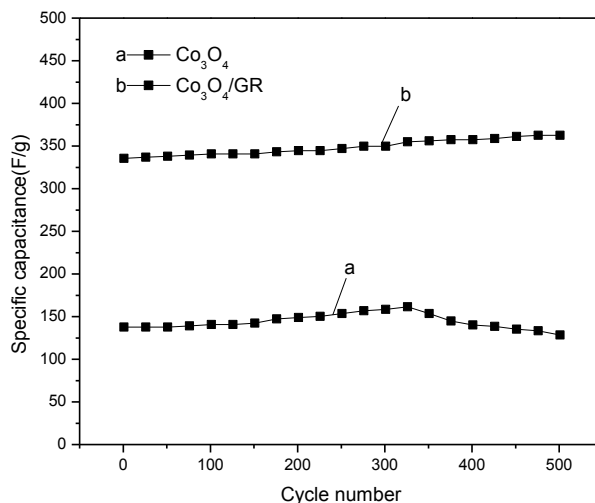


Figure 5. Cycling performances of Co_3O_4 and $\text{Co}_3\text{O}_4/\text{graphene}$ at 1.6 and 0.72 A/g, respectively

More importantly, the discharge time of $\text{Co}_3\text{O}_4/\text{graphene}$ is much longer than that of Co_3O_4 . By calculation, the $\text{Co}_3\text{O}_4/\text{graphene}$ delivers a discharge capacitance of 362.6 F/g, while the bare Co_3O_4 only show a value 161.6 F/g, suggesting the $\text{Co}_3\text{O}_4/\text{graphene}$ is more suitable for Co_3O_4 as supercapacitor material.

Besides the discharge capacitance, the cycling stability is also very important, as shown in Fig. 5. After 500 cycles, the $\text{Co}_3\text{O}_4/\text{graphene}$ can reach capacitance retention of 108.1%, while the Co_3O_4 only keep 79.5% of initial value. As we know, the electrode materials will experience severe volume change during charge-discharge process, resulting from continuous insertion/extraction of electrolyte ions. This volume change should lead to poor cycling stability. Herein, the existence of graphene, especially uniform mixing with Co_3O_4 , can effectively buffer the volume change. Furthermore, the high specific surface area nature of graphene can also enlarge the discharge capacity of original Co_3O_4 .

4. CONCLUSION

The $\text{Co}_3\text{O}_4/\text{graphene}$ composition has been successfully prepared by a simple low-temperature oxidation route. The Co_3O_4 nanospheres with spinel structure are uniformly loaded on the single layer of 2D graphene. Using the CV and charge-discharge methods, it is found that the $\text{Co}_3\text{O}_4/\text{graphene}$ has a high discharge capacitance of 362.6 F/g, which is 2.2 times as large as the bare Co_3O_4 . What's more, the cycling stability and electrochemical reversibility of $\text{Co}_3\text{O}_4/\text{graphene}$ is also excellent. Maybe, the $\text{Co}_3\text{O}_4/\text{graphene}$ prepared by the low-temperature oxidation route is suitable as high-performance supercapacitor materials, deserved to be conducted continuously.

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