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Preparation of reduced graphene oxide/cobalt oxide composites and their enhanced capacitive behaviors by homogeneous incorporation of reduced graphene oxide sheets in cobalt oxide matrix

Huan-Wen Wang, Zhong-Ai Hu*, Yan-Qin Chang, Yan-Li Chen, Zi-Yu Zhang, Yu-Ying Yang, Hong-Ying Wu

Key Laboratory of Eco-Environment-Related Polymer Materials of Ministry of Education, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, PR China

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ABSTRACT

Incorporation of reduced graphene oxide (rGO) in Co₃O₄ matrix is systematically investigated through a chemical route for supercapacitors. The α -Co(OH)₂ supported by graphene oxide is first fabricated by a chemical precipitation approach. Thermal decompositions of these precursors at the given temperature (150°C) lead to rGO/Co₃O₄ composites. Measurement results show that the morphology and electrochemical activity of the rGO/Co₃O₄ composites are influenced significantly by the mass ratios of rGO to Co₃O₄. When used as electrode materials in supercapacitors, the composite with mass ratio of 0.22:1 (rGO:Co₃O₄) achieves the specific capacitance as high as 291 Fg⁻¹ at 1 Ag⁻¹ in the potential range of -0.4 to 0.55 V, as compared with each individual counterpart (56 and 161 Fg⁻¹ for rGO and Co₃O₄, respectively). In addition, the excellent rate capability and well cycling ability are observed in the composite electrodes. The enhanced electrochemical performance is indicative of a positive synergistic effect between rGO and Co₃O₄. These results suggest the importance and great potential of graphene based composites in the development of high-performance energy-storage systems.

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1. Introduction

Over the past few years, the worsening energy depletion and growing concerns about air pollution and global warming have stimulated intense research on the development of alternative energy storage/conversion devices with high power and energy densities [1,2]. Supercapacitors as a kind of attractive energystorage/conversion device are attracting wide interest owing to their higher power density and longer life cycle compared with batteries and higher energy density than conventional dielectric capacitors. Supercapacitors can be applied in a large variety of applications, including consumer electronics, memory back-up systems, industrial power, energy management, public transportation, military devices and electric vehicles [3]. Generally, there are two types of supercapacitors based on the electrode materials: (1) high surface area, inert and conductive carbon materials that store and release energy by nanoscopic charge separation at the electrochemical interface between an electrode and an electrolyte and (2) some redox active materials such as conducting polymers and transition metal oxides that undergo fast, reversible redox reactions at the surface of active materials, which is known as the pseudocapacitance [4,5].

As is well known, graphene has triggered an exciting new area in the field of carbon nanoscience with ever-increasing scientific and technological impetus [6-8]. Because of its high specific surface area, good chemical stability, and excellent electrical and thermal conductivity as well as remarkably high mechanical strength and Young's modulus [9], graphene is predicted to be an excellent electrode material candidate for energy-conversion/storage systems [10]. Recent progress in large-scale synthesis of graphene sheets [11,12] has promoted extensive exploration of using single-layer graphene sheets or graphene-based composites for supercapacitors. Although the specific capacitances of tens to 264 Fg^{-1} have been obtained in different graphene systems [13-15], graphene sheets usually suffer from agglomeration and restacking due to the van der Waals interactions, which leads to a great loss of effective surface area and consequently a lower capacitance than as expected. In order to enhance the performance of graphene based energy storage, some researchers are trying to combine doublelayer capacitance of graphene sheets and pseudocapacitance of the loaded redox-active materials. It is reported that the Ni(OH)₂ hexagonal nanoplates grown on graphene sheets display both high power and energy capabilities [2]. Besides, graphene coupled with conducting polymers [16-19] or metal oxides [20-25] shows a

^{*} Corresponding author. Tel.: +86 931 7973255; fax: +86 931 8859764. *E-mail address*: zhongai@nwnu.edu.cn (Z.-A. Hu).

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promising application in the electrode materials of supercapacitors. In the most of graphene-based composites, which are prepared by reduction of graphene oxide followed with load of pseudocapacitive nanomaterials, the excellent electric and surface properties of graphene sheets are not completely revealed due to the agglomerations. Therefore, seeking for the effective strategies to synthesize well-dispersed graphene-based composites remains a major topic of interest.

Graphite oxide (GO), one of the most important derivatives of graphene, is characterized by its special surface properties and layered structure [26,27]. Specifically, owing to the introduction of oxygen-containing functional groups (hydroxyl, carboxyl and epoxy groups) on carbon nanosheets (CNS), GO can be exfoliated under appropriate treatment and forms quasi-two-dimensional CNS [28]. These exfoliated GO sheets possess large surface areas and thus may be potential support materials to load some nanocrystals. Meanwhile, the aforementioned oxygenated functional groups can be acted as nucleation centers to anchor active materials onto graphene sheets. So it should be reasonably feasible to synthesize well-dispersed graphene-based composites directly starting from GO. However, little research involved in this strategy indicates that the correlative exploration is not nearly enough so far.

In the present work, we demonstrate that rGO sheets can well be dispersed within the Co_3O_4 matrix. The GO/Co(OH)₂ composites with different mass ratios, which were prepared by a chemical precipitation route, were used as precursors to produce graphenebased composites. To our surprise, the mass ratios of rGO to Co_3O_4 influence dramatically the morphologies and electrochemical performance of the resultant composites. In the appropriate mass ratio, rGO dispersed in the composites is clearly identified and the resultant materials show excellent electrochemical capacitive performance. However, when the mass ratio of rGO to Co_3O_4 is more than 0.22:1, rGO sheets from composites seem to be in high agglomeration and concurrently the specific capacitances become observably low. This suggests that there is a scientific requirement to explore relative factors associated with it.

It is documented that graphene is an excellent supercapacitor electrode material, giving consistently good electrochemical performances over a wide range of voltage scan rates [13]. Cobalt oxide is an important electrochemically active material [29–31]. Therefore, a high electrochemical performance can be expected for rGO/Co₃O₄ composite electrodes by taking the full advantage of graphene-based double-layer capacitance and cobalt oxide pseudocapacitance.

2. Experimental

2.1. Synthesis of GO

GO was synthesized from graphite powder by a modified Hummers method [32,33], in which pre-oxidation of graphite was followed by oxidation with Hummers' method. In the pre-oxidation, the graphite power (4.0g) was added with stirring into the concentrated H_2SO_4 (40 mL) solution in which $K_2S_2O_8$ (2.0 g) and P2O5 (2.0g) were completely dissolved at 80 °C. The mixture, in a beaker, was kept at 80 °C for 4.5 h using an oil bath after that the mixture was cooled down and was diluted with 1 L of distilled deionized (DDI) water. The pretreated product was filtered and washed until the pH of filtrate water became neutral. The shiny, dark-gray, pre-oxidized graphite was dried in air overnight. Then, it was dispersed by stirring into chilled H₂SO₄ (92 mL) in a flask in an ice bath. KMnO₄ (12 g) was added slowly with stirring to keep the temperature of reaction mixture below 20 °C. The resulting thick, dark green paste was allowed to react at 35 °C for 3 h followed by addition of H₂O (184 mL) to give a dark brown solution. After additional stirring for 2 h, the dark brownish solution was further diluted with distilled water (560 mL) and then H₂O₂ (30%, 40 mL) was added slowly and the color of the mixture turned into brilliant yellow. The mixture was allowed to settle overnight and the supernatant was decanted. The remaining product was washed with 10% HCl solution with stirring and the brownish solution was allowed to settle overnight. The supernatant was decanted and the remaining product was centrifuged and washed with deionized (DI) water. The washing process was repeated until the pH of the solution became neutral. After filtration and dry under vacuum, GO was obtained as a gray powder.

2.2. Synthesis of GO/Co(OH)₂ composites

The GO/Co(OH)₂ composites with different mass ratios were synthesized. Taking the rGO/Co₃O₄ composite with mass ratio (rGO:Co₃O₄) of 0.22:1 for example, the typical route is as follows. 0.1 g of GO was dispersed to 100 mL of distilled water and ultrasonicated for 1 h. 1.45 g of CoCl₂·GH₂O was dissolved in 10 mL water. The above CoCl₂·GH₂O solution was dropwise added into the GO suspension with vigorous stirring for 24 h. Afterwards, the aqueous solution of NH₃·H₂O (25–28%) was dropwise added into the above solution with continuous stirring until the pH of the solution reached 9. After aging for 12 h, the resulting product was separated by suction filtration and rinsed with distilled water and ethanol several times to remove the excess CoCl₂, and then dried at 60 °C for 12 h under vacuum. For comparison, pure Co(OH)₂ was synthesized by the same procedure in the absence of GO.

2.3. Synthesis of rGO/Co₃O₄ composites

The GO/Co(OH)₂ composites and pure Co(OH)₂ were used as precursors to subject to thermal treatment in air atmosphere at 150 °C for 6 h, resulting in the formation of the end products.

2.4. Acid leaching of the composites

In order to analyze GO and rGO in the precursor and product, the $GO/Co(OH)_2$ and rGO/Co_3O_4 composites were subjected to acid treatment by soaking composites (20 mg) in 100 mL of 1:1 HCl for 24 h to remove the Co_3O_4 . The acid-leached samples were separated by suction filtration and rinsed with distilled water and ethanol several times, and then dried at $60 \,^\circ$ C for 12 h under vacuum.

2.5. Characterization

The morphology of products was observed by field emission scanning electron microscopy (FESEM; JEOL, JSM-6701F, Japan) and transmission electron microscope (TEM; JEOL, JEM-2010, Japan). The structure of the samples was examined by X-ray diffraction (XRD; D/Max-2400) with Cu K\alpha radiation (λ = 1.5418 Å) operating at 40 kV, 100 mA. Fourier transform infrared spectroscopy (FT-IR) test was carried out by a Nicolet Nexus 670 FT-IR instrument. Thermogravimetric (TG) analysis was carried out using a Perkin-Elmer TG/DTA-6300 instrument in the temperature range of 25–800 °C. A heating rate of 10 °C min⁻¹ in air with a flow rate of 20 mL min⁻¹ was used.

2.6. Preparation of electrodes and electrochemical measurement

The working electrodes were prepared by pressing mixtures of the as-prepared samples, acetylene black, conducting graphite and polytetrafluoroethylene (PTFE) binder (weight ratio of 75:10:10:5) onto a nickel foam $(1 \text{ cm} \times 1 \text{ cm})$ current collector. The mass of electroactive materials in the working electrode was obtained through weighting bare nickel foam and nickel foam on which the above mixtures were pressed. Each working electrode contained about 3 mg of electroactive material and had a geometric surface area of about 1 cm². A typical three-electrode experimental cell equipped with a working electrode, a platinum foil counter electrode, and an Hg/HgO reference electrode was used for measuring the electrochemical properties of working electrode. All electrochemical measurements were carried out in 6 mol L⁻¹ aqueous KOH solution as electrolyte on a CHI660B electrochemical working station. Cyclic voltammetry (CV) was obtained at different scan rates of 5, 10, 15 and 20 mV s⁻¹ in the potential range of -0.4 to 0.55 V (vs. Hg/HgO). Galvanostatic charge–discharge was carried out at different constant current densities from 1 to 8 Ag⁻¹ in the voltage up to 0.95 V.

3. Results and discussion

3.1. Material characterization

TG analyses were carried out to determine the chemical composition of the as-prepared composites. Fig. 1 shows the TG curves of the rGO/Co₃O₄ composites with different mass ratios. Only one significant weight loss on the TG curves is found around 300 °C, except for the composite with low Co₃O₄ content, which exhibits a slight weight loss at about 150 °C due to the removal of the physisorbed water. This may be due to a little H₂O adsorbed on rGO sheets of rGO/Co₃O₄ composites, which are obtained through thermal treatment of GO/Co(OH)₂ in air atmosphere at 150 °C. Such phenomenon can also be found in other reference [34]. The large weight loss at about 300 °C is attributed to the removal of rGO from the composites. After 400 °C, the TG traces are stable with no further weight loss, indicating the complete removal of rGO. The estimations based on the TG curves indicate that the rGO/Co₃O₄ mass ratios of the five



Fig. 1. TG curves of as-prepared rGO/Co_3O_4 composites with different mass ratios under air atmosphere.

composites are 0.15:1, 0.22:1, 0.39:1, 0.78:1, and 1.78:1, respectively. In addition, it is pointed out that the burning temperatures of the samples in air atmosphere (around 300 °C) are much lower as compared with those of other CNS composites such as CNS-silica [35]. This can be attributed to the oxidizing activity of carbon due to the contained Co_3O_4 [36].

The crystal phase and structure information of the products were obtained by XRD measurements. Fig. 2 shows XRD patterns of GO, the GO/Co(OH)₂ composite, and the residual sediment obtained from the HCl leaching of the GO/Co(OH)₂ composite. The XRD pattern (curve a) of GO has a dominant peak centered at $2\theta = 10.3^{\circ}$, corresponding to the (001) reflection with the basal spacing of 8.6 Å and it matches well with the values reported in the literature [37]. The saw tooth-shaped broad reflection at 42.3° indicates that GO exhibits turbostratic disorder. The XRD pattern (curve b) of the as-prepared GO/Co(OH)₂ composite can be indexed to α -type cobalt hydroxide (JCPDS 38-0715), and the reflections of GO (001) and graphite (002) almost disappear. This is consistent with the previous studies that the diffraction peaks become weakened or even disappear whenever the regular stacks of GO are exfoliated [23,38]. In addition, the XRD pattern (curve c) of the residual sediment almost matches that of GO, although it is slightly disordered. Therefore, we speculate that the regular lamellar structure of GO sheets has been broken in the as-synthesized composite, forming exfoliated GO sheets.



Fig. 2. XRD patterns of GO (a), the $GO/Co(OH)_2$ composite (b), and the residual sediment obtained from the HCl leaching of the $GO/Co(OH)_2$ composite (c).



Fig. 3. XRD patterns of the rGO/Co_3O_4 composites with different rGO/Co_3O_4 mass ratios of 0.15:1 (a), 0.22:1 (b), 0.39:1 (c), 0.78:1 (d), and 1.78:1 (e) and the residual sediment obtained from the HCl leaching of the rGO/Co_3O_4 composite (f).

XRD patterns of rGO/Co₃O₄ composites with different mass ratios and the residual sediment obtained from the HCl leaching of the rGO/Co₃O₄ composite are shown in Fig. 3. In the XRD patterns of composites, the diffraction peak for C (002) is relatively weak, indicating that face-to-face stacking is absent [39] due to the existence of Co_3O_4 on both sides of rGO sheets. All the other diffraction peaks can be unambiguously indexed to the cubic spinel Co₃O₄ (JCPDS card No. 43-1003). The relative weak intensity of the peaks indicates that the size of Co₃O₄ particles is small. In addition, it is clearly seen that the peak intensity gradually decreases with increasing the content of rGO, indicating that homogeneous or amorphous phase is formed in the composites with high mass ratio of rGO:Co₃O₄ or the particle size is decreasing. Also, no peaks from other phases have been detected, indicating that the product is of high purity. To further verify if GO is converted to rGO in the composite, rGO/Co₃O₄ composites are also subjected to acid treatment. The XRD pattern of the residual sediment is shown in Fig. 3 (curve f). A broad peak with a basal spacing of 0.37 nm at $2\theta = 23.7^{\circ}$ is observed, and it can be ascribed to the characteristic peak of graphene [40]. This result suggests that GO nanosheets are almost reduced into rGO after the thermal treatment.

To further support the XRD study, the FT-IR spectra of the products are presented in Fig. 4. As shown on the FT-IR spectrum (curve a) of GO, the peaks at 3400 and $1624 \, \text{cm}^{-1}$ are attributed to O–H stretching and bending vibration, respectively. The other oxygencontaining functional groups are revealed by the bands at 1725, 1065, 1245 and 1375 cm^{-1} , which correspond to C=O in COOH, C-O, C-OH and C-O-C (epoxy), respectively [41]. The rGO/Co₃O₄ composite shows strong absorptions at 662 and 568 cm⁻¹ due to decomposition of the hydroxide to Co₃O₄ (curve b). For the residual sediment obtained from the HCl leaching of the rGO/Co₃O₄ composite, all the bands related to the oxygen-containing functional groups become very weak or even vanished (curve c), revealing that these functional groups are almost removed during the process of thermal treatments, and thus the GO is converted into rGO. In addition, a new absorption band at about 1572 cm^{-1} in the IR spectrum of the residual sediment may be attributed to the skeletal vibration of the rGO sheets.

The surface morphologies of pure Co_3O_4 and rGO/Co_3O_4 composites with different mass ratios are imaged by FESEM, as shown in Fig. 5. It can be seen from Fig. 5a that the sample of pure Co_3O_4 consists of fine particles. After rGO is incorporated in Co_3O_4



Fig. 4. The FTIR spectra of GO (a), the composite with mass ratio of 0.22:1 (rGO:Co₃O₄) (b) and the residual sediment obtained from the HCl leaching of the rGO/Co₃O₄ composite (c).

matrix, each rGO/Co₃O₄ composite displays an interesting and distinctive morphology. In the composite with mass ratio of 0.15:1 (rGO:Co₃O₄), a relatively loose packed structure assembled by particles is clearly revealed (Fig. 5b). When the rGO/Co₃O₄ mass ratio is equal to 0.22:1, the composite shows binary morphology which comprises rGO sheets and Co₃O₄ clusters assembled by different sizes of layers (Fig. 5c and d). We also call the Co₃O₄ cluster a thinwalled cell configuration, in which small sheets, acting as a wall, joined large sheets to form various cells. When the mass ratio is of 0.39:1, the composite presents closely packed filamentous network (Fig. 5e). However, the composite with mass ratio of 0.78:1 is particles of average size of 60-70 nm (Fig. 5f). As the rGO/Co₃O₄ mass ratio reaches 1.78:1, a higher agglomeration results in cementation of rGO and Co₃O₄ nanoparticles (Fig. 5g). To further verify that the rGO sheets exist in the composites, we use 1 M HCl to dissolve the inorganic matter (Co_3O_4) and extract rGO from composites. Fig. 5h shows the FESEM image of the rGO sheets after HCl leaching, which are curled and entangled together.

In order to further confirm the binary structure of the rGO/Co_3O_4 composite with mass ratio ($rGO:Co_3O_4$) of 0.22:1, TEM study was carried out (Fig. 6). As compared with TEM image of the residual sediment after HCl leaching (Fig. 6c), Co_3O_4 nanoparticles from rGO sheets are clearly distinguished (Fig. 6a). Besides, Co_3O_4 clusters assembled by different sizes of layers are displayed in Fig. 6b. That is, the interesting binary morphology can also be revealed by TEM, which is in agreement with FESEM images (Fig. 5c and d).

It is worth pointing out that the rGO sheets are clearly observed only in the composite with mass ratio (rGO:Co₃O₄) of 0.22:1. When the mass ratio of rGO to Co₃O₄ is more than 0.22:1, rGO sheets in composites are agglomerated together to form clusters or aggregates covered by Co₃O₄ particles (Fig. 5). Although many factors are associated with this interesting phenomenon, we think that dispersion of graphene oxide in the reaction process may be dominant. Usually, there are two interactions between GO sheets, that is, the electrostatic repulsion and van der Waals interaction. If the electrostatic repulsion is dominant, then graphene oxides could well disperse in the reaction systems [42,43]. On the contrary, if the van der Waals interaction dominates, the irreversible coagulation of the exfoliated GO occurs during the reaction process. This suggests that exfoliated GO can enable to form well-dispersed colloids if it carries enough positive (or negative) charges. At the initial stage of the reaction, some cobalt ions are adsorbed on graphene oxide sheets through coordination interactions of the C-O-C and -OH or ion-exchange with H⁺ from carboxyl. It is obvious that the adsorption quantity of cobalt ions (directly relative to the charge quantity carried by GO) is proportional to the ratio of free cobalt ions in the solutions to GO. With the continuous increment of the ratio of the free cobalt ions to GO, the electrostatic repulsion interaction between the charged GO gradually reaches and finally exceeds the van der Waals interaction. Consequently, there exists a critical ratio of the free cobalt ions to GO to achieve well-dispersed colloids of exfoliated graphene oxide through the electrostatic repulsion mechanism. If the relative amount of cobalt ions is lower than the critical ratio, coagulation of GO occurs during the reaction process because negative charges on reduced GO are partially or fully neutralized by cobalt ions, and thus there are fewer rGO sheets in the resultant composites in the SEM images. On the other hand, if the amount of cobalt ions exceeds the critical level described above, rGO sheets are also in high agglomeration because the rGO is locked up in a less porous Co₃O₄ matrix. So the critical ratio is important to synthesize well-dispersed graphene/metal oxide composites directly starting from GO. On the basis of the above analysis, a schematic representation of the formation process of the rGO/Co_3O_4 composite is shown in Fig. 7.

3.2. Electrochemical characterization

The potential of using the rGO/Co₃O₄ composites as electrode materials for supercapacitors is tested by CV and galvanostatic charge–discharge technique. The CVs of as-synthesized samples with a potential window from -0.4 to 0.55 V (vs. Hg/HgO) at 5 mV s⁻¹ are shown in Fig. 8. The CV curve of rGO after HCl leaching is not a perfect rectangle, compared to those reported by Stoller et al. [13]. This interesting behavior and the existence of redox peaks may be attributable to the redox reaction of OH⁻ with the residual functional groups (e.g., epoxyl, hydroxyl, and carboxyl function groups) in the rGO [44], suggesting the incomplete reduction of graphene oxide.

Moreover, there are two redox peaks observed in the CV curve of Co_3O_4 due to the following faradaic reactions [30]:

$$Co_3O_4 + OH^- + H_2O \Leftrightarrow 3CoOOH + e^-$$
(1)

 $CoOOH + OH^{-} \Leftrightarrow CoO_2 + H_2O + e^{-}$ (2)

As shown in Fig. 8a, the peaks of rGO and Co_3O_4 are so close to each other that we cannot make a clear distinction between the overlapped peaks, and therefore only two well-resolved redox peaks can be observed in CVs for the rGO/Co₃O₄ composites. It is known that the specific capacitance is proportional to the integral area of CVs [30]. It is notable that the composite with mass ratios of 0.22:1 gives the highest integral area in comparison with single component (rGO or Co_3O_4) and the composites with other mass ratios (Fig. 8b). In addition, from the inset zooming in Fig. 8b, we find that the change in the double layer capacitances is not clear. That is, the Co_3O_4 inclusion does not increase the double layer capacitance by increasing the accessible surface area of the rGO. It is possible that the improvement of capacitance is due to improving the conductivity and morphology of the Co_3O_4 electrode material.

Fig. 9a shows galvanostatic discharge curves of the rGO/Co_3O_4 composites with different mass ratios. It can be seen obviously that there are two clear voltage stages included in all the curves: -0.4 to 0.3 and 0.3-0.55V, respectively. During the former, short charge/discharge duration is ascribed to the electric double-layer capacitance of the electrode. During the latter, the combination of electric double-layer capacitance and faradaic capacitance is responsible for the longer charge/discharge duration. These results are in accordance with those deduced from the CV tests.



Fig. 5. FESEM images of pure $C_{0_3}O_4$ (a), rGO/Co₃O₄ composites with mass ratios (rGO:Co₃O₄) of 0.15:1 (b), 0.22:1 (c and d), 0.39:1 (e), 0.78:1 (f), and 1.78:1 (g) and the residual sediment after HCl leaching of the rGO/Co₃O₄ composite (h). Inset of Fig. 5(a, b and e) shows the corresponding high-magnification FESEM images of rGO/Co₃O₄ composites.

The specific capacitance is calculated by $I \times t/(V \times m)$, where *I* is the discharging current, *t* is the discharging time, *V* is the potential drop during discharge, and *m* is the mass of active material in a single electrode. As seen in Fig. 9b, the composite with mass

ratio of $0.22:1(rGO:Co_3O_4)$ achieves the highest specific capacitance of $291 \, Fg^{-1}$, which is much higher than that of the pure Co_3O_4 ($161 \, Fg^{-1}$). Moreover, when the mass ratio is more than 0.22, the specific capacitance deceases with increasing rGO content. This



Fig. 6. TEM images of rGO/Co₃O₄ composites with the mass ratio (rGO:Co₃O₄) of 0.22:1 (a and b) and the residual sediment after HCl leaching of the rGO/Co₃O₄ composite (c).

result is consistent with the morphology analysis of the rGO/Co₃O₄ composites. As shown in Fig. 5, the composite with mass ratio of 0.22:1(rGO:Co₃O₄) has a unique binary morphology, that is, rGO sheets on which grow Co₃O₄ and Co₃O₄ clusters with thin-walled cell configuration. In this structure, graphene layers interact with each other to construct an open pore network, through which electrolyte ions can easily access the surface of rGO to form electric double layers. On the other hand, cobalt oxides well dispersed in and grown on rGO sheets reduce diffusion length of OH- inside of the cobalt oxide and enhance a fast electron transfer between the electroactive materials and rGO matrix during the charge/discharge process, thus improving the electrochemical utilization of Co₃O₄. In the composites with other mass ratios, the excellent electric and surface properties of rGO sheets are not completely revealed due to the agglomerations. So they display relatively low capacitive behaviors.

On the basis of the above results, further electrochemical investigation is focused on the rGO/Co₃O₄ composite with mass ratio of 0.22:1. Fig. 10a shows the CVs of the composite at different scan rates of 5, 10, 15 and 20 mV s^{-1} in 6 M KOH solution. As seen from Fig. 10a, the characteristic CV shapes of the rGO/Co₃O₄ composite are not significantly influenced with the increasing of the scan rates. This indicates an excellent capacitive behavior, and the fast diffusion of electrolyte ions into the composite electrode. Fig. 10b shows galvanostatic discharge curves of the composite with mass ratio of 0.22:1 at various specific currents. This composite achieves a specific capacitance as high as 291 F g^{-1} at a specific current of 1 A g^{-1} . Its specific capacitance is up to 232 F g⁻¹ even at 8 A g⁻¹, 80% of that 1 Ag^{-1} (Fig. 10b and c). This implies that this rGO/Co₃O₄ composite has a good rate capability at a large specific current, which is very important for the electrode materials of a supercapacitor to provide high power density.

Long cycle life of supercapacitor is important for its practical applications. To evaluate the stability of the rGO/Co_3O_4 composite with mass ratio of 0.22:1 during the charge–discharge cycle, the values of specific capacitance with respect to charge–discharge cycle number (up to 1000 cycles) at 1 Ag^{-1} were measured in Fig. 10d. The composite can maintain 90% of the initial value over 1000 cycles, demonstrating excellent electrochemical stability of such electrode material. This confirms that the charge and discharge processes do not induce significant micro-structural changes of the rGO/Co₃O₄ composite electrode.



Fig. 7. A schematic representation of the formation process of the rGO/Co_3O_4 composite.



Fig. 8. CVs of rGO after HCl leaching, Co₃O₄ and rGO/Co₃O₄ composite with mass ratio (rGO:Co₃O₄) of 0.22:1 (a), rGO/Co₃O₄ composites with different mass ratios (b) at the sweep rate of 5 mV s⁻¹.



Fig. 9. Galvanostatic discharge curves of rGO/Co₃O₄ composites with different mass ratios at 1 A g⁻¹ and charge–discharge curves (inset) of the rGO/Co₃O₄ composite with mass ratio (rGO:Co₃O₄) of 0.22:1 at 1 A g⁻¹ (a). Specific capacitance variation of the rGO/Co₃O₄ composite with the weight percentage of rGO (b).



Fig. 10. CVs of the rGO/Co₃O₄ composite with mass ratio of 0.22:1 at various scan rates (a), galvanostatic discharge curves (b), specific capacitance of the rGO/Co₃O₄ composite with mass ratio of 0.22:1 at various specific currents (c) and cycle life measured at 1 A g⁻¹ (d).

4. Conclusions

It has been demonstrated that the rGO/Co₃O₄ composite can be successfully prepared directly starting from GO. There exists a crit-

ical ratio of rGO/Co₃O₄ to achieve well-dispersed graphene/cobalt oxide composite. Meanwhile, the rGO/Co₃O₄ composite with the optimal ratio reveals good pseudocapacitance of the loaded redoxactive materials, which produce positive synergistic effects and consequently enhance capacitive performance of the electrode materials.

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