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Reduced Graphene Oxide/Nickel Oxide/Polyaniline: Preparation and Properties Investigation as Supercapacitor Electrode Material

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Reduced graphene oxide/nickel oxide/polyaniline (GNP) was prepared by a two-step method. First, the reduced graphene oxide/nickel oxide composite material is prepared, and then the conductive polyaniline is loaded on the surface. The electrode materials were characterized by XRD, Raman spectra, TEM and HRTEM. Adopting a three electrode test system, the electrochemical properties of the materials were measured by cyclic voltammetry, constant current charge/discharge and AC impedance. The results showed that the characteristic peaks of graphene oxide were not detected in the XRD spectra of the reduced graphene oxide/nickel oxide composite, which shows that graphene oxide films with good dispersity was obtained in the process of the composite. High resolution transmission electron microscopy shows that the reduced graphene oxide / nickel oxide/polyaniline with a rough surface, indicating that the polyaniline was successfully loaded on the reduced graphene oxide/nickel oxide surface. The specific capacitance of GNP is 638Fg^{-1}. Under the current density is 500 mA g^{-1}, the specific capacitance maintained 100% after 1000 cycles while it reduced only 9% after 5000 cycles.

Keywords: Graphene oxide, nickel oxide, polyaniline, electrode material, three element composites

1. INTRODUCTION

Nickel oxide has a high theoretical specific capacitance and low cost, making it one of the candidate materials for the electrode material of the supercapacitor. However, only a few literatures have reported the usage of nickel oxide as supercapacitor material, due to the relatively poor electrical conductivity of nickel oxide [1-3]. To solve this problem, conductive polymer [4-6], carbon nanotube

[1, 7] and other conductive materials have been added to the nickel oxide, so composite materials were prepared with improved electrochemical performance. Xia *et al.* reported that graphene sheet/porous NiO was used as the electrode material of supercapacitor and the specific capacitance of this electrode material was about 84 Fg^{-1}, which maintained about 80% after 1000 cycles. [8] Graphene is considered as a type of novel carbon substrate material, due to its high electrochemical conductivity, large specific surface area (2630 m^2g^{-1}), strong mechanical strength and chemical stability. [9-11] However, the carbon structure was destroyed by the oxidation-reduction treatment [12-14] during the process of chemical synthesis.[11-12] In the process of charging and discharging nickel oxide, volume expansion or agglomeration may be encountered, leading to the reduction the cycle performance of the electrode material.

In this study, graphene oxide/nickel oxide/polyaniline (GNP) was prepared by a two-stepped method. First, the reduced graphene oxide/nickel oxide composite material is prepared, and then the conductive polyaniline is loaded on the surface. So, electrode material of supercapacitor with excellent performance was obtained.

2. EXPERIMENTAL

2.1 Preparation of graphene oxide (RGE)

Graphene oxide (RGE) was prepared through a two-step method:

1) Graphite (20 g, 12500 mesh) was added to a mixed solution containing concentrated sulfuric acid (30 mL), potassium sulfate (10 g) and P_2O_5 (10 g). The mixture was heated at 80 °C for 8 h. After reaction, the reaction mixture was filtrated and the resulted product was washed until the pH value of the filtrate was neutral and left for overnight.

2) The pre-oxidized graphite was added to 460 mL concentrated sulfuric acid. 60 g of potassium permanganate was added to the above solution and the feeding speed was controlled to make the temperature not exceed 20 °C. Then the mixture was heated at 35 °C for 2h with stirring. Ultrapure water (920 mL) was slowly added and the temperature was controlled in the range of 95-100 °C and maintained for 30 minutes. Then, the experiment was terminated by the addition of 2.8 L of water and 50mL 30% hydrogen peroxide. After reaction, the product was filtrated and the washed with 5 L HCl solution (v/v, 1:10).

2.2 Preparation of reduced graphene oxide /NiOx (GN)

The reduced graphene oxide/nickel oxide composite was prepared through hydrothermal method: 100 mg graphite oxide was added to 50 mL of anhydrous alcohol and dispersed under ultrasonic for 3 h. 0.7456 g of nickel nitrate was dissolved in 10 mL anhydrous ethanol at room temperature with stirring for 30 min. The two solutions above were blended and stirred for 30 min. Then, 10 mL 10% ammonia was added and the color of the mixture turned to black green. The mixture was transferred into hydrothermal kettle and heated at 180 ºC for 10 h. After cooling to room temperature, the product was washed thoroughly and dried under vacuum at 60 ºC.

2.3 Preparation of graphene /NiOx/ polyaniline (GNP)

Graphene/NiOx/polyaniline (GNP) was prepared by immobilization of polyaniline on the surface of reduced graphene oxide/nickel oxide. The mass ratio of graphene oxide/nickel oxide and aniline was 1: 10, 1: 5, 1: 1, 2: 1 and the corresponding product were named as GNP_{10}, GNP_5, GNP_1 and $GNP_{0.5}$, respectively.

The graphene/nickel oxide was dispersed uniformly. To this suspension, aniline monomer was slowly dropped (The mass ratio of graphene/nickel oxide and aniline was 0.5). The mixture was stirred under ice bath for 2 h, making the uniform dispersion of aniline in the system. The polymerization reaction was initiated by the addition of hydrochloric acid and ammonium sulfate under the condition of ice bath and the reaction lasted for 10h with the molar mass ratio of hydrochloric acid, ammonium perchlorate and aniline set at 1: 1: 1. After reaction, the product was collected by centrifugal and washed with ethanol and water.

As a control, polyaniline was synthesized adopting the same conditions without the presence of reduced graphene oxide/nickel oxide; Nickel oxide was synthesized with hydrogen peroxide as oxidant. Reduced graphene oxide (RGE) is prepared by the immersion of GN in 1 $molL^{-1}$ hydrochloric acid solution with ultrasonication for 2 h and stirring for 10 h successively. This process was repeated 4 times and nickel oxide nanoparticles were removed. Graphene/polyaniline (GP) and nickel oxide/polyaniline (NP) were synthesized by the same method of $GNP_{0.5}$, in which GN was replaced by the reduced graphene oxide and nickel oxide.

2.4 Characterization

Morphology: Transmission electron microscopy (JEOL); accelerating voltage set at 200KV; Synthesized products were first fully dispersed in ethanol under ultrasonic and the mixture was dropped on the supported carbon membrane for measurement;

FT-IR spectrum: FT-IR spectrometer (BRUKER Vector 22, Germany); Potassium bromide tablets method was used for sample preparation; the test wavenumber in the range of 400 ~ 4000 cm^{-1};

Raman spectroscopy: Renishaw Invia laser Raman spectrometer (England); the laser wavelength set at 514.5 nm, the test range is 100-4000 cm^{-1};

XRD: Ray powder diffractometer (Bruker Vector 22X, Germany); Condition: Cu_{Ka} target (λ=1.5406 Å); the test range is 5 ~70°.

2.5 Preparation of electrode and performance test

A three electrode system was adopted for the test: platinum sheet electrode as the counter electrode and saturated calomel electrode as a reference electrode and the working electrode.

The preparation of working electrode: foam nickel was used as current collector, washed with ethanol and ultra pure water under ultrasonic for 3 times, respectively, dried and weighed; the sample, conductive carbon black and adhesive were taken according to the mass ratio of 85:10:5. After fully blending, the mixture was evenly coated on the foam nickel, and painting area was controlled to be 1 cm^2. Then it was dried under vacuum at 60 ^oC. After drying, it was compressed (10MPa) and weighted.

Electrochemical test: The test electrolytes were 1 mol L^{-1} sulfuric acid and sodium sulfate solution with test temperature is 22 ^oC. The cyclic voltammetry and AC impedance were tested on CHI760C (Shanghai Chenhua Instrument Co., Ltd.). The cyclic voltammetry test ranges were -0.4 - 0.6 V for H_2SO_4 and -0.2 - 1 V for Na_2SO_4. The test frequency for the AC impedance is 1×10^5 to 1×10^{-3} Hz with the test voltage at 0 V and the amplitude at 5 mV. Constant current charge/discharge test was preformed on Land (CT2001A Wuhan Jinnuo Electronics Co Ltd) and the current density is 200, 500, 1000 mA g^{-1}.

3. RESULTS AND DISCUSSION

3.1 Structural characterization of graphene /NiOx/ Polyaniline

Figure 1a and b were the transmission electron microscope of GN.

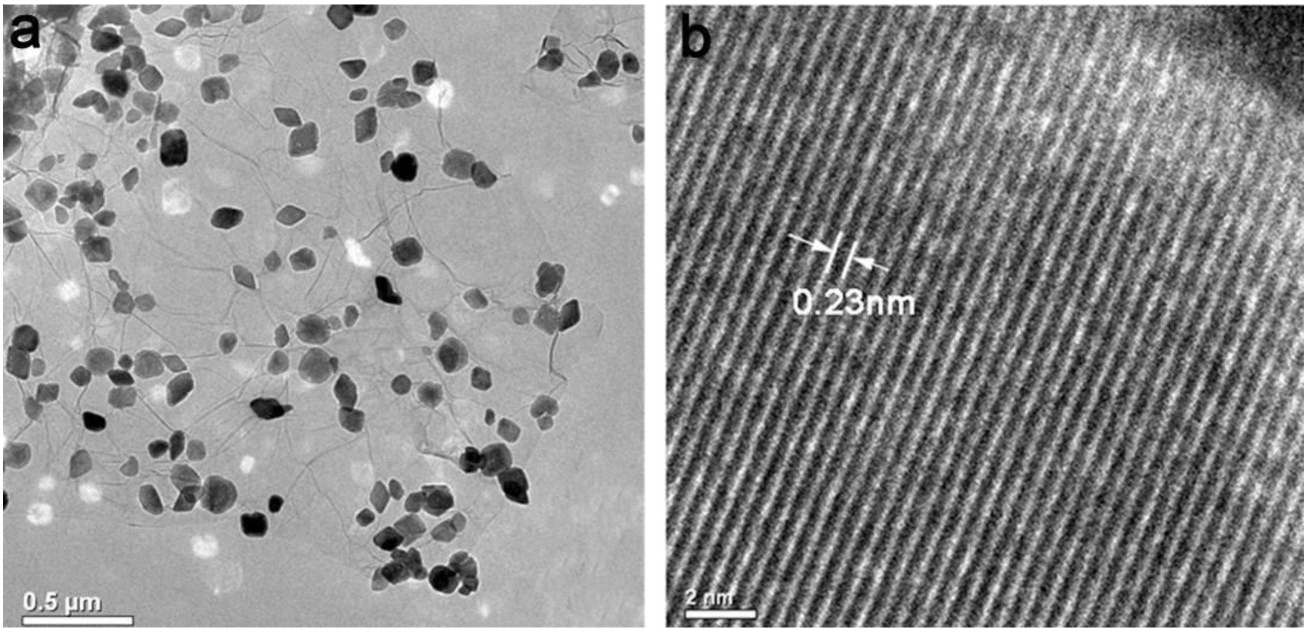

Figure 1. The TEM (a), HR-TEM (b) images of GN.

Figure 1a shows that the GN has the characteristic fold of graphene, which has a very small contrast with the substrate carbon support film, indicating that the thin carbon film is obtained by load of in the material, and nickel oxide nanoparticles with diameter in the range of 20~70 nm can be obtained. As shown in Fig.1b, the spacing of lattice line of nickel oxide was 0.23 nm, corresponding to the crystal surface (001) of nickel oxide (see XRD analysis).

Figure 2 shows the XRD and Raman spectra of GN and graphene oxide.

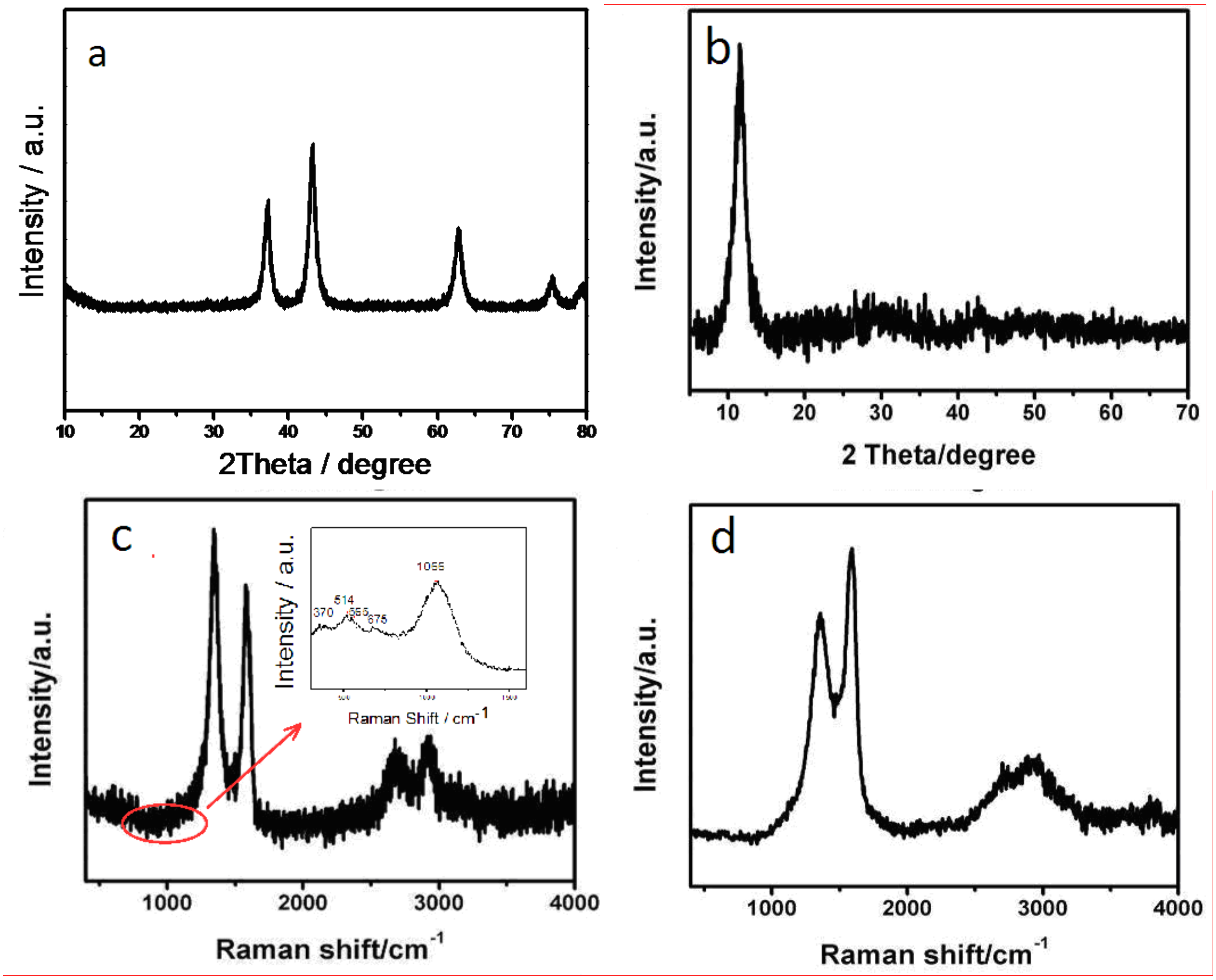

Figure 2. XRD patterns (a) and (b), Raman spectra (c) and (d) of GN and GO

Fig. 2a is the XRD spectrum of graphene oxide/nickel oxide, which demonstrated the Characteristic spectrum of nickel oxide. The card number is 89-7130, and no other object is detected. As shown in figure 2b, the characteristic peak of graphene oxide appears at 10.5, which corresponds to (001) diffraction and was not detected in the XRD GN complex, indicating that reduced graphene oxide film with excellent dispersity was obtained in the process of the complex.

Figure 2c and d were the Raman spectra for reduced graphene oxide/ Nickel oxide and graphene oxide, respectively. In Fig. 2, five main characteristic peaks of NiO could be observed at 370 cm^{-1}, 514 cm^{-1}, 565 cm^{-1}, 675 cm^{-1} and 1066 cm^{-1} respectively. The peaks at 370 cm^{-1} and 565 cm^{-1} could be attributed to one order transverse (1TO) and one order longitudinal (1LO) vibration respectively. The peaks at 1066 cm^{-1} and 675 cm^{-1} attributed to the vibration coupling of 2TO and 2LO while the peak at 514 cm^{-1} is the superimposed vibration peak of 1TO and 1LO. In addition, the peaks at 1341, 1593, 2685 and 2930 cm^{-1} correspond to D, G, 2D and D+D ' of the carbon materials[14]. G peak was caused by the SP^2 hybrid carbon atoms of graphene oxide, and the D peak was derived from the SP^2 hybrid to SP^3 hybrid. The ratio of D peak and G peak is usually used to explain the extent of the destruction of carbon materials and to be reduced. In addition, the peak at 2685 cm^{-1} indicated that the reduced graphene oxide had been stripped well in the material [14].

Figure 3 was the TEM spectra of GNP.

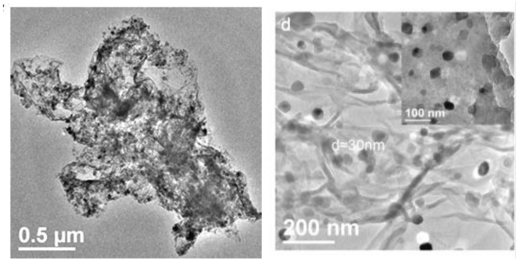

Figure 3. The TEM images of GNP.

Adopting reduced graphene oxide/nickel oxide as support material, polyaniline was attached on the surface. High resolution TEM shows that the GNP has a rough surface, demonstrating that polyaniline was successfully loaded on the surface of reduced graphene oxide/nickel oxide.

3.2 Electrochemical properties of graphene/NiOx/polyaniline

Under the three electrode test system, cyclic voltammetry, constant current charge/discharge and AC impedance were used to test the electrochemical properties of the composite materials as electrode materials of supercapacitor.

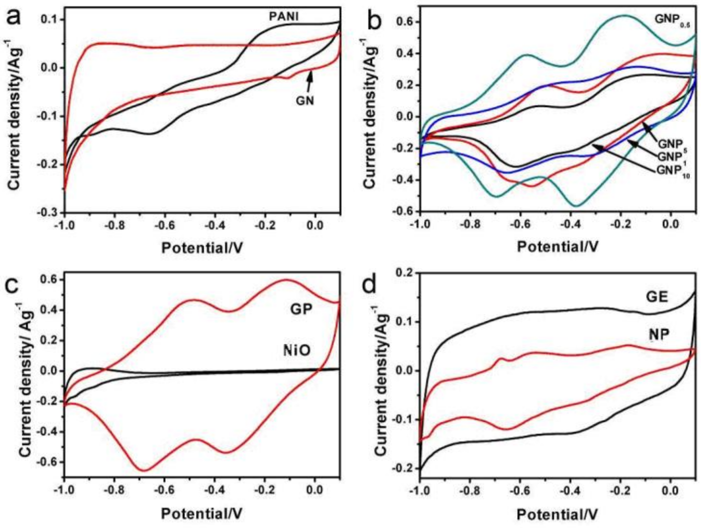

Figure 4. CV curves (a, b, c and d) of PANI, GN, GNP$_{0.5}$, GNP$_1$, GNP$_5$, GNP$_{10}$, GP and NiO in 1 mol/L KOH at a scan rate of 1 mV s^{-1},respectively.

Figure 4a cyclic voltammetry curves of reduced graphene oxide/nickel oxide in alkaline electrolyte under 1 mVs^{-1}. As shown, the curve was approximated a rectangular box and there was a small peak at the -0.1 V, indicating that the capacitance of this material in alkaline electrolyte was mainly derived from the double layer capacitance of the electrode material and the electrolyte interface. Double electric layer capacitance had good stability, and its specific capacitance was far less than the pseudo capacitance [15]. So the introduction of polyaniline could further improve the specific capacitance of the composite material. In figure 4a, the cyclic voltammetry curve of polyaniline had a pair of redox peaks (-0.67/-0.19V), corresponding to the conversion of polyaniline from the semiconductor state to the electric conduction state [16]. The potential difference between the oxidation peak and the reduction peak was usually used to indicate the reversibility of the redox reaction of the electrode material [17]. The potential difference of pure polyaniline was 0.46V, which is consistent with the values reported in the literature [18]. After being immobilized on the surface of reduced graphene oxide/nickel oxide, the cyclic voltammetry curves (Fig. 4b) of the polyaniline exhibited two pair of redox peaks. The redox peaks of $GNP_{0.5}$ were -0.7/-0.57 V and -0.38/-0.18 V, attributing to the state change of polyaniline among reduced/doped/oxidation states. Through calculation, the potential difference between the two pairs of redox peaks were 0.21 and 0.14 V, respectively, indicating that polyaniline showed better reversibility after it was loaded onto the reduced graphene oxide/nickel oxide while the utilization of polyaniline was improved at the same time. In addition, compared with pure polyaniline and reduced graphene oxide / nickel oxide, the cyclic voltammetry curves of GNP electrode materials showed a greater current response under the same test condition, indicating that the three elements composite had excellent electrochemical specific capacitance. With the increase of the content of polyaniline, the cyclic voltammetry curves of GFP are becoming more and more same as the cyclic voltammetry curves of pure Polyaniline and the current response decreased, attributing mainly to the load of a large amount of polyaniline which decreased the electrochemical activity of the polyaniline and reduced the full play of the pseudo capacitance of polyaniline.

In contrast, nickel oxide, reduced graphene oxide/polyaniline, reduced graphene oxide and nickel oxide/Polyaniline were tested under the same conditions and the results were shown in Figure 4c Figure 4d. Similar to GNP curve, reduced graphene oxide/Polyaniline also had two pairs of redox peaks (-0.38/-0.18 V, -0.7/-0.57 V). And the current response of the reduced graphene oxide/polyaniline was much larger than that of the reduced graphene oxide and pure polyaniline, which was equivalent to $GNP_{0.5}$. The results showed that the excellent electrochemical specific capacitance was mainly derived from the synergistic effect of reduced graphene oxide and polyaniline and the reversibility and high utilization rate of polyaniline was mainly due to the conductive properties of reduced graphene oxide. The cyclic voltammetry curves of nickel oxide/polyaniline had three cathodic peaks at -0.69, -0.54, -0.15 V and two anodic peaks at -0.66 and -0.98 V, respectively. The redox peak at -0.66/-0.15 V was consistent with that of the pure polyaniline while the -0.98/-0.69 V peak was the redox peak of the nickel oxide. The peaks at -0.54 V could be considered as the peak of polyaniline, which was similar to that of $GNP_{0.5}$ (-0.57 V). When reduced graphene oxide was in the presence of the three-element composite, no peaks of nickel oxide was observed, which might be due to the high electrochemical activity of polyaniline and coating of polyaniline on the periphery, causing that the redox reaction of nickel oxide could not be reflected in the cyclic voltammetry curve.

By calculation, the specific capacitance of reduced graphene oxide/nickel oxide, polyaniline, nickel oxide, reduced graphene oxide/polyaniline, reduced graphene oxide, nickel oxide/polyaniline as well as GNP were 96 Fg^{-1}, 58 Fg^{-1}, 33 Fg^{-1}, 678 Fg^{-1}, 198 Fg^{-1}, 87 Fg^{-1}, 202 Fg^{-1} (GNP_{10}), 339 Fg^{-1} (GNP_5), 366 Fg^{-1} (GNP_1), 638 Fg^{-1} ($GNP_{0.5}$) under a scan rate of 1 mVs^{-1}. After the load of nickel oxide onto graphene oxide, its specific capacitance was 3 times of pure nickel oxide, which was mainly due to the conductivity of reduced graphene oxide. The electrochemical specific capacitance of GNP was higher than that of polyaniline, reduced graphene oxide/nickel oxide, graphene oxide and nickel oxide/polyaniline, which was related to the morphology of materials and the interaction between materials. However, the specific capacitance of $GNP_{0.5}$ was a little smaller better than that of reduced graphene oxide/polyaniline and the possible reason was the poor conductivity of nickel oxide and the content of polyaniline reduced graphene oxide in GNP was less than that of reduced graphene oxide/polyaniline with the same electrode quality.

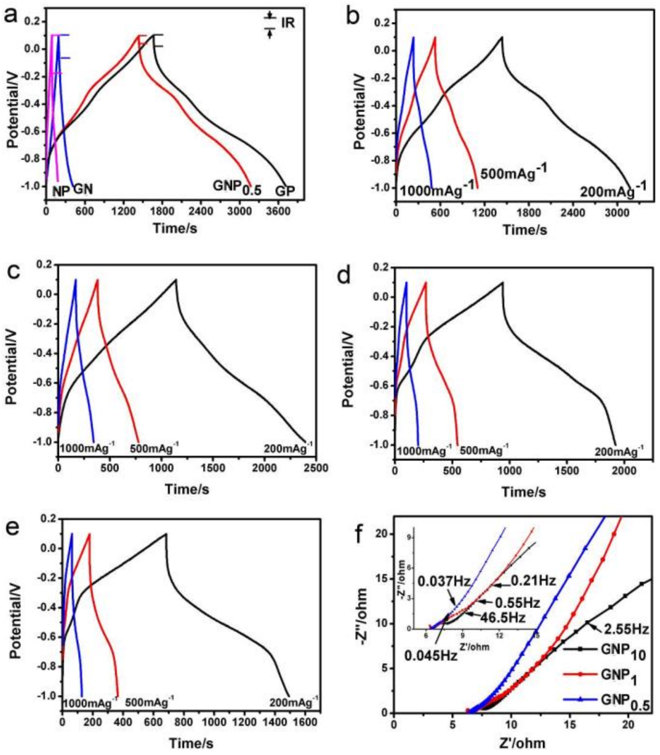

Figure 5. Galvanostatic charge–discharge curves of GP, GN, NP and $GNP_{0.5}$ at 200 mA g^{-1} (a).The galvanostatic charge–discharge curves of $GNP_{0.5}$ (b) GNP_1 (c), GNP_5 (d), GNP_{10} (e) at different current densities. EIS (f) of GNP_{10}, GNP_1, and $GNP_{0.5}$

Fig. 5a was the charge/discharge curve of the reduced graphene oxide/polyaniline, reduced graphene oxide/nickel oxide, nickel oxide/polyaniline and $GNP_{0.5}$ electrode material at the current density of 200 mA g^{-1} while b-e were the charge/discharge curves of GNP under different current densities. The curve of reduced graphene oxide/nickel oxide was approximate isosceles triangle, indicating that the electrochemical capacitance of the material was mainly attributed to the double layer capacitance, and the polyaniline/nickel oxide showed charge/discharge curves of with different slopes. The charge/discharge curves of reduced graphene oxide / Polyaniline and $GNP_{0.5}$ showed three voltage platforms in the ranges of -0.1~-0.1 V, -0.1~-0.6 V and 0.6~-1 V. The voltage platform at the highest voltage was caused mainly by the electric double layer capacitance. The later two platforms had a more extended charge and discharge time, mainly because of the electrode material featured mainly of the two aspects of electrochemical characteristics- electric double layer capacitance and pseudo capacitance [17]. In addition, the voltage drop of $GNP_{0.5}$ was smaller than that of the reduced graphene oxide/nickel oxide and nickel oxide/polyaniline and close to that of reduced graphene oxide/polyaniline, indicating that the resistance of $GNP_{0.5}$ and reduced graphene oxide/polyaniline were smaller than that of reduced graphene oxide/nickel oxide and nickel oxide/polyaniline. So, $GNP_{0.5}$ and the reduced graphene oxide/polyaniline were more suitable than the other two materials as electrode material of the supercapacitor. Figure 5f was the AC impedance spectra of GNP. In the high frequency region, the $GNP_{0.5}$ and GNP_1 showed almost no arc, and GNP_{10} showed a resistance of about 1 Ω, demonstrating the good electrical conductivity of the three-element composite. The slope in the middle frequency region of the curve was close to 45 degrees and the resistance in this part was called the Warburg impedance. The Warburg $GNP_{0.5}$ (0.045~0.037 Hz) was far less than those of GNP_1 (0.55~0.21 Hz) and GNP_{10} (46.5~2.55 Hz). This result demonstrated that when compared with other materials, $GNP_{0.5}$ had the fastest diffusion speed, due to the thin layer of polyaniline film on the surface of the $GNP_{0.5}$, which was consistent with the results of the TEM test.

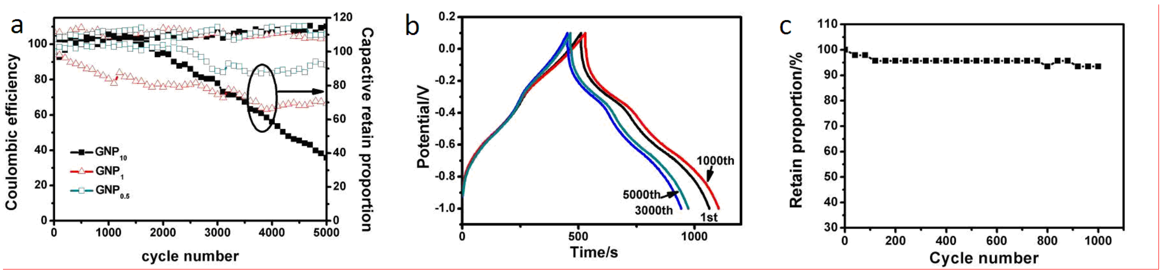

Figure 6. Coulombic efficiencies and capacitive retention proportions (a) of GNP_{10}, GNP_1, $GNP_{0.5}$ at 500 mA g^{-1} The different cycles of $GNP_{0.5}$ at 500 mA g^{-1}(b). Capacitive retain proportions of GN (c)

Figure 6a and Figure 6c were the cycle life spectra of GNP and reduced graphene oxide/nickel oxide with current density at 500 mA g^{-1}. After 1000, the specific capacitance GNP0.5 was maintained almost 100%. And after 5000 cycles, the specific capacitance attenuation was only 9%. And as shown in figure 6b, the different cycle charge/discharge curves all contained three voltage platforms. This showed that the reversible redox pseudo capacitance of polyaniline was also maintained, demonstrating that $GNP_{0.5}$ had excellent cyclic performance. Under the same test conditions, after 5000 cycles, the specific capacitance of GNP_1 and GNP_{10} remained only 69% and 37%. The decay of the two materials was due to extension of polyaniline chain in the thick film of polyaniline in the process of circulation, which limits their applications. However, the lifetime of $GNP_{0.5}$ was much higher than that of graphene/nickel oxide (Figure 6c) and showed more excellent cyclic performance that the reported electrode materials, such as graphene/polyaniline (79%, 800 cycles), graphene/carbon nanotubes/polyaniline (94%, 1000 cycles), and graphene/manganese oxide/poly ethylene 3,4- two oxygen thiophene [18-21]. The excellent cyclic performance of $GNP_{0.5}$ was mainly due to nano-structure design of the composite and the synergistic effect between materials. The graphene/nickel oxide was adopted as substrate for the load of polyaniline and beards the mechanical stress of polyaniline chain in the process of circulation. It improved the conductivity of the composite material. As polyaniline was embedded in the reticular structure of graphene/nickel oxide, the proliferation and migration paths of the ions in the electrolyte was effectively shortened in the process of rapid charge and discharge. This could increase the electrochemical utilization of the active material during the process of circulation. Moreover, as polyaniline was embedded uniformly in the reticular structure of grapheme, it could prevent the size expansion and agglomeration of nickel oxide during the long cycle of charge and discharge. Thus the synergy of these conditions improved the stability of the material.

4. CONCLUSIONS

Adopting a two-step method, reduced graphene oxide/nickel oxide/polyaniline three element composite materials was synthesized. Using two valence nickel ion as reducing agent and a stripping agent, graphene oxide was reduced and reduced graphene oxide with excellent dispersity was obtained. With this method, nickel oxide nanoparticles with diameter of 20~70 nm and reduced graphene oxide/nickel oxide composite materials were obtained. By adjusting the mass ratio of aniline monomer and reduced graphene oxide, three element composite materials with different thickness of polyaniline film were prepared. And the structure and morphology of the composite materials were characterized. Through the introduction of polyaniline, the carbon structure damage in the process of preparation of the reduced graphene oxide was repaired. The electrochemical performance of the three element composite materials with different proportions was investigated. The three element composite materials gave full play to the Faraday capacitance and nonfaradaic capacitance at the same time in nanometer size, so excellent electrochemical performance was shown. Its specific capacitance reached 638 Fg^{-1} and after 5000 cycles, its specific capacitance attenuation was only 9%. All these results showed that the reduced graphene oxide/nickel oxide/polyaniline was a kind of supercapacitor material with excellent cyclic performance.

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