



Preparation and Electrochemical Properties of Polyaniline Grafted Graphene Composites

Sayed Shokoth, Hossain Baten and Taoyu Yang*

School of Materials and Textile Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, PR China

Abstract

In order to improve the cycle stability of polyaniline and graphene composites, the hummers method was used to prepare graphene oxide (GO), which was modified by amination. On the basis of this, polyaniline was prepared by in situ oxidative polymerization. Aniline grafted graphene (rGO-PANI) composite. The morphology of the structure was characterized by scanning electron microscopy (SEM). X-ray diffraction (XRD) was used to characterize its crystal structure. The infrared (FTIR), Raman and Ra-Vi (UV-vis) spectra were used to characterize the functional structure. The conductivity was tested by four probes, and the electrochemical performance of the electrochemical workstation was tested and compared with the non-grafted polyaniline/graphene composite (rGO/PANI). The results show that polyaniline in the polyaniline grafted graphene composite is covalently bonded to graphene. The polyaniline grafted graphene composite material has improved cycle stability, and the capacity is only lost by 5% after 100 cycles, while the non-graft type loss is 15%. At the same time, the material has good electrical conductivity, the resistivity can reach $0.3\Omega\cdot\text{cm}$, and has good charge storage performance, and the mass ratio capacitance can reach 603F/g.

Keywords: Graphene; Polyaniline; Covalent grafting

Introduction

As a new type of energy storage device that combines the advantages of conventional capacitors and secondary batteries, super capacitors can provide higher energy density than conventional capacitors and have superior power density and cycle life compared to secondary batteries [1]. According to the working principle, the super capacitors can be divided into an electric double layer capacitor and a tantalum capacitor with a Faraday reaction [2]. The electrode material is the core component of the super capacitor, and its performance directly determines the performance of the capacitor, so the electrode Research on materials has received much attention. Graphene is a new type of carbon material with high specific surface area. It is generally used as an electrode material for electric double layer capacitors. However, when a single graphene is used as an electrode material for an electric double layer capacitor, the specific capacitance is usually not more than 200 F/g [3,4]. Polyaniline is the electrode material of the popular tantalum capacitors, which has the advantages of good conductivity, low cost and redox reversibility. However, when polyaniline is used as an electrode material, the repeated chemical process during the cycle causes its own volume to expand and contract, eventually leading to electrode shedding, which greatly affects its cycle stability [5]. In recent years, many studies have reported the use of in-situ polymerization to prepare composites of graphene and polyaniline with different morphological features. The characteristics of the electric double layer capacitor of graphene and the high tantalum capacitor of polyaniline greatly increase the capacitance [6,7]. However, the non-covalent bond between graphene and polyaniline in the general composite material is weak, and the polyaniline is easily detached during use, resulting in deterioration of electrochemical performance and cycle stability [8]. In order to overcome these problems, it is necessary to design a composite material for studying polyaniline grafted graphene. In this paper, graphene oxide was prepared from graphite and modified by amination. On the basis of this, in-situ oxidative polymerization of aniline monomer was added to prepare polyaniline grafted graphene composite [9], and non-grafted type. Graphene/polyaniline composites were compared [10].

Materials and Methods

Materials

Graphite powder (Aladdin product), aniline (AR, Wuxi Prospect Chemical Reagent Co. Ltd.), Hydrochloric acid (HCl) (AR, Huadong Pharmaceutical Co. Ltd.), sulfuric acid (H_2SO_4) (AR, Zhejiang Sanying Chemical Reagent Co, Ltd. Company, potassium permanganate (AR, Zhejiang Sanying Chemical Reagent Co. Ltd.), phosphorus pentoxide (AR, Tianjin Komi Chemical Reagent Co., Ltd.), ammonium persulfate (APS) (AR, Tianjin Yongda Chemical Reagents Ltd.) Hydrogen peroxide (30%, Tianjin Yongda Chemical Reagent Co. Ltd.), thionyl chloride (AR, Macleans products), tetrahydrofuran (AR, Shanghai Zhanyun Chemical Co. Ltd.), 4-(BOC-amino) phenol (including BOC) Is tert-butoxycarbonyl) (98%, Shanghai Maclean Biochemical Technology Co. Ltd.), trifluoroacetic acid (AR, Aladdin products), methanol (AR, Hangzhou Gaojing Fine Chemical Co. Ltd.), acetone (AR, Zhejiang Sanying) Chemical Reagent Co. Ltd. Toluene (AR, Zhejiang Sanying Chemical Reagent Co. Ltd.), Ethanol (AR, Hangzhou Gaojing Fine Chemical Co. Ltd.), Perfluorosulfonic acid (Suzhou Yilong Energy Technology Co. Ltd.).

Methods

EL electronic analytical balance (Japan Shimadzu company), DLK-2007 rapid low temperature cooling cycle machine (Ningbo Xinzhi Biotechnology Co. Ltd.), JBSC-6 constant temperature stirring water bath (Gongyi City Yuhua Instrument Co. Ltd.), H1805 Desktop high-

*Corresponding author: Taoyu Yang, School of Materials and Textile Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, PR China, Tel: +86-2345874688; E-mail: tyang41@illinois.edu

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speed centrifuge (Xiangyi Centrifuge Instrument Co. Ltd.), JP-040S ultrasonic cleaning machine (Shenzhen Jiemeng Cleaning Equipment Co. Ltd.), FD-1D-80 Freeze Dryer (Beijing Bo Yikang Experimental Instrument Co. Ltd.), VERTEX 70 infrared spectrometer (scanning range 4000-400 cm^{-1} , Bruker, Switzerland), Phenom pro desktop scanning electron microscope (Reeding Scientific Instruments (Shanghai) Co. Ltd.), Renishaw inVia Raman microscope (scanning range 100-3500 cm^{-1} , Renishaw, UK), D8 discover X-ray diffractometer (scan range 5°-70°, scan rate 5°/min, Platinum Instruments (Shanghai) Co. Ltd.), UV-2600 UV-visible spectrophotometer (integration) Ball (scanning range 300-800 nm, Shimadzu Corporation, Japan), RTS-9 dual-electric measurement four-probe tester (Guangzhou four-probe technology), CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd.).

Preparation of Polyaniline Grafted Graphene Composite

Preparation of graphene oxide

The graphene oxide was prepared by the modified hummer's method [11]. The first step was the pre-oxidation stage. 15 ml of concentrated sulfuric acid was added to a 500 ml four-necked flask and placed in a water bath at 80°C, 2.5 g of phosphorus pentoxide and 2.5 g were weighed. Ammonium sulfate was slowly added to the flask and stirred vigorously for a while. After being completely dissolved, 3 g of graphite powder was weighed and added to the flask, and stirring was continued for 5 hours at 80°C. After the reaction was completed, it was cooled to room temperature, diluted with a small amount of deionized water, then transferred to a 500 ml beaker, and a large amount of deionized water was added to the beaker and allowed to stand overnight. The supernatant was decanted and filtered through a Buchner funnel and deionized water was repeatedly washed until neutral. Finally, the obtained product was dried in a vacuum oven at 50°C to obtain pre-oxidized graphite. The second step is the oxidation stage; 120 ml of concentrated sulfuric acid is added to a 500 ml four-necked flask and placed in an ice water bath. The pre-oxidized graphite was slowly added to the flask and added with stirring. After it was completely dispersed, 15 g of potassium permanganate was weighed and added very slowly to the flask, and kept in an ice water bath and stirred. After stirring for a while to stabilize, the temperature was raised to 35°C and stirred for 4 h. After the completion of the reaction, the mixture was stirred, and 100 ml of deionized water was added drop wise with a constant pressure dropping funnel. After 15 minutes, 25 ml of hydrogen peroxide was added drop wise, and when the dispersion turned bright yellow, the reaction was completed. After stirring for a while, let stand for one night. The upper layer of liquid was removed, and the lower layer of the precipitate was washed by centrifugation, washed three times with 10% hydrochloric acid, and washed repeatedly with deionized water until near neutral. The product is dried in a freeze dryer to obtain a graphene oxide product (GO) [12].

Preparation of aminated graphene: 40 ml of thionyl chloride was added to a 250 ml four-necked flask, and 500 mg of graphene oxide was weighed and added to a four-necked flask, and ultra-sonicated for 1 h to uniformly disperse the graphene oxide. After refluxing for 24 hr under nitrogen atmosphere, after refluxing, an appropriate amount of toluene was added and distilled under reduced pressure three times to remove excess thionyl chloride. Immediately thereafter, the obtained solid was added to a flask of an appropriate amount of anhydrous tetrahydrofuran, and ultrasonically dispersed to obtain a dispersion. 3 g of 4-(BOC-amino) phenol (wherein BOC is tert-butoxycarbonyl) was added to the dispersion, and refluxed under nitrogen for 12 hr. Then,

excess trifluoroacetic acid and dichloromethane were added and mixed for 1 hour to remove the protecting group. Finally, it was washed three times with methanol, and lyophilized to obtain a product of graphene grafted p-aminophenol (rGO-NH₂).

Preparation of Polyaniline Grafted Graphene Composite

20 mg of rGO-NH₂ powder was added to 40 ml of hydrochloric acid solution (1 mol/L), and dispersed by ultra-sonication for 30 minutes to obtain a dispersion. The dispersion was placed in an ice water bath and cooled to 0°C, and then a certain amount of aniline monomer was added and stirred for a while. According to the ratio of ammonium persulfate to aniline of 1:1, ammonium persulfate was weighed and formulated into X% ammonium persulfate solution, and ammonium persulfate solution was slowly added dropwise. After a few minutes the black dispersion turned green, indicating that the aniline graft polymerization started. The ice water bath was kept stirring and reacted for 6 hours. After the reaction, the product was washed with 1 mol/L hydrochloric acid solution, washed with acetone and deionized water for 3 times, and finally dried in a freeze dryer to obtain a graphene-grafted polyaniline product (rGO)-PANI). In order to compare the structure and properties, the non-grafted graphene/polyaniline composite was also prepared. The preparation process was as follows: firstly, the same method was used to prepare graphene oxide, and then a certain amount of graphene oxide was placed in 8M. The sodium hydroxide solution was gently sonicated at a temperature of 80°C for 1 h, and then freeze-dried to obtain a reduced graphene oxide (rGO) powder. Finally, the aniline monomer was polymerized in the rGO dispersion in the same manner as above, and then freeze-dried. A graphene/polyaniline composite (rGO/PANI) was obtained.

Structural Characterization and Performance Testing of rGO-PANI

Structural characterization: Infrared spectroscopy (FTIR) VERTEX 70 infrared spectrometer was used to grind the sample with the spectral grade potassium bromide powder in a ratio of 1:100, and then the infrared absorption peak of the substance was measured. The scanning range was 4000 cm^{-1} -400 cm^{-1} resolution 4 cm^{-1} , 32 times of scanning. Sample surface topography analysis, Phenom pro desktop scanning electron microscope (SEM) was used to adhere the sample to the sample platform for observation. Ultraviolet spectroscopy, TU-1950 dual-beam UV-visible spectrophotometer (UV-vis) with UV wavelength range of 300-800 nm. Raman spectroscopy, using a Renishaw inVia Raman microscope from Renishaw, UK, with an excitation wavelength of 633 nm. X-ray diffraction spectroscopy, X-ray diffraction spectroscopy (XRD) was used to test the samples under the conditions of incident light source Cu K α ray (wavelength 1.5405Å), test voltage 40 kV, test current 100 MA, scan rate It is 5/min and the scanning range is 5-70°.

Performance Test

Conductivity test

For the preparation of the powder test sample, the sample powder was subjected to tableting treatment using a 769YP-15A tablet press; the resistivity test of the powder was performed using an RTS-9 type double electrical test four probe tester.

The resistivity is determined by the standard four-probe method and its resistivity is calculated by the following formula:-

$$\rho = \frac{Vlh}{Id}$$

Where ρ is the resistivity ($\Omega \cdot \text{cm}$), V is the measured voltage value, l is the diameter (cm) of the sample, h is the thickness (cm) of the sample, I is the current (A), d is the middle two probes between the width (cm).

Electrochemical performance test

Tested by Shanghai Chenhua 660E electrochemical workstation. Preparation of electrode material sample: First, about 5 mg of the sample was weighed, and 200 μl of perfluorosulfonic acid and 300 μl of ethanol were added, followed by ultrasonic dispersion for 20 min. Approximately 40 μl of the suspension was uniformly loaded on a glassy carbon electrode and dried to serve as a working electrode. The reference electrode is a saturated calomel electrode, the auxiliary electrode is a platinum electrode, and the electrolyte is a 1M H_2SO_4 solution.

Results and Discussion

Structural analysis of polyaniline grafted graphene

Scanning electron micrograph analysis: The scanning electron micrographs of rGO/PANI and rGO-PANI are shown in Figure 1 (rGO/PANI and rGO-PANI correspond to Figures 1a and 1b, respectively). The sheet structure in the figure is graphene, and the rod-like structure is polyaniline. In the graph a, the graphene of the sheet structure was not observed, and only the polyaniline agglomerates of the rod structure were observed. This may be a polymerization of aniline into polyaniline-coated graphene, indicating that the polyaniline polymerization is disordered when there is no reaction site for graft polymerization. The graphene structure of graphene in Figure 1b remains relatively intact, and the polyaniline of the rod structure is distributed around the graphene. This is mainly because the edge of the graphene is modified into a reaction site, and the aniline is grafted and polymerized from the reaction site, and the polyaniline is uniformly distributed around the graphene.

Analysis of infrared spectrum: The infrared spectrum of GO, rGO/PANI and rGO-PANI is shown in Figure 2. In the spectrum of GO, 1720 cm^{-1} is the stretching vibration peak of C=O in the COOH at the edge of the GO, the stretching vibration peak of -OH at 3446 cm^{-1} , and the absorption peak at 1625 cm^{-1} is the carbon on the GO. Skeleton vibration of the ring plane. At 1220 cm^{-1} and 1058 cm^{-1} , an epoxy group and an also xy group on GO are respectively represented. In the spectrum of rGO-PANI, 1750 cm^{-1} is the stretching vibration peak of the C=O group in the ester bond, which is the carbonyl group in which the 4-(BOC-amino) phenol is esterified with the carboxyl group on GO to form an ester bond peak. The stretching vibration

peak of the C-N group at 1302 cm^{-1} and the C=C skeleton vibration peak of the benzene ring at 1464 cm^{-1} . The absorption peak at 1560 cm^{-1} and 1113 cm^{-1} is the characteristic absorption peak of the N-Q-N group on the PANI molecular chain, and the C-H bending vibration peak of 804 cm^{-1} belongs to the benzene ring. These characteristic peaks indicate that the aniline is polymerized into polyaniline and grafted onto the graphene. The rGO/PANI spectrum also has a characteristic absorption peak of polyaniline and a characteristic absorption peak representing the vibration of the graphene carbocyclic plane skeleton. However, the characteristic absorption peak indicating the ester bond is absent in the spectrum of rGO/PANI, and infrared analysis proves that the rGO-PANI complex is obtained by graft polymerization.

X-ray diffraction spectroscopy: The X-ray diffraction spectrum of GO, rGO/PANI and rGO-PANI is shown in Figure 3. In the spectrum of GO, the characteristic peak of graphene oxide appears at $2\theta=9.9^\circ$. According to the Bragg equation, $2d\sin\theta=n\lambda$, the layer spacing of graphene oxide can be calculated as 0.89 nm from $n=1$, $\lambda=1.5405\text{\AA}$. It is obviously larger than the interlayer spacing of natural graphite (0.34 nm), indicating that under the action of strong oxidant, oxygen-containing functional groups such as hydroxyl group, epoxy group and carboxyl group are formed on the surface and edge of graphite, which increases the interlayer spacing of graphene oxide. In the spectrum of rGO-PANI, three characteristic diffraction peaks appeared at 14.6° , 20.9° and 25.4° , corresponding to the characteristic diffraction peaks of polyaniline, indicating the presence of polyaniline in the composite.

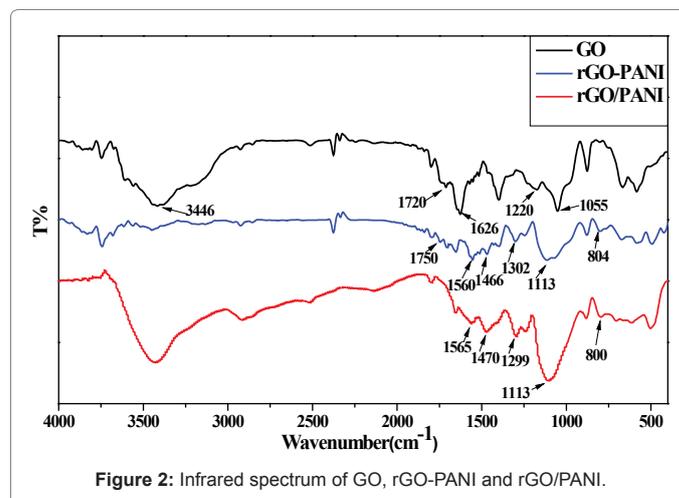


Figure 2: Infrared spectrum of GO, rGO-PANI and rGO-PANI.

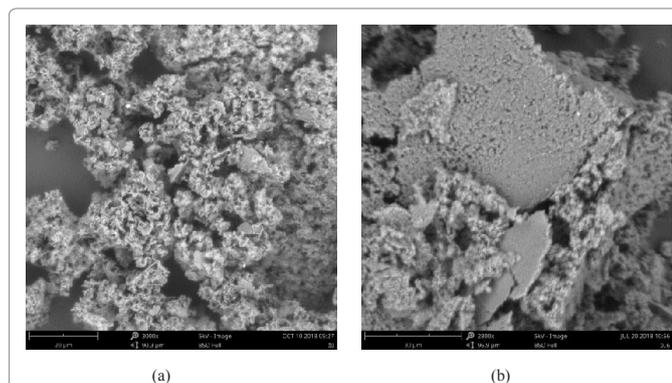


Figure 1: Scanning electron micrograph of rGO/PANI and rGO-PANI.

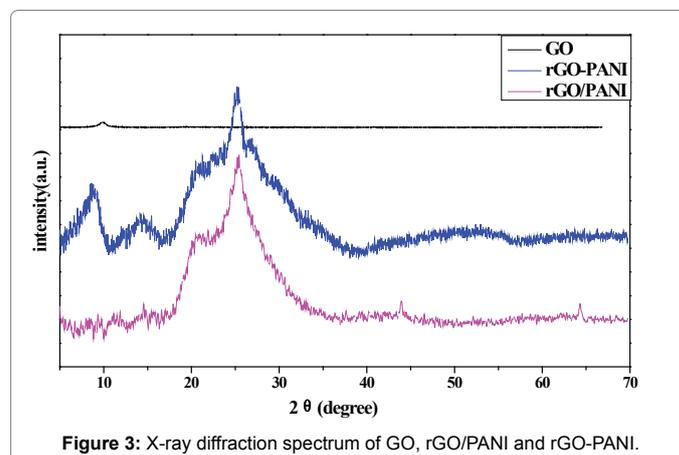
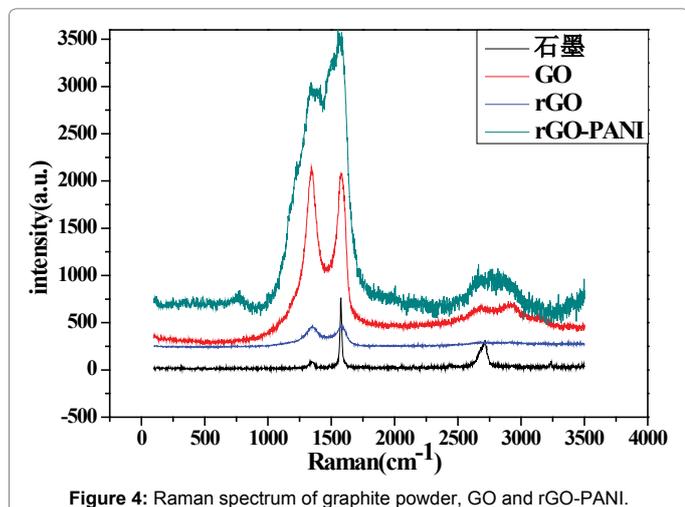


Figure 3: X-ray diffraction spectrum of GO, rGO/PANI and rGO-PANI.

The diffraction peak corresponds to the graphene structure at $2\theta=8.5^\circ$, and the interlayer spacing is calculated to be 1.03 nm according to the Bragg equation, indicating that the embedding of polyaniline increases the interlayer spacing of the graphene structure. In the line of rGO/PANI, three characteristic diffraction peaks were also observed at 14.6° , 20.9° and 25.4° , indicating that polyaniline was also present in the composite. There is a weak diffraction peak around $2\theta = 11^\circ$, corresponding to the structure of graphene. According to the Bragg equation, the layer spacing can be calculated to be 0.79 nm, and the layer spacing of the graphene structure becomes smaller, indicating that the graphene structure in the polymerization of aniline A reunion may have occurred. By comparing the peak shapes of rGO-PANI and rGO/PANI, it can be found that the peak of rGO-PANI composite is sharp and obvious, indicating that during the polymerization of rGO-PANI composite, aniline is ordered polymerized at the reaction site, making the crystal form The structure of the structure is regular and orderly, while the peak of the rGO/PANI composite is weaker and wider, indicating that the aniline polymerization is disordered and disordered during the polymerization of the rGO/PANI composite, and may contain more oligomers.

Raman spectroscopy: The Raman spectra of graphite powder, GO, rGO and rGO-PANI are shown in Figure 4. Graphene materials generally have two characteristic peaks D and G in the Raman spectrum, and the D peak generally appears around 1350 cm^{-1} , indicating the degree of disorder of the graphene structure, that is, defects. The G peak generally appears around 1580 cm^{-1} , and the E2g vibration derived from the first-order scattering of phonons is caused by the in-plane vibration of the Sp² carbon atom. The intensity ratio of the D peak and the G peak to the ID/IG can reflect the disorder of the graphene material. In the spectrum of graphite powder, there is a G peak at 1580 cm^{-1} , and the D peak is not obvious, indicating that the graphite powder is composed of Sp² carbon atoms, and the structure is stable and defect-free. In the spectrum of GO, 1343 cm^{-1} and 1580 cm^{-1} correspond to D peak and G peak, respectively, ID/IG=1.02, indicating that many oxygen-containing functional groups are formed in GO, and there are many defects. In the spectra of rGO and rGO-PANI, the ID/IG is 0.96 and 0.81, respectively, indicating that the oxygen-containing functional groups in the graphene oxide are reduced in these two substances, and the reduction effect of rGO-PANI is better, which is beneficial to A more coherent conductive plane is formed [13].

UV-visible spectroscopy: The UV-Vis spectra of rGO/PANI and rGO-PANI are shown in Figure 5. In the spectra of rGO/PANI and



rGO-PANI, the $\pi-\pi^*$ transition of the benzene ring is at 300-360 nm, and the absorption peak at 420-460 nm and 680 nm-800 nm is attributed to the transition of the polaron and the bipolaron. It is related to the degree of polyaniline doped with hydrochloric acid, which indicates that polyaniline in both grafted and non-grafted composites is doped polyaniline with conductivity [14]. Compared with rGO/PANI, the UV absorption peak position of rGO-PANI is red-shifted, which is the result of graft polymerization of polyaniline and graphene.

Conductivity analysis

In order to investigate the electrical conductivity of the composite, the electrical resistivity of the rGO/PANI composite was compared with that of the rGO, PANI, and rGO-PANI composites. The results are shown in Table 1. It can be seen from the table that the resistivity of the rGO-PANI composite is smaller than that of the rGO/PANI composite, because the polyaniline grafts the graphene to facilitate electron transport and improve conductivity. At the same time, the resistivity of the composites is less than rGO and PANI, indicating that the combination of the two materials can effectively improve the electrical conductivity.

Electrochemical performance analysis

CV curve analysis: In order to investigate the electrochemical properties of the composites, the rGO-PANI composite and rGO/PANI composites were subjected to cyclic voltammetry in a 1M H₂SO₄ solution using a three-electrode system with a scanning potential of -0.8 V-1.6V. Figure 6 is the cyclic voltammetry curve of rGO-PANI composites at different scanning speeds. At different scanning speeds, the cyclic voltammetry curves of composites have two distinct peaks, corresponding to the redox reaction of polyaniline, and peaks. The potential did not move substantially, indicating that the polyaniline grafted graphene composite material has good cycle stability.

Figure 7 is the cyclic voltammetry curve of rGO-PANI composite material and rGO, PANI, rGO/PANI composite material at a sweep speed of 100mv/s. It can be seen from the figure that the shape of the RV CV curve is close to a rectangle, indicating its performance. The double-layer capacitor is available. The cyclic voltammetry curves of PANI, rGO/PANI composites and rGO-PANI composites all have obvious redox peaks and exhibit tantalum capacitance characteristics.

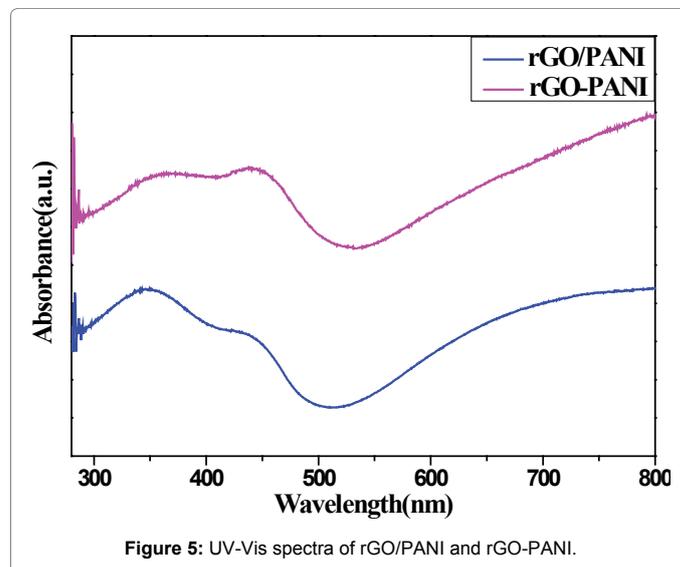


Table 1: Resistivity comparison.

Sample	rGO-PANI	rGO/PANI	rGO	PANI
Resistivity ($\Omega \cdot \text{cm}$)	0.3	7.9	213.1	37.5

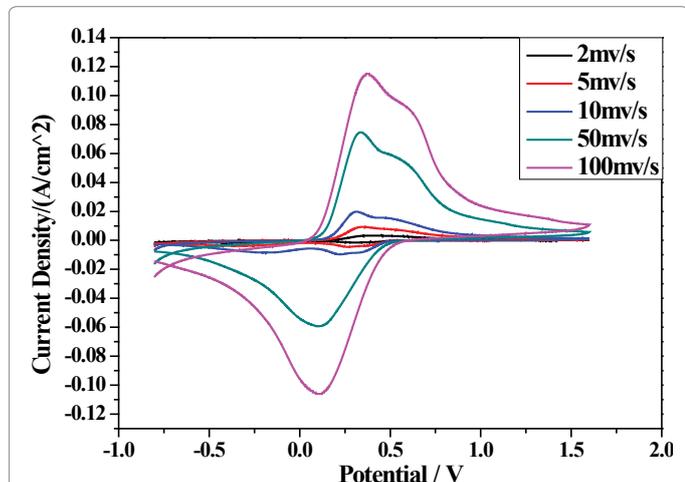


Figure 6: Cyclic voltammetry curve of rGO-PANI at different scanning speeds.

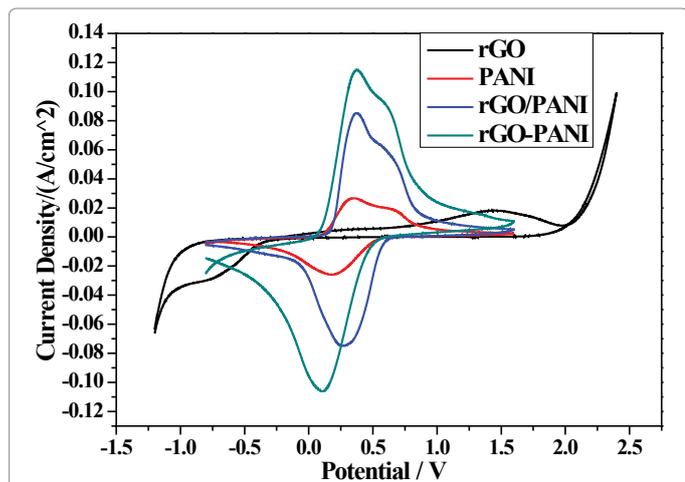


Figure 7: Cyclic voltammetry curves of rGO, PANI, rGO/PANI and rGO-PANI.

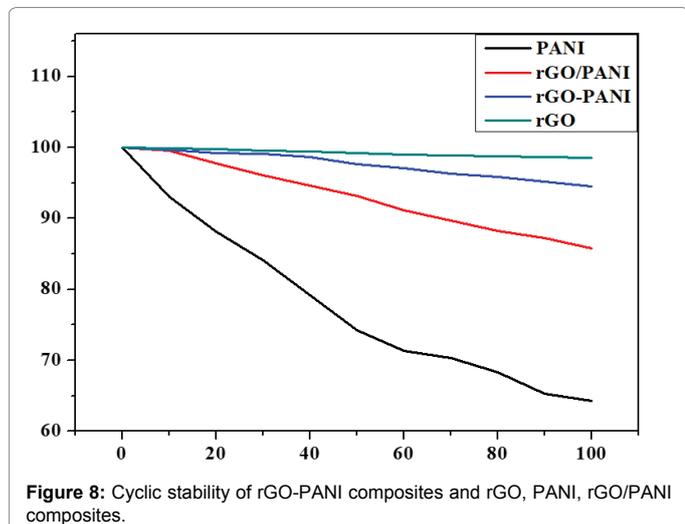


Figure 8: Cyclic stability of rGO-PANI composites and rGO, PANI, rGO/PANI composites.

The size of the area contained in the CV curve indicates the capacitance of the material. It can be seen that the capacitance of the composite is significantly larger than that of the single component, and the capacitance of rGO-PANI is greater than that of rGO/PANI. The formula for calculating the capacitance by cyclic voltammetry (where S is the integral area, m is the sample mass, V is the scanning speed, and U is the potential difference), and the mass of rGO-PANI composite, rGO, PANI, rGO/PANI composite is calculated. The specific capacitance is 603F/g, 117F/g, 64F/g, 408F/g. It can be seen more intuitively that the polyaniline and graphene are grafted and composited with a larger capacity than the non-grafted.

Cycle Stability Analysis: By recycling the composite material multiple times and observing the loss of its capacitance to judge its cycle stability, the capacitance changes of rGO-PANI composite material and rGO, PANI, rGO/PANI composite material after 100 cycles is shown in Figure 8. It can be seen from the figure that the capacity loss of rGO-PANI composite material is 5% after 100 cycles, while the capacity loss of rGO/PANI composite material after 15 cycles is 15%, which indicates that graphene and polyaniline pass covalent. The key connections are stronger and the cycle stability is improved during use. The cycle stability of rGO is very good because it exhibits an electric double layer capacitance, and only charge accumulation occurs without chemical reaction. The loss of capacitance of PANI in the first 50 cycles is serious. The main reason is that the electrolyte ions are repeatedly doped and dedoped in the PANI bulk phase, causing the expansion and contraction of their own volume, resulting in the electrode being easy to fall off. Reduced cycle stability, PANI capacitance loss of 36% after 100 cycles.

Conclusion

In this paper, graphene oxide was prepared by modified hummers method and its amination was modified. On the basis of this, polyaniline grafted graphene composites were prepared by in situ oxidative graft polymerization of aniline. Polyaniline grafted graphene has good cycle stability, and the capacitance is only lost 5% after 100 cycles, which is better than non-grafted graphene/polyaniline composite. At the same time, the polyaniline grafted graphene composite material has excellent electrical conductivity and electrical capacity, and the resistivity can reach $0.3 \Omega \cdot \text{cm}$. When the scanning speed is 100 mV/s, the mass ratio capacitance can reach 603 F/g. The polyaniline grafted graphene composite material prepared by the method not only effectively solves the problem that the cyclic stability of the non-covalently bound graphite dilute aniline is deteriorated during use, but also improves the conductivity and the electric capacity.

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