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**Novel layered polyaniline-poly(hydroquinone)/graphene film as
supercapacitor electrode with enhanced rate performance and
cycling stability**

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Abstract:

It is a challenge to fabricate polyaniline (PANI) materials with high rate performance and excellent stability. Herein a new special supercapacitor electrode material of polyaniline-poly(hydroquinone)/graphene (PANI-PHQ/RGO) film with layered structure was prepared by chemical oxidative polymerization of aniline and hydroquinone (H_2Q) in the presence of RGO hydrogel film. The synergistic effect and loose layered structure of the composite film facilitate fast diffusion and transportation of electrolyte ions through unimpeded channels during rapid charge-discharge process, resulting in high rate capability and stable cycling performance. As a result, the PANI-PHQ/RGO-61 film electrode exhibited 356 F g^{-1} at a current density of 0.5 A g^{-1} and high capacitance retention of 83% from 0.5 to 30 A g^{-1} . Moreover, it presented an excellent cycling stability with 94% of capacitance retention in comparison with 60% of pure PANI electrode and an outstanding Coulombic efficiency of 99% after 1000 cycles of galvanostatic charge-discharge. These superior electrocapacitive properties make it one of promising candidates for electrochemical energy storage.

Keywords: Polyaniline; Polyaniline-poly(hydroquinone)/graphene film; Electrode material; Pseudocapacitance

Introduction:

Supercapacitors as clean energy-storage devices have attracted great attention owing to their high power density, long cycling life, and high charge-discharge rate [1-3]. Electrode materials are the key components, which determine the whole performance of full devices. When being used as an electrode material for supercapacitors, graphene (RGO) is stable but the capacitance is relatively low (around 100 to 270 F g⁻¹) because it mainly stores energy through the electric double-layer capacitor mechanism [4-6]. Pseudocapacitance materials are alternative electrode materials based on a Faradic mechanism and have much higher specific capacitance but poor stability [7-9]. To combine the virtues of the two types of materials, composites of RGO and nanostructured pseudocapacitance materials were prepared and studied [10-13].

Polyaniline (PANI), as one of the typical conducting polymers, has been extensively studied for pseudocapacitors mainly due to its high specific pseudocapacitance, ease of synthesis, good environmental stability, and low cost [14]. However, the cycling life and rate capability of PANI electrodes are unsatisfactory due to their large volume changes and slow redox reactions during charge-discharge processes [15]. Furthermore, the low conductivity of PANI also weakens its performance in supercapacitors [16]. To solve these problems, PANI was frequently blended with carbon nanomaterials to improve its conductivity, mechanical and electrochemical stabilities, and the kinetics of redox reactions [17]. Recently, researches on developing flexible and binder-free RGO-based PANI composite films

have been attracted a great deal of interest owing to their enhanced performance [18, 19, 20]. However, the cycling stability of most PANI/RGO composite films usually unsatisfactory. The flexible RGO/PANI paper was prepared by Yu group with capacitance retention of 82% after 1000 cycles [18]. Li group have prepared RGO-wrapped PANI nanofibers film, which only maintained up to 74% of its capacitance over 1000 cycles [19].

Herein, we report an extremely special PANI-PHQ/RGO film with a layered structure for the first time, and the schematic formation process is presented in Figure 1. Poly(hydroquinone) (PHQ), is very attractive as redox polymer due to the unique two-electron redox behavior and stable reversibility [21, 22], which is added in PANI/RGO composite material in order to achieve higher cycling stability. Additionally, the loose layered structure of PANI-PHQ/RGO-61 film offers intrinsic porous channels and promotes the transportation of charges and ions [18, 23]. Consequently, The PANI-PHQ/RGO-61 film electrode exhibits 356 F g^{-1} at a current density of 0.5 A g^{-1} and an enhanced capacitance retention of 83% (dropped from 356 to 294 F g^{-1} upon increase of current density from 0.5 to 30 A g^{-1}) compared with those of PANI (59%) and PANI/RGO-60 film (67%) electrodes. Furthermore, the PANI-PHQ/RGO-61 film electrode presents a good cycling stability with 94% of capacitance retention after 1000 cycles, much higher than those of PANI (60%) and PANI/RGO-60 film (74%) electrodes. The excellent rate performance and cycling stability make it one of promising candidates for electrochemical energy storage.

2. Experimental

2.1 Chemicals

Aniline (analytical grade) was distilled until color-less under reduced pressure before use. Other chemicals (analytical grade) were used as received without further treatment.

2.2 Sample Preparation

2.2.1 Preparation of RGO hydrogel film

The RGO hydrogel film was fabricated by following the method reported in literature [24]. RGO dispersion was prepared by the following process firstly. Graphite oxide (GO) (Nanjing XFNANO Materials Tech Co., Ltd) was dispersed into deionized water and treated by ultrasonic treatment for 2 h, the GO homogeneous dispersion was obtained. Then the GO suspension (0.5 mg mL^{-1} , 100 mL) was mixed with 140 μL hydrazine (50 wt% in water) and 350 μL ammonia (28 wt% in water) solution in a glass vial. After being vigorously shaken for a few minutes, the vial was put in an oil bath ($\sim 100^\circ\text{C}$) for 3 h. Then 30 mL as-obtained RGO dispersion was vacuum filtrated through alumina membrane (Whatman, $0.2 \mu\text{m}$ pore size). The filtrate cake immediately transferred to a Petri dish and immersed in water for 10 h to further remove the remaining ammonia and hydrazine.

2.2.1 Preparation of PANI-PHQ/RGO film

The obtained RGO hydrogel film was immersed in 5 mL 1 M HCl aqueous solution containing 150 μL aniline monomer and different mass of hydroquinone (28, 40, 55, and 110 mg). The mixture was stored at refrigerator for 2 h ($\sim 5^\circ\text{C}$). 5 mL 1 M pre-cooled HCl aqueous solution containing 90 mg ammonium peroxydisulfate was

then poured into the above mixture, and the mixture was left at refrigerator for another 2 h. Then the film was immersed in water for 10 h and air-dried at room temperature. The contents of RGO in the composites were calculated by measuring the different masses before and after polymerization reaction. The present recipes yielded PANI-PHQ/RGO films with RGO mass contents of 40, 52, 61, and 66 wt%, respectively, which were denoted as PANI-PHQ/RGO-x with x representing the mass percentage of RGO in the composite. PANI/RGO-60 film was obtained by the above same procedure without H₂Q for 1.5 h. Pure PANI sample was prepared under the identical conditions except that RGO hydrogel film and H₂Q were not included in the solution. PHQ was prepared according to the method reported previously [21].

2.3 Characterization

The morphology of the samples was observed by field-emission scanning electron microscopy (FESEM) on SU8020 F equipped with an energy dispersive spectrum (EDS) analyzing. Raman spectra were measured on a Renishaw inVia Raman microscope with an excitation wavelength of 758 nm. Infrared spectra were obtained by KBr method on a Fourier Transform Infrared Spectrometer EQUINX55. The electrochemical performance of the electrode materials was characterized on a CHI 660 E (Chenhua, Shanghai) electrochemical workstation.

2.4 Electrochemical Measurement

The electrochemical tests of cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) were performed using 1 M H₂SO₄ as electrolyte solution in a three-electrode cell, in which platinum

foil and Ag/AgCl electrode were used as counter and reference electrodes, respectively. The as-prepared film materials (1 cm^2) were directly used as working electrode without adding additives such as binder or conducting agent, which were directly attached to the interlayer of two stainless steel cloths (2 cm^2). The specific capacitance was calculated from the galvanostatic discharge process according to the following equation: $C = I \times \Delta t / (m \times \Delta V)$, where I is the discharge current (A), Δt is the discharge time (s), ΔV is the voltage change (V) excluding the IR drop during the discharge process, and m is the mass of the active material for working electrode (g). The electrochemical impedance spectroscopy (EIS) was used to investigate the electrochemical behavior of electrode materials with amplitude of 5 mV at the frequency range of 100 kHz to 0.01 Hz.

Results and discussion:

As shown in Figure 2a, pure PANI has nanofiber morphology with the diameter of $\sim 80\text{ nm}$ and $\sim 1\text{ }\mu\text{m}$ long. The RGO film has a layered structure as shown in its cross-section (Figure 2b), which is caused by the flow assembly effect of RGO sheets during filtration. The strong sheet-to-sheet Van Der Waals interaction leads to a severe layer restacking, which not only greatly reduces the ion accessible surface area, but also brings a large ion diffusion resistance between the adjacent RGO sheets [25, 26]. In contrast, PANI-PHQ/RGO-61 film has more loose layered structure than RGO film (Figure 2c). Although it is difficult to distinguish PANI-PHQ from RGO film by FESEM, the overall uniform structure of its cross-section and the elemental mapping of C, O, N across the film indicate that the PANI-PHQ coating is rather even. Due to

the presence of a continuous flexible RGO network, the PANI-PHQ/RGO-61 film provides sufficient mechanical properties and high electrical conductivity, allowing direct use as a binder-free electrode for characterizing its electrochemical property.

The Raman spectra of as prepared materials were shown in Figure 3. The Raman spectrum for RGO film shows a disorder induced band (D-band) at 1310 cm^{-1} and a first order-allowed band (G-band) at 1600 cm^{-1} , which is consistent with the literature [27]. The two broad bands appear at 1580 and 1350 cm^{-1} for PHQ, resulting from the stretching and deforming of aromatic ring, which agrees well with the reported literature [28]. In contrast, many bands are observed for PANI. The band at 1592 cm^{-1} corresponds to the C–C deformation bands of semiquinone rings, while the band at 1462 cm^{-1} is characteristic of the N–H bending deformation band of the protonated amine, other bands at 1160 and 1335 cm^{-1} ascribed to the C–H vibrations in quinoid/phenyl groups and the semiquinone radical cation structure in PANI [29, 30]. The presence of these bands suggests the successful preparation of PANI. The characteristic peaks of PANI are noticed from PANI-PHQ/RGO-61 film, and the intensities of the bands at 1580 and 1350 cm^{-1} are enhanced compared to pure PANI due to the existence of RGO and PHQ in PANI-PHQ/RGO-61 film. The results demonstrate the coating of PANI-PHQ on RGO sheets.

The infrared spectra of the PHQ, PANI, and PANI-PHQ/RGO-61 film were measured to further verify the composite film. As shown in Figure 4, in particular for PHQ, the band at 1623 cm^{-1} is assigned to C=O stretching vibration, indicating the presence of quinone. The bands at 1540 , 1477 and 1431 cm^{-1} can be assigned to the

vibrations of aromatic rings and C=C bonds in the backbone of PHQ. The bands at 1242 and 1200 cm^{-1} are attributed to C–O stretching vibration, confirming the existence of phenolic OH groups [21]. While for PANI powder, the typical bands at 1566 and 1477 cm^{-1} are assigned to C=C stretching vibration modes in quinoid and benzene rings, respectively, whereas the bands at 1290 and 1240 cm^{-1} are related to the C–N and C=N stretching modes, respectively [29]. Accordingly, the typical bands of PANI and PHQ appear in the spectrum of PANI-PHQ/RGO-61, indicates the existence of PANI and PHQ in composite film.

The electrochemical properties of as prepared materials were evaluated by CV, galvanostatic charge-discharge, and EIS in 1 M H_2SO_4 . Figure 5 (a-c) compare the electrochemical properties of the PANI-PHQ/RGO-61 film with RGO film, PANI, and PANI/RGO-60 film. The CV profiles of different electrodes at a scan rate of 5 mV s^{-1} are significant differently, the RGO film electrode shows a nearly rectangular CV behavior, characteristic of double layer capacitance [31, 32]. In contrast, the CV profiles of PANI and PANI/RGO-60 film electrodes have distinct two pairs of redox peaks, which are attributed to the leucoemeraldine/emeraldine and emeraldine/ pernigraniline transitions of PANI [18, 33]. While the CV profiles of PHQ electrode at different scan rates have a pair of redox peak (Figure S1a), which agrees well with the reported literature [34]. Additionally, the CV profile at a high scan rate of 200 mV s^{-1} keeps well indicates the good rate performance and excellent reversibility of PHQ electrode. More interestingly, the CV profile of PANI-PHQ/RGO-61 film electrode shows three pairs of redox peaks, which is caused

by the synergistic effect among PANI, PHQ, and RGO in the composite film [18, 35, 36]. Moreover, three of the redox peaks are well separated and symmetric in shape, indicating that the electrochemical reactions involved are reversible.

Figure 5b shows galvanostatic charge-discharge curves of RGO film, PANI, PANI/RGO-60 and PANI-PHQ/RGO-61 film at a current density of 0.5 A g^{-1} , and the specific capacitance are 189, 450, 398, and 356 F g^{-1} , respectively. Although the specific capacitance of PANI-PHQ/RGO-61 film electrode is lower than those of PANI and PANI/RGO-60 film electrodes at 0.5 A g^{-1} , PANI-PHQ/RGO-61 film electrode maintains 294 F g^{-1} at 30 A g^{-1} with capacitance retention of 83%, while the capacitance retention of PANI and PANI/RGO-60 film electrodes are only 57% (from 450 to 255 F g^{-1}) and 67% (from 398 to 266 F g^{-1}), respectively (Figure 5c). Obviously, the specific capacitance of PANI-PHQ/RGO-61 film electrode at high current density of 30 A g^{-1} is larger than others, which shows its excellent rate performance. The rate capability is also higher than most of the PANI/RGO films without PHQ in reported literatures [18, 19, 23, 37-40]. RGO-wrapped PANI nanofibers paper has a capacitance retention of only 40% from 0.5 to 4 A g^{-1} [19]. The freestanding RGO/PANI paper with a capacitance retention of 53% from 1 to 8 A g^{-1} [38]. The high rate capability guarantees high power density, the highest capacitance retention of PANI-PHQ/RGO-61 film electrode could be ascribed to the positive synergistic effect in composite film and the loose layered structure, which provides a short and unimpeded diffusion channel for electrolyte ions.

In order to obtain more information for PANI-PHQ/RGO film, the CV profiles and

galvanostatic charge-discharge of PANI-PHQ/RGO film composites with different contents of RGO are shown in Figure 6. They both have distinct redox peaks, indicating that the specific capacitance primarily originates from Faradaic capacitance [41, 42]. Most interestingly, the CV profile of PANI-PHQ/RGO-40 film electrode is different from other three electrodes. With the increase of H₂Q in reaction system, the mass ratio of RGO increases due to H₂Q partly acts as polymerization inhibitor [43]. When the mass ratio of RGO is beyond 52%, one more redox peak appears and the surrounded area of CV loop is smaller than PANI-PHQ/RGO-40 film electrode but slightly increases with the increase of RGO and PHQ. The galvanostatic charge-discharge curves of the composite electrodes at a current density of 0.5 A g⁻¹ have evident voltage stages, which are caused by the combination of double layer capacitance with the pseudocapacitance [37]. The specific capacitances of composite films are 448, 345, 356, and 362 F g⁻¹ at a current density of 0.5 A g⁻¹ from PANI-PHQ/RGO-40 to PANI-PHQ/RGO-66, which agree well with the areas of their corresponding CV loops. Although PANI-PHQ/RGO-40 film electrode has the largest original specific capacitance at 0.5 A g⁻¹, the specific capacitance of PANI-PHQ/RGO-61 film electrode is almost the same with that of PANI-PHQ/RGO-40 when the current density increases to 20 A g⁻¹ and exceeds it dramatically at 30 A g⁻¹ (Figure S2a). Moreover, the cycling stability of PANI-PHQ/RGO-61 and PANI-PHQ/RGO-66 are much higher than PANI-PHQ/RGO-40 and PANI-PHQ/RGO-52 (Figure S2b).

To understand the high rate performance of PANI-PHQ/RGO-61 film electrode, the

CV profiles at different scan rates from 5 to 200 mV s^{-1} were tested. As shown in Figure 7a, the peak currents increase with the increase of scan rate. Furthermore, the redox peaks and symmetric shape are maintained obviously even at high scan rate up to 200 mV s^{-1} . Whereas, an obviously distorted CV curves are observed at scan rate of 200 mV s^{-1} for PANI and PANI/RGO-60 film electrodes (Figure S2c), which indicates that the PANI-PHQ/RGO-61 film electrode processes low resistance, excellent rate ability and ideal supercapacitive properties. In addition, its good linear relationship between the evolved charge-discharge current densities and scan rates also signifies a remarkably fast charge-discharge capability even at a high scan rate of 200 mV s^{-1} (Figure 7b). [44, 45]. These indicate much faster electron transfer kinetics for the PANI-PHQ/RGO-61 film electrode. While the galvanostatic charge-discharge curves at different current densities are shown in Figure 7c, the charge-discharge curves maintained the same shape, implying sustainable behavior in a broad current range. Furthermore, the charge curves are generally symmetrical to their discharge counterparts without obvious IR drop even at higher current density, demonstrating small resistance, excellent reversibility and high Coulombic efficiency for PANI-PHQ/RGO-61 film electrode [45].

A long cycle life is another critical criterion for supercapacitor electrode materials in practical applications, which was evaluated by repeating galvanostatic charge-discharge test for 1000 cycles at 10 A g^{-1} . As shown in Figure 8a, it can be seen that RGO film electrode maintains good charge-discharge performance, and the capacitance retention is 99% due to the stable double layer capacitance [4]. On the

other hand, PHQ electrode also has good cycling stability (Figure S1b). Accordingly, the PANI-PHQ/RGO-61 film electrode has much higher cycling stability and presents extremely high capacitance retention of 94% than PANI (60%) and PANI/RGO-60 (74%) film electrodes, which is higher than most of the PANI/RGO films (Table 1). Moreover, the CV profile with a tiny decreased integrated area (Figure 8b) and the slightly enlarged semicircles as shown in Nyquist plots (Figure 8c) after 1000 cycles also support the excellent electrochemical cycle ability. In addition, a very stable Coulombic efficiency of 99% is maintained (Figure 8d). As we can see in Figure S3, the loose layered structure of PANI-PHQ/RGO-61 film remains after long-term cycling test. The conducting RGO layers in the composite film material serve as a flexible supporter, which greatly slow down the structure swelling and shrinking of PANI. All of these make PANI-PHQ/RGO-61 composite film as an outstanding supercapacitor electrode material with superb rate capability, good cycling stability and outstanding Coulombic efficiency.

Conclusion:

In summary, we demonstrated an effective route to prepare layered PANI-PHQ/RGO-61 film with high rate capability and stable cycling performance. In contrast to the conventional PANI/RGO film, the obtained film can accommodate reversible electrochemical reactions due to the synergistic effect among PANI, PHQ, and RGO in the composite film. In addition, the loose layered structure facilitates fast diffusion and transport of electrolyte ions during rapid charge-discharge process. Consequently, the PANI-PHQ/RGO-61 film electrode exhibited an excellent rate

capability, outstanding Coulombic efficiency of 99% and a substantially improved electrochemical stability with 94% capacitance retention after 1000 continuous galvanostatic charge-discharge cycles. Furthermore, the performance of RGO composite film decorating other conducting polymers can be further enhanced by chemical oxidative polymerization of polymer monomers and H₂Q on flexible RGO film substrate. Such composite film electrode material with superior electrochemical properties represents one of the promising candidates for high-performance supercapacitors.

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Figure captions

Figure 1. A schematic formation process of PANI-PHQ/RGO film.

Figure 2. Cross-section FESEM images of (a) PANI, (b) RGO film, (c) PANI-PHQ/RGO-61 film (photograph, inserted), and the elemental mappings of C, O, N in PANI-PHQ/RGO-61 film.

Figure 3. Raman spectra of RGO film, PHQ, PANI, and PANI-PHQ/RGO-61 film.

Figure 4. FTIR spectra of PHQ, PANI, PANI-PHQ/RGO-61 film.

Figure 5. Electrochemical properties of RGO film, PANI, PANI/RGO-60 film, and PANI-PHQ/RGO-61 film electrode materials: (a) CV profiles at a scan rate of 5 mV s^{-1} , (b) galvanostatic charge-discharge curves at a current density of 0.5 A g^{-1} , (c) capacitance retention from 0.5 to 30 A g^{-1} .

Figure 6. CV profiles at a scan rate of 5 mV s^{-1} (a) and galvanostatic charge-discharge curves at various current densities (b) of PANI-PHQ/RGO film electrodes with different RGO contents.

Figure 7. Electrochemical properties of PANI-PHQ/RGO-61 film electrode. (a) CV profiles at different scan rates, (b) the dependence of the current density (extracted from the CV profiles of middle redox peaks for the charge and discharge) on the applied scan rates, (c) galvanostatic charge-discharge curves at different current densities.

Figure 8. (a) Variation of the specific capacitance with respect to cycle numbers of RGO film, PANI, PANI/RGO-60 film, and PANI-PHQ/RGO-61 film electrodes at a current density of 10 A g^{-1} , CV profiles (b) and Nyquist plots (c) of

PANI-PHQ/RGO-61 film electrode before and after 1000 cycles, (d) dependence of Coulombic efficiency on cycle number at 10 A g^{-1} and galvanostatic charge-discharge curves at 1st and 1000th cycles (inserted) of PANI-PHQ/RGO-61 film electrode.

Table 1. Comparative electrochemical performance of PANI/RGO film electrodes reported in the literatures.

Figure S1. CV profiles at different scan rates from 5 to 200 mV s^{-1} (a) and cycling performance during 1000 cycles at 10 A g^{-1} (b) of PHQ electrode.

Figure S2. Capacitance retention from 0.5 to 30 A g^{-1} (a) and cycling performance during 1000 cycles at 10 A g^{-1} (b) of PANI-PHQ/RGO film electrodes with different RGO contents. (c) CV profiles of PANI, PANI/RGO-60 film, and PANI-PHQ/RGO-61 film electrodes at a scan rate of 200 mV s^{-1} .

Figure S3. FESEM images of PANI-PHQ/RGO-61 electrode material (a) before and (b) after 1000 charge-discharge cycles.

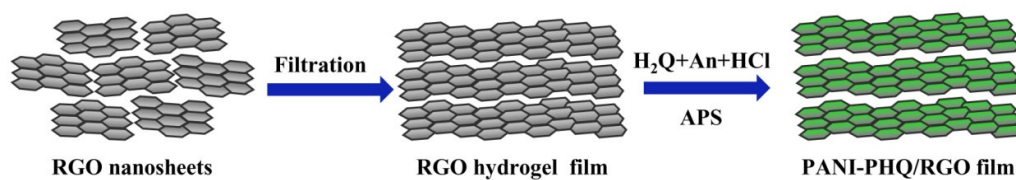


Figure 1. A schematic formation process of PANI-PHQ/RGO film.

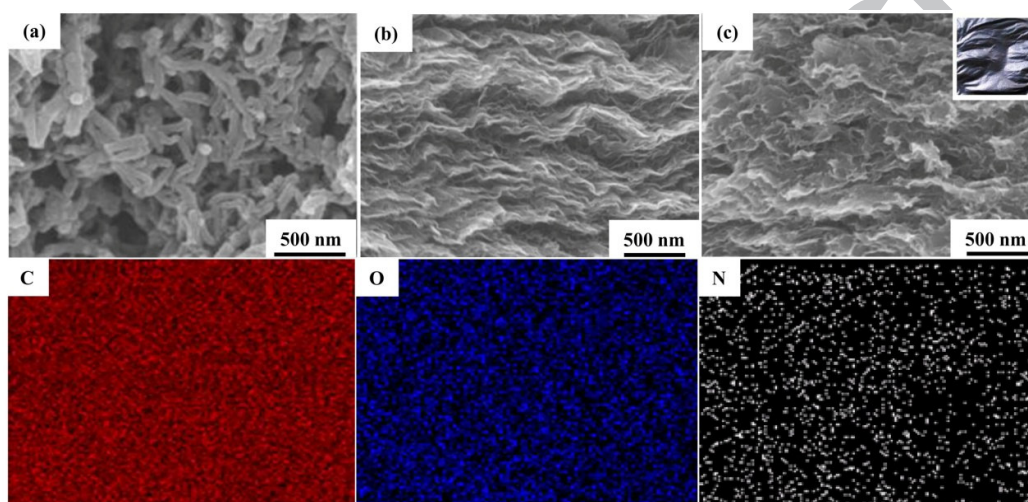


Figure 2. Cross-section FESEM images of (a) PANI, (b) RGO film, (c) PANI-PHQ/RGO-61 film (photograph, inserted), and the elemental mappings of C, O, N in PANI-PHQ/RGO-61 film.

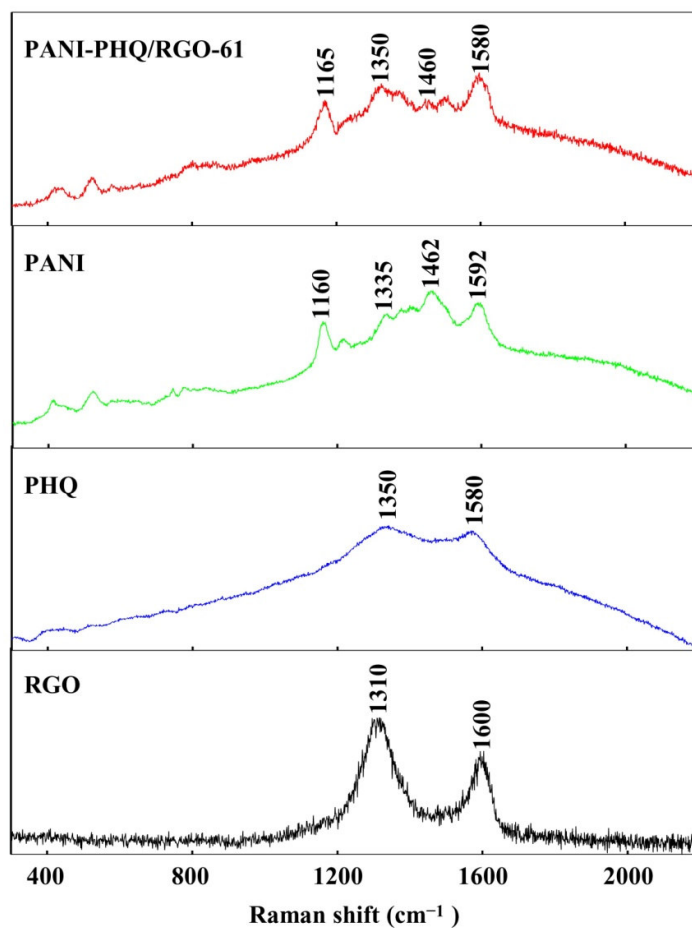


Figure 3. Raman spectra of RGO film, PHQ, PANI, and PANI-PHQ/RGO-61 film.

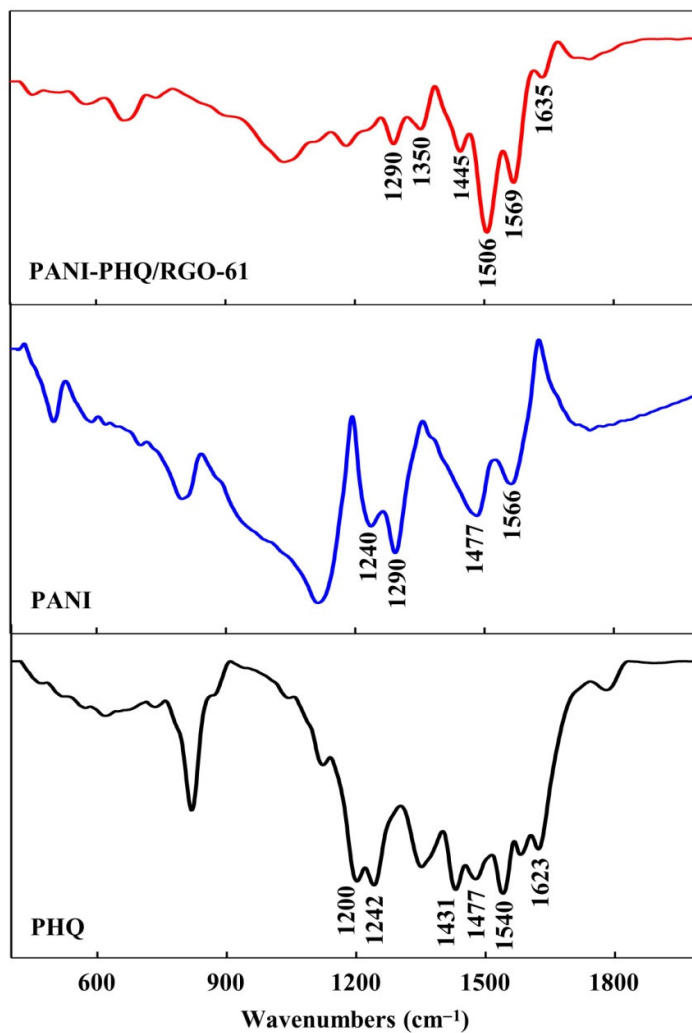


Figure 4. FTIR spectra of PHQ, PANI, PANI-PHQ/RGO-61 film.

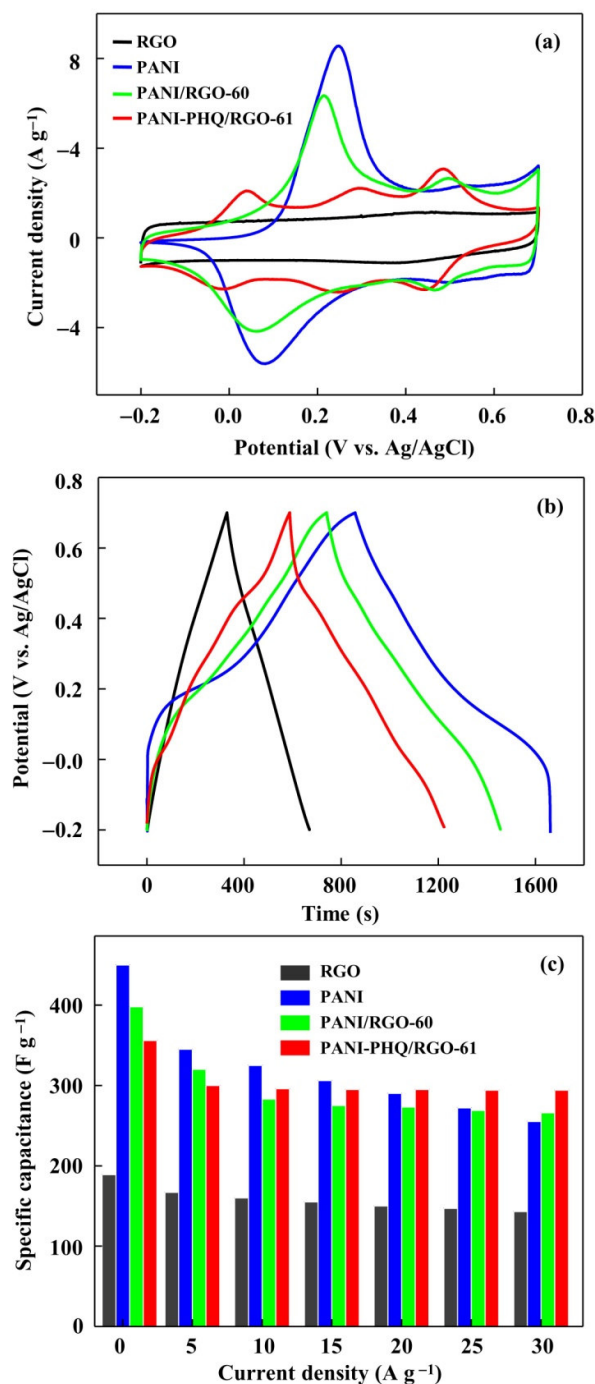


Figure 5. Electrochemical properties of RGO film, PANI, PANI/RGO-60 film, and PANI-PHQ/RGO-61 film electrode materials: (a) CV profiles at a scan rate of 5 mV s⁻¹, (b) galvanostatic charge-discharge curves at a current density of 0.5 A g⁻¹, (c) capacitance retention from 0.5 to 30 A g⁻¹.

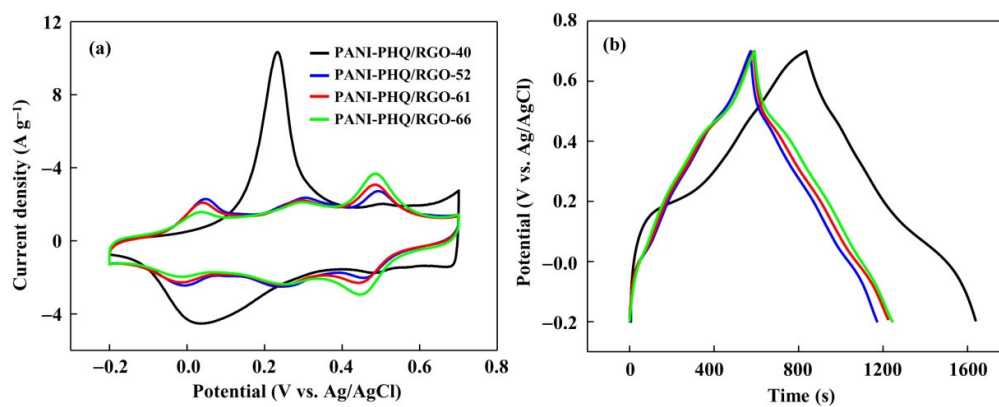


Figure 6. CV profiles at a scan rate of 5 mV s^{-1} (a) and galvanostatic charge-discharge curves at various current densities (b) of PANI-PHQ/RGO film electrodes with different RGO contents.

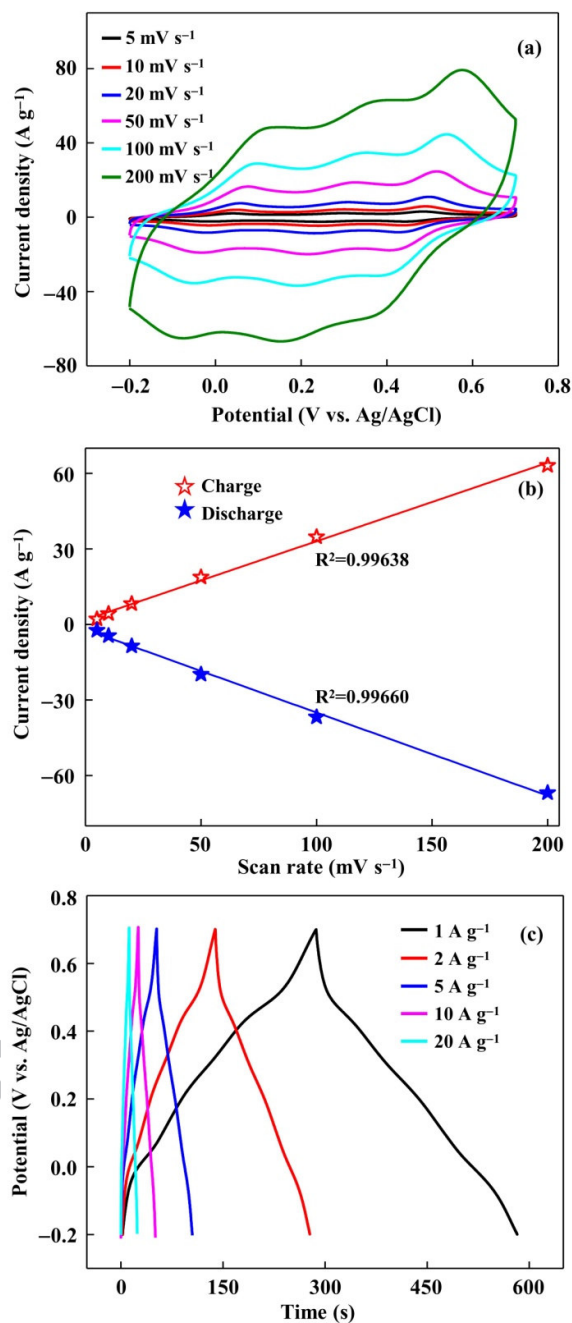


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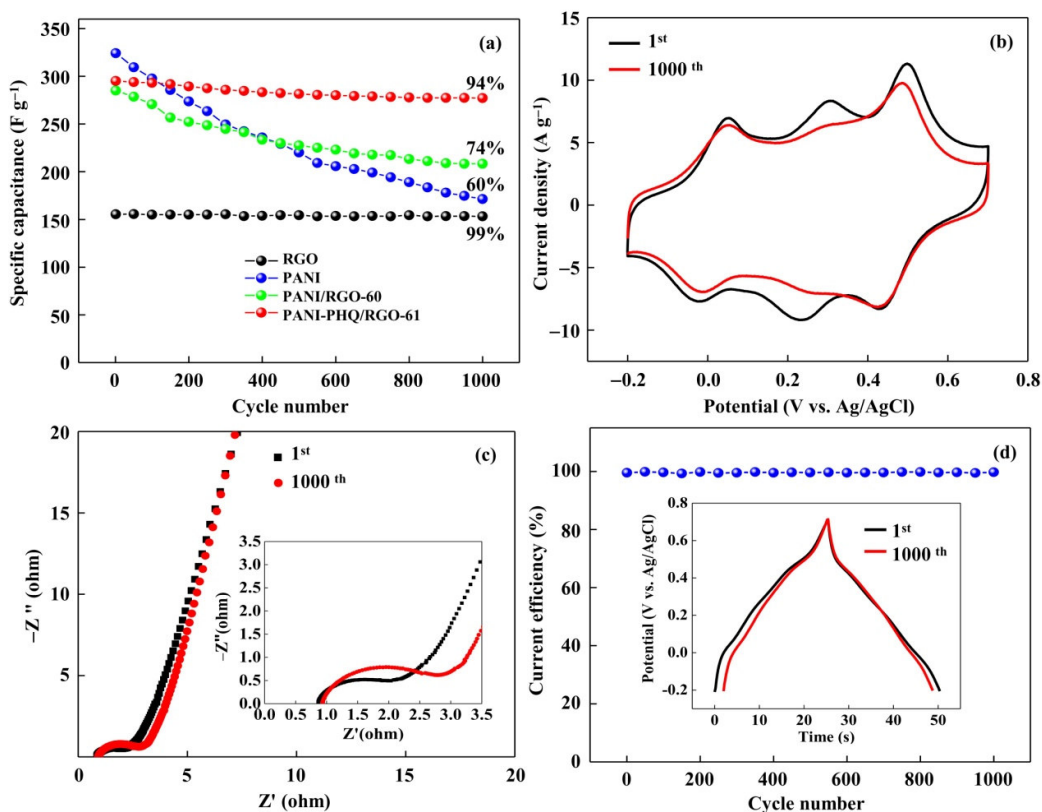


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Table 1. Comparative electrochemical performance of PANI/RGO film electrodes reported in the literatures.

Electrode materials	Rate capability	Cycling stability	References
RGO/PANI composite paper	1~10 A g ⁻¹ 64%	5 A g ⁻¹ 1000 C 82%	[18]
RGO wrapped PANI nanofibers paper	0.5~4 A g ⁻¹ 40%	1 A g ⁻¹ 1000 C 74%	[19]
RGO/PANI nanofiber film	0.3~6 A g ⁻¹ 82%	3 A g ⁻¹ 800 C 79%	[37]
RGO/PANI paper	1~8 A g ⁻¹ 53%	8 A g ⁻¹ 5000 C 86%	[38]
RGO/PANI paper	3~30 A cm ⁻³ 50%	3 A cm ⁻¹ 1000 C 82%	[39]
RGO/PANI nanocomposite paper	0.5~4 A g ⁻¹ 58%	0.5 A g ⁻¹ 2000 C 88%	[40]
PANI-PHQ/RGO film	0.5~30 A g ⁻¹ 83%	10 A g ⁻¹ 1000 C 94%	Our work

Graphical Abstract

