

Short communication

Electrochemical supercapacitor electrode material based on poly(3,4-ethylenedioxythiophene)/polypyrrole composite

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Abstract

Poly (3,4-ethylenedioxythiophene)/polypyrrole composite electrodes were prepared by electropolymerization of 3,4-ethylenedioxythiophene (EDOT) on the surface of polypyrrole (PPy) modified tantalum electrodes. The morphology observation of PPy and poly(3,4-ethylenedioxythiophene)/polypyrrole composite (PEDOT/PPy) was performed on Field Emission Scanning Electron Microscope (SEM). The electrochemical capacitance properties of the composite were investigated with cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) techniques in the two- or three-electrode cell system. The results show that the PEDOT/h-PPy (PPy with horn-like structure) composite films were characterized with highly porous structure, which leads to their specific capacitance as 230 Fg^{-1} in 1 M LiClO_4 aqueous solutions and even 290 Fg^{-1} in 1 M KCl aqueous solutions. Moreover, the composite exhibits a rectangle-like shape of voltammetry characteristics even at scanning rate 100 mV s^{-1} , a linear variation of the voltage with respect to time without a clear ohm-drop phenomenon in galvanostatic charge–discharge process and almost ideal capacitance behavior in low-frequency in 1 M KCl solutions. Furthermore, specific power of the composite would reach 13 kW kg^{-1} and it had good cycle stability. All of the above imply that the PEDOT/h-PPy composites were an ideal electrode material of supercapacitor.

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1. Introduction

Electrochemical supercapacitors have various applications not only coupling with batteries to provide peak power, but also replacing batteries for memory backup and electric vehicles [1–5].

Many researchers have extensively studied to use electrically conducting polymers (ECPs), such as polyaniline (PANi), polypyrrole (PPy), polythiophene (PTh), and their derivatives for electrochemical supercapacitor electrode materials [6–29]. Among them, the PANi family stands out for high specific capacitance and high power density as well as relatively low cost [8–10]. Unfortunately, because of the possible presence of benzidine moieties in the polymer backbone, which might yield toxic (carcinogenic) products upon degradation, the research in polyaniline chemistry have been limited by numerous industrial

and academic groups [30]. In contrast, the PPy family and PTh family are possibly more environmentally “friendly” systems. They have attracted considerable attention in electrochemical supercapacitor application in the last decade [11–29]. In particular, poly(3,4-ethylenedioxythiophene) (PEDOT) [22–29], a derivative of PTh, is an interesting material in view of its good thermal and chemical stability, fast electrochemical switching, and a high electrical conductivity in the p-doped state (easily up to 550 S cm^{-1}) [31]. However, the specific capacitance of PEDOT was smaller than that of PPy and PANi, due to monomer units (3,4-ethylenedioxythiophene, EDOT) with the greater molecular weight than pyrrole (Py) and aniline (ANi). In addition, the ECP/C composites are often prepared with active carbon, carbon nanotubes (CNTs), or carbon fiber to enhance their specific capacitance further [15–20,29]. However, there is little literature available on ECP/ECP composite in supercapacitor application.

In the present study, PEDOT/PPy composite electrodes were prepared by the galvanostatic polymerization of PEDOT on the PPy modified electrode. The aim was to obtain the PEDOT/PPy

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composite with its rapid response like PEDOT while its specific capacitance and cost close to those of PPy. Their relevant electrochemical properties were measured by means of cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) tests.

2. Experimental

2.1. Materials

EDOT (Baytron, 99%) and Py (Fluka, 99%) were distilled prior to use and stored at -10°C in a nitrogen atmosphere. All other reagents were obtained from commercial sources and were used as received. Sodium *p*-toluenesulfonate (PTSNa) was used as a surfactant and supporting salt for all the electrochemical polymerizations. LiClO_4 or KCl was used as a supporting salt in the electrochemical tests.

2.2. Electrode preparation and characterization

PPy electrodes were galvanostatically prepared on tantalum electrodes (Ta, $10\text{ mm} \times 10\text{ mm} \times 0.1\text{ mm}$) in aqueous solution containing 0.3 M Py and 0.1 M PTSNa. By adjusting the electrolytes pH and the current density, PPy films with typical cauliflower-like structure (c-PPy) [32] and PPy films with novel horn-like structure (h-PPy) were obtained. PEDOT/PPy composite electrodes were obtained by galvanostatic polymerization of EDOT on the PPy electrodes. The molar ratio of the composite was controlled by the electropolymerization charge of PPy and PEDOT.

The mass of PEDOT/PPy composite ranged from 3.6 mg to 10 mg, which was determined by the electronic balance (AG 135, Mettler-Toledo). Scanning electron microscope (SEM) observations of samples were carried out on Field Emission Scanning Electron Microscope (JSM-6700F, JEOL).

2.3. Electrochemical tests

The electrochemical performance was investigated by using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge–discharge techniques. All electrochemical tests were performed on the Versatile Multichannel Potentiostat 2/Z (VMP2, Biologic) with the ability for impedance measurements. In three-electrode system, a platinum sheet was used as counter electrode and saturated calomel electrode (SCE) as reference electrode. Two-electrode system consisted of two almost identical PEDOT/PPy composite electrodes.

The scanning rates of CV tests ranged from 2 mV s^{-1} to 200 mV s^{-1} . Current (i) in the CV plots was replaced by specific capacitance (i/sm , where s represents the scanning rate and m is the mass of the polymers). The capacitance, C , is calculated from CV according to Eq. (1):

$$C = \int i \frac{dt}{dv}, \quad (1)$$

where i is current, t the time and v is the voltage.

The current density of charge–discharge ranged from 0.5 mA cm^{-2} to 50 mA cm^{-2} . The discharge capacitance C is calculated from the linear part of discharge curves using the following formula:

$$C = i \times \Delta t \times \Delta V^{-1} \quad (2)$$

where i is the current and Δt is the time interval for the change in voltage ΔV .

In three-electrode system, the specific capacitance C_m is obtained by Eq. (3):

$$C_m = \frac{C}{m}, \quad (3)$$

where m is the mass of the polymers.

In two-electrode system, C_m is calculated by Eq. (4):

$$C_m = \frac{2C}{m}. \quad (4)$$

The specific power of electrode materials (P_m) can be obtained by Eq. (5),

$$P_m = \frac{C_m V^2}{2t}, \quad (5)$$

where V represents the potential window and t is the discharge time.

EIS measurements were made in the frequency range from 100 000 Hz down to 0.005 Hz, using an ac voltage of 10 mV at different dc potentials. We made sure that the electrochemically steady state was attained in the composite films by waiting 10 min between the application of the dc potential and the data recording. During the waiting time, the current passing through the electrochemical cell reached undetectable values. This procedure produced a homogeneous distribution of counterions inside the composite films. The analysis of EIS was performed on the ZSIMPWIN, the software attached to VMP2.

3. Results and discussion

The c-PPy films were obtained with 1 mA cm^{-2} in pH 1.5 electrolytes, while the h-PPy films were obtained with 5 mA cm^{-2} in pH 9 electrolytes, as shown in Fig. 1(a) and (b). The PEDOT/c-PPy composite displayed cauliflower-like morphology while PEDOT/h-PPy composite showed highly porous structure, as shown in Fig. 1(c) and (d). The porous structure may be caused by the electropolymerization of EDOT on the interface of horn and electrolyte, as shown in Fig. 1(e).

Fig. 2(a) shows the CV curves of PEDOT (curve 1), PEDOT/c-PPy (curve 2) and PEDOT/h-PPy (curve 3) composite (5:1) in 1 M LiClO_4 solution with scanning rate at 2 mV s^{-1} . From Fig. 2(a), their specific capacitance was 110 Fg^{-1} , 160 Fg^{-1} and 230 Fg^{-1} , respectively. It is shown that the composite was characterized with greater specific capacitance than PEDOT, due to the synergy effect of PPy and PEDOT. In addition, the specific capacitance could be further improved by the highly porous structure of PEDOT/h-PPy. This might result from that the porous structure enhanced the rates of ionic

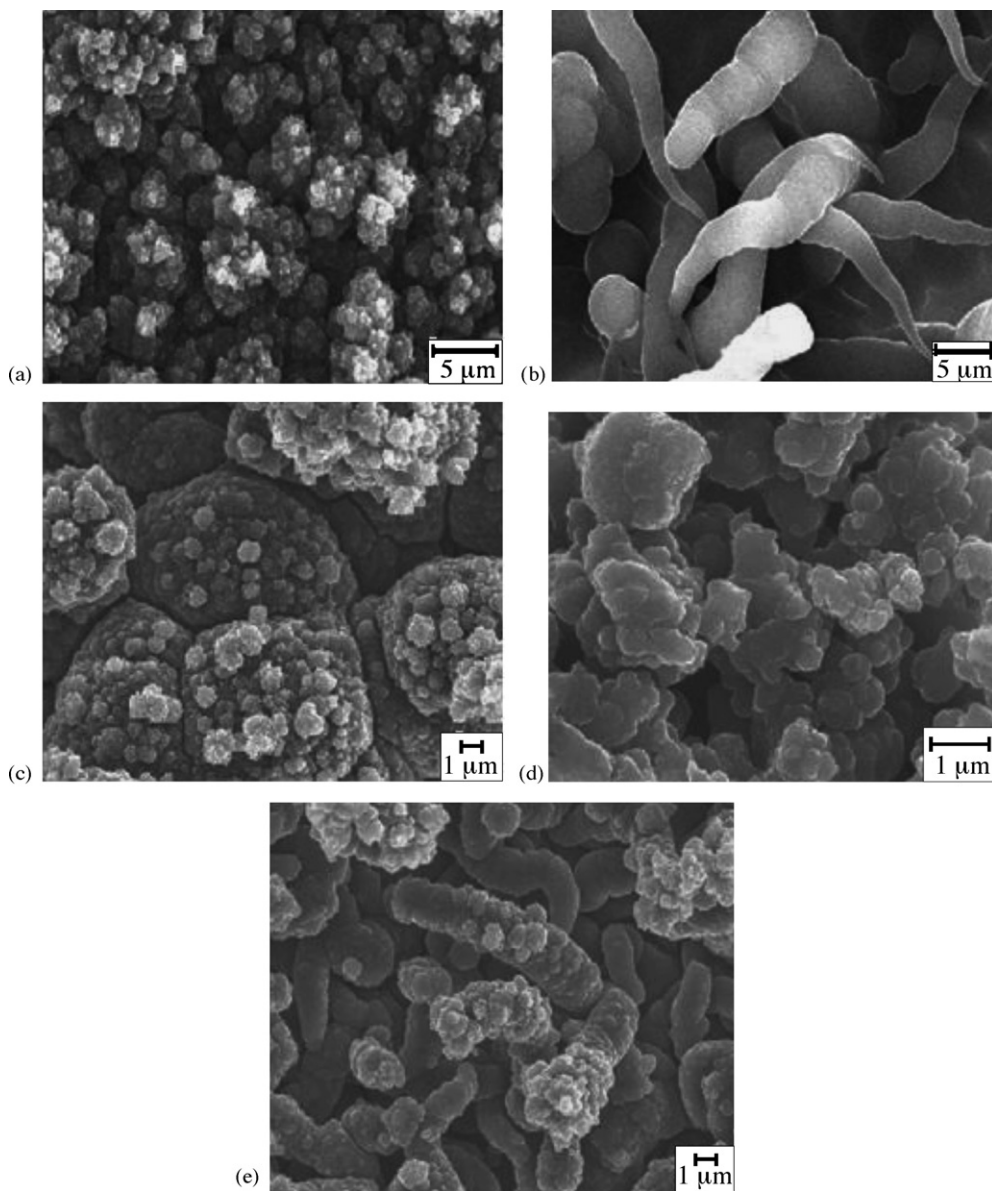


Fig. 1. SEM images of c-PPy (a), h-PPy (b), PEDOT/c-PPy (electropolymerization of PEDOT on c-PPy at 1 mA cm^{-2} for 1 h) (c), PEDOT/h-PPy (electropolymerization of PEDOT on h-PPy at 1 mA cm^{-2} for 1 h) (d), PEDOT/h-PPy (electropolymerization of PEDOT on h-PPy at 1 mA cm^{-2} for 15 s) (e).

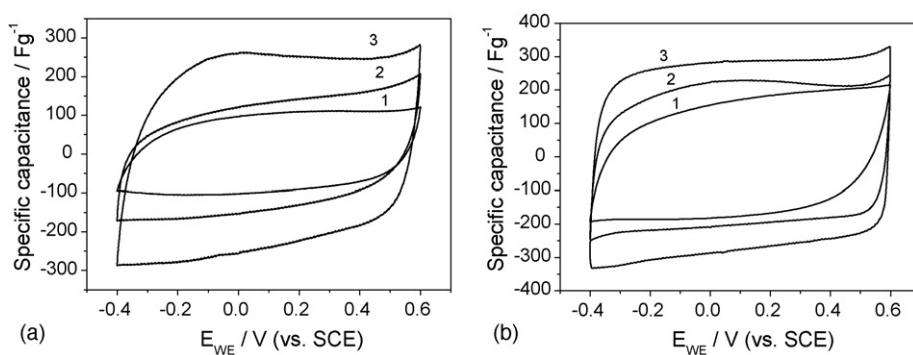


Fig. 2. CV curves at 2 mV s^{-1} of PEDOT (curve 1), PEDOT/c-PPy (5:1, curve 2) and PEDOT/h-PPy films (5:1, curve 3) in 1 M LiClO_4 solution (a) and 1 M KCl solution (b).

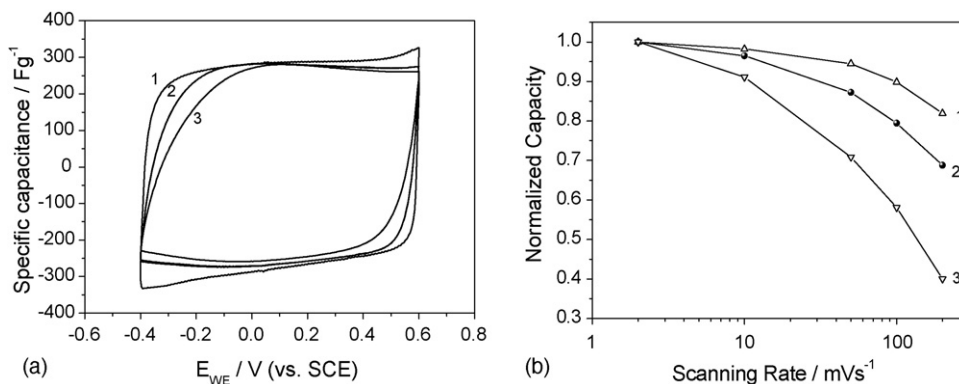


Fig. 3. CV curves of PEDOT/h-PPy films (5:1) at scanning rate 10 mV s^{-1} (curve 1), 50 mV s^{-1} (curve 2) and 100 mV s^{-1} (curve 3) (a); normalized capacitance as function of the scanning rate of PEDOT/h-PPy (5:1, curve 1), PEDOT (curve 2) and PEDOT/h-PPy (1:1 curve 3) (b).

mass transport during the charge–discharge process [33]. Moreover, their specific capacitances were 180 Fg^{-1} , 210 Fg^{-1} and 290 Fg^{-1} in 1 M KCl solution, as shown in Fig. 2(b). The curves of PEDOT/h-PPy displayed rectangle-like shape, which exhibited a very fast electrochemical switch as expected. Comparing Fig. 2(a) with (b), we could find that the specific capacitances in KCl solution were greater than those in LiClO_4 solution. The increase of specific capacitance was contributed to the smaller size of Cl^- than that of ClO_4^- , which might lead to the fast transport of ions in the polymer chains. Therefore, the following tests were all carried out in 1 M KCl solution.

Charge–discharge rate can be further evaluated by performing the CV scans at different scanning rates. The CV curves of PEDOT/h-PPy (5:1) in 1 M KCl solution are depicted in Fig. 3(a). The curve shapes at 10 mV s^{-1} (curve 1), 50 mV s^{-1} (curve 2), and even 100 mV s^{-1} (curve 3) were all close to rectangle. Although the specific capacitance decreased slightly with the increase of scanning rate, the value at 100 mV s^{-1} could reach 260 Fg^{-1} . The specific capacitances of PEDOT/h-PPy (5:1), PEDOT, and PEDOT/h-PPy (1:1) in the ranges of $2\text{--}200 \text{ mV s}^{-1}$ were normalized with respect to the value obtained at 2 mV s^{-1} . The results in Fig. 3(b) showed that the charge–discharge rate of PEDOT/h-PPy (5:1) was obviously greater than that of PEDOT films, though PEDOT was well known for fast charge–discharge response [22–29]. The enhanced response rate may be attributed to the highly porous structure of PEDOT/h-PPy, as mentioned previously. But the response rate of PEDOT/h-PPy (1:1) was smaller than that of PEDOT, which might be due to the relatively slower response of PPy.

The power output capability of electrochemical supercapacitor depends strongly on not only the rates of ionic mass transport [33] but also the series resistance (R) [34]. The R is the sums of two major parts, an electronic resistance and an ionic one. EIS has been widely used to study the redox processes of ECPs and to evaluate their electronic and ionic conductivities. The EIS curves of PEDOT/h-PPy (5:1) composite at open circuit voltage (OCV), 0.6 V (versus SCE), and -0.4 V (versus SCE) are shown by curve 1, curve 2, and curve 3 in Fig. 4, respectively. Two well-separated patterns were observed: an arc was obtained at frequencies high enough, as shown in the up-right

corner of Fig. 4, which is related to interfacial processes; the low-frequency region of such plots indicated a capacitive behavior related to the film charging mechanism. The difference in the real part of the impedance between low and high frequencies could be used to evaluate the value of electrochemical charge transfer resistance (R_{CT}) [35–36], which would be mainly part of the R of supercapacitor. The value of PEDOT/h-PPy (5:1) composite from Fig. 4 was only 1.2Ω at OCV, because of the high electronic conductivity and fast response ability of the composite. Slight increase occurring at 0.6 V (versus SCE), R_{CT} was up to 1.5Ω . Further increase would occur at -0.4 V (versus SCE), due to the reduced volume [37] and the relatively lower electronic conductivity [38] of polymer at dedoped state. It could eventually reach 2.5Ω only. On the other hand, the imaginary part of the impedance at low frequencies was almost perpendicular to the real part, which verified a good capacitance behavior of the system.

The specific capacitance calculated from Fig. 4 is 280 Fg^{-1} at OCV, which is slightly smaller than the value calculated from the CV curve due to the redox switching hysteresis of conducting polymer [35].

Fig. 5 illustrates the charge–discharge curves of the PEDOT/PPy (5:1) composite in 1 M KCl solutions in two-electrode system. The curves were linear in the whole range of potential without a clear ohm-drop phenomenon, which sig-

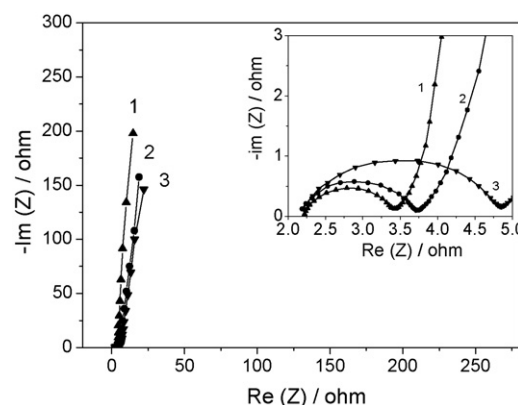


Fig. 4. EIS spectra of PEDOT/h-PPy (5:1) at open circuit voltage (curve 1), 0.6 V (vs. SCE) (curve 2), and -0.4 V (vs. SCE) (curve 3) in 1 M KCl solution.

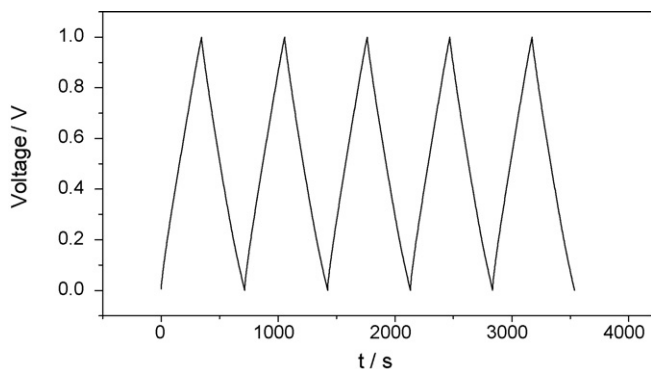


Fig. 5. Galvanostatic charge–discharge curves of PEDOT/h-PPy (5:1) in 1 M KCl solution with current density 3 mA cm^{-2} , two-electrode system.

nified an ideal supercapacitor system. The specific capacitance calculated from Fig. 5 was about 290 Fg^{-1} .

Fig. 6 shows the CV curves of PEDOT/h-PPy (5:1) composite with scanning rate 50 mV s^{-1} (curve 1) and 100 mV s^{-1} (curve 2) in 1 M KCl solution in two-electrode system. The curves were both rectangle-like shapes. The specific capacitance of the composite was about 260 Fg^{-1} at 100 mV s^{-1} . That is, the specific power could reach 13 kW kg^{-1} . Furthermore, the value remained stable during 1000 cycles, as shown by curve 1 in Fig. 7.

The cyclic performance was further examined by galvanostatic charge–discharge tests for 1000 cycles with the load of 3 mA cm^{-2} in two-electrode system (charging until 1 V). The results were shown by curve 2 in Fig. 7. The specific capacitance of the composite was 276 Fg^{-1} after 1000 cycles, only decreasing by 5%. Although the potential window of PPy in 1 M H_2SO_4 , according to the reference [39], was only 0.4 V with good durability, the potential window of the PPy/PEDOT composite was up to 1 V in 1 M KCl. The reasons may lie in two aspects. On one hand, PEDOT had the broad potential window (up to 1.2 V in 1 M H_2SO_4 solution and 0.8 V with good durability) [29]. On the other hand, PPy could obtain broader potential window in neutral aqueous solution (e.g. KCl) [13]. In addition, the neutral electrolyte is less corrosive and so more applicable compared to the strongly acidic electrolyte (e.g. H_2SO_4).

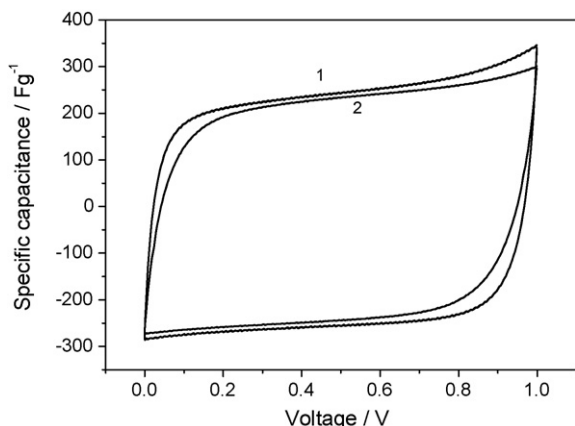


Fig. 6. CV curves of PEDOT/h-PPy (5:1) at 50 mV s^{-1} (curve 1), 100 mV s^{-1} (curve 2) in 1 M KCl solution, two-electrode system.

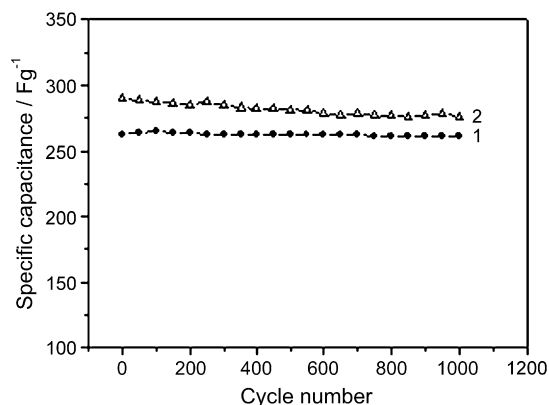


Fig. 7. Variation of capacitance of PEDOT/h-PPy (5:1) as a function of cycle number in CV test with 100 mV s^{-1} in 1 M KCl solution, two-electrode system.

4. Conclusions

PEDOT/PPy composite electrodes have greater specific capacitance than that of pure PEDOT electrodes. In particular, PEDOT/h-PPy composite (5:1) electrodes show a specific capacitance of 290 Fg^{-1} and a good cycling performance in 1 M KCl solution. Furthermore, the composite electrodes are characterized with better response ability than pure PEDOT electrodes do, so that its specific power could reach 13 kW kg^{-1} . It is confirmed that PEDOT/h-PPy composite is a kind of very promising electrode materials for electrochemical supercapacitors.

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