

Enhanced electrochemical performance of PEDOT film incorporating PEDOT: PSS

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Abstract: For effective use of conducting polymers, a hybrid film composed of poly (3,4-ethylenedioxythiophene) : poly (styrenesulfonate) (PEDOT:PSS) and poly (3,4-ethylenedioxythiophene) (PEDOT) has been fabricated by a in situ polymerization method. Each component in the hybrid film provides unique and crucial function to achieve optimized electrochemical properties. In the presence of PEDOT:PSS, the PS/PEDOT hybrid film is found to possess the better energy storage ability. Volumetric capacity of composite film (97.51 F/cm³) is much higher than that of pure PEDOT:PSS (37.75 F/cm³) and PEDOT (50.52 F/cm³) films. The hybrid film also exhibits excellent charge/discharge rate and good cycling stability, retaining 92.4% of its initial charge after 1000 cycles. The electrochemical performance improvement is primarily due to the synergistic effect between PEDOT:PSS and PEDOT. It is anticipated that this flexible procedure could be a promising large scale fabrication method for supercapacitor electrodes.

1. Introduction

Supercapacitors due to their high power density, long life cycles, and high efficiency have aroused great research interest in recent years[1-3]. Generally, supercapacitors can be divided into two types based on the kind of the electrode materials: one is the electrical double-layer capacitor which utilizes mainly the separation of the electronic and ionic charges at the interface between electrode materials and the electrolyte solution[4]. The other is the pseudo-capacitor based on the Faradaic redox reactions occurring within the active materials of electrodes[5]. Comparing with Carbon materials and Transition metal oxides materials, conducting polymers have attracted great interest for being candidates in fabrication of various electronic devices because of their various structures, high conductivity, excellent stability for redox and the benign property to environment[6]. Recent research efforts have been focused on to synthesize nanocomposite based on conducting polymers. The polymer nanocomposite exhibits fast charge-discharge behavior, large surface to volume ratio and superior chemical stability[7,8].

Here, we developed a in situ polymerization deposition based technology synthesizing composite materials with well distribution of PEDOT:PSS into PEDOT matrix. In this hybrid film, PEDOT:PSS as a framework provides the improved electrical conductivity and facilitates the hybrid film fabrication. The PEDOT film with porous structure supplies ion transport corridor and desired high specific capacitance. Synergistic effect between PEDOT:PSS and PEDOT results in enhanced electrochemical performance.

2. Experiments

A solution of oxidant iron (III) p-toluenesulfonate (FeTos) 40 wt% in butanol and 3,4-ethylenedioxythiophene (EDOT) were obtained from HC Starck (under the respective trade names Clevios CB40 and Clevios M). PEDOT:PSS (1.3wt% dispersion in H₂O) solution was purchased from Sigma-Aldrich(USA).

First, 6wt% EDOT monomer and 6wt% PEDOT:PSS was added in the FeTos solution. The blend of PEDOT:PSS, EDOT, FeTos and IPA reacted with the assistance of ultrasonic for 2 h. Then the reactant was spin coated at 2000 rpm for 20 s onto ITO substrate. Subsequently, the PEDOT:PSS/PEDOT film was annealed on the hotplate at 50°C for 30 min. The resulting film denoted by PS/PEDOT was thoroughly washed with ethanol to remove the unreacted monomer, FeTos and IPA. The PEDOT film had also been synthesized without the use of PEDOT:PSS and was labeled by PEDOT.

The crystallographic information of the films was investigated by a X-ray diffraction system (XRD, X'Pert Pro MPD). Raman spectra were measured on a laser Raman spectroscopy (Advantage 633nm). The morphology and microstructure of the films were examined using a scanning electron microscopy (SEM, HITACHI S4800). Electrochemical properties were carried out in a three-electrode system (CHI660D electrochemical workstation, Chenhua, Shanghai) with 1 M H₂SO₄ aqueous solution as electrolyte. A platinum plate and an Ag/AgCl electrode were used as the counter and reference electrode, respectively.

3. Results and discussion

In Fig. 1a, for the Raman spectrum of PEDOT:PSS, five bands at 1258 cm⁻¹, 1365 cm⁻¹, 1438 cm⁻¹, 1538 cm⁻¹ and 1569 cm⁻¹ are assigned to C-C inter-ring stretching, C-C single bond stretch, C=C symmetric stretch, C=C asymmetric stretch, and C=C anti-symmetric stretch, respectively[9]. In the Raman spectrum of PEDOT, the bands at 522 cm⁻¹ and 579 cm⁻¹ are associated with C-O-C bond deformation and the bands at 699 cm⁻¹ and 857 cm⁻¹ are assigned to C-S-C stretching[10]. The peaks at 991 cm⁻¹ and 1256 cm⁻¹ are due to oxyethylene ring deformation and thiophene C-C inter-ring stretching in plane modes, respectively. Vibrational modes observed at 1098, 1368, 1429 and 1509 cm⁻¹ correspond to C-O stretching, C-C stretching in plane modes, C=C stretching in plane modes (symmetric) and C=C stretching in plane modes (antisymmetric), respectively[10]. For the PS/PEDOT film, the features of PEDOT dominate the Raman spectroscopy of PS/PEDOT hybrid film. Moreover, the presence of the bands at 1538 and 1569 cm⁻¹ in the spectrum of PS/PEDOT clearly indicates the successful incorporation of PEDOT:PSS in the PEDOT structure[11]. These results suggest the successful preparation of PS/PEDOT composite film. To explore the structural properties of the as prepared films, XRD patterns of PEDOT:PSS, PEDOT and PS/PEDOT are presented in Fig. 1b. For the pattern of pure PEDOT film, no characteristic peaks appear except the low angle peak at 6.9°, indicating the amorphous structure of PEDOT material[12]. Peaks at 2θ=6.9° and 28.4° are all observed in the spectrum of PS/PEDOT film and the peak at 2θ=25.6° belonged to PEDOT:PSS disappears. This clearly shows that the PEDOT:PSS is wrapped by the the close package of PEDOT material.

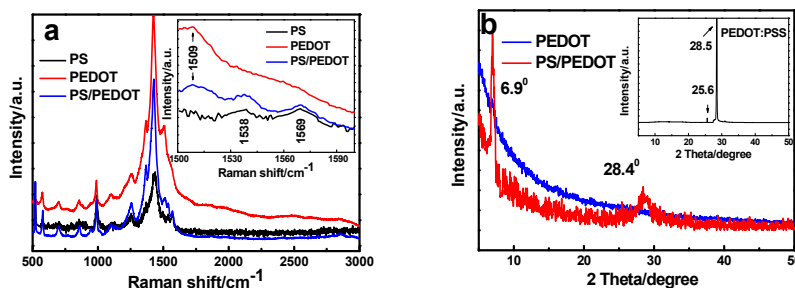


Fig. 1: (a) Raman spectroscopy of PEDOT:PSS, PEDOT and PS/PEDOT films, Inset represents Raman spectra in the range of 1500-1600 cm⁻¹; (b) XRD patterns of PEDOT and PS/PEDOT films; Inset represents the XRD spectrum of PEDOT:PSS.

Surface morphologies of pure PEDOT:PSS, PEDOT and PS/PEDOT films are characterized by scanning electron microscopy (SEM). Fig. 2a shows that the PEDOT:PSS nanoparticles are scattered across the substrate surface. Fig. 2b shows a close package of PEDOT film displaying a compact and rough morphology. In Fig. 2c, the surface morphology of as-prepared PS/PEDOT film shows nanoporous network structure. It is clearly that when incorporating PEDOT:PSS into PEDOT matrix, porous microstructure appears during in situ polymerization process. Moreover, this porous structure is able to enlarge the surface areas and facilitate the fast diffusion of electrolyte components inside the composite film.

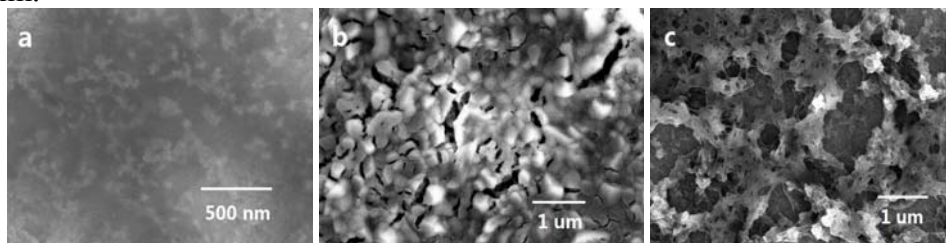
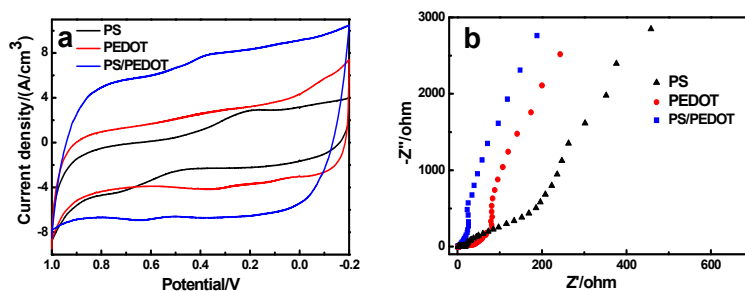


Fig. 2: SEM images of (a) PEDOT:PSS, (b) PEDOT and (c) PS/PEDOT films.

As shown in Fig. 3a, the CV curves of different electrodes are presented at a scan rate of 100 mV/s within a potential window from -0.2 to 1 V. With the same scan rate, the great larger current response of the PS/PEDOT film suggests a higher capacitance than those of pure PEDOT film and PS film. EIS measurements are carried out in the frequency range from 100 kHz to 0.01 Hz at open circuit potential with an ac perturbation of 5mV (Fig. 3b). The R_e values for PS, PEDOT and PS/PEDOT films are measured to be 1.36, 1.29 and 1.18 Ω , respectively. For PS/PEDOT film, the straight line in the low frequency almost parallels with imaginary axis which indicates that the PS/PEDOT composite film exhibits an ideal capacitive behavior. Fig. 3c depicts charge-discharge curves of PS, PEDOT and PS/PEDOT films at a current density of 3 A/cm². The PS/PEDOT film displays more symmetric triangular charge-discharge curves and longer discharge time which is consistent with the specific capacitance behavior, confirming that the composite film presents higher specific capacitance, better reversibility as well as charge-discharge properties. The volumetric capacitances of electrode films are calculated from the discharge plot of charge-discharge curves through an equation:

$$C_v = (I \times \Delta t) / (V \times \Delta V)$$

where C_v is volumetric capacitance (F/cm³), I and Δt are charge-discharge current and time, respectively, ΔV is the potential drop during discharge, and V is the volume of the films[13]. From the discharge curves shown in Fig 3c, the volumetric capacitances of PS, PEDOT and PS/PEDOT are 37.75, 50.52 and 97.51 F/cm³, respectively. The value of volumetric capacitance for PS/PEDOT achieves 97.51 F/cm³, which is approximately two times higher than that of PEDOT film. The volumetric capacitance of the cells assembled by PS, PEDOT and PS/PEDOT retains 91%, 92.1% and 92.4% of the initial capacitance after 1000 cycles. This indicates that the stability of the ternary film is strengthened with the dopant of PEDOT:PSS. It is clearly that synergistic effect reveals by introducing PEDOT:PSS into PEDOT matrix, which can prevent high rate degradation of hybrid film.



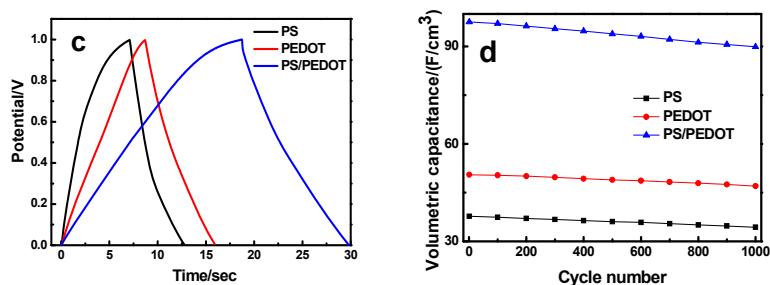


Fig. 3: (a) CV curves of PS, PEDOT and PS/PEDOT films at 100mV/s; (b) Nyquist plots for all the samples in the frequency range of 100 kHz-0.01 Hz; (c) Galvanostatic charge-discharge curves of all the sample films at a current density of 0.1 A/cm³; (d) stability plots for all the samples at current density of 3 A/cm³.

4. Summary

A in situ polymerization approach to preparing hybrid film consisting of PEDOT:PSS and PEDOT is demonstrated. The as-prepared hybrid film presents super capacitive behavior with excellent electrochemical performance. At a current density of 3 A/cm³, the volumetric capacitance (97.51 F/cm³) is improved compared to PEDOT:PSS (37.73 F/cm³) and PEDOT (50.52 F/cm³). It would be reasonable to expect that this high-performance PS/PEDOT film is a promising electrode for energy storage devices.

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