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Electrochemical preparation of nano-composites of poly(*o*-methoxyaniline) and carbon nanotubes

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Abstract Composite films of poly(*o*-methoxyaniline) (POMA) and carbon nanotubes (CNTs) were prepared via electrochemical co-deposition from the aqueous solutions containing *o*-methoxyaniline and acid-treated CNTs. The addition of small amounts of CNTs to *o*-methoxyaniline can accelerate significantly the electrochemical polymerization rate of the monomer. As-prepared composite films are characterized by thermal analysis, SEM, and the electrochemical methods. The results of the thermal analysis show that the composites have an enhanced thermal stability relative to POMA. SEM revealed that CNTs had been uniformly coated with POMA, forming dense nanoporous networks composite films.

Introduction

Conducting polymers (CPs) with good electrical conductivity and large pseudo-capacitance have aroused wide interests as the electrode material in supercapacitors which are unique for provision of pulsed high power [1–6]. They undergo conducting–insulating switch during charge–discharge cycles. Carbon nanotubes (CNTs) with excellent structural, mechanical, and electronic properties have recently attracted considerable interest in consequence of their potential applications in field emitters, nanoelectronic devices, probe tips for scanning probe microscopies, and nanotube-based composites [7–11]. Introducing CNTs into CPs could significantly improve the mechanical and electrical properties of CPs [12, 13]. Therefore, the formation of polymer/CNTs composites can be considered as a useful approach for the fabrication of polymer-based devices [14, 15].

Composites of CPs and CNTs have been prepared by chemical or electrochemical polymerization method from the mixtures of the corresponding monomers and CNTs. For chemical approach, an oxidant is needed and converted to a reduction product that may affect the properties of the product. The reaction product is always a powder which means a binder has to be used for the construction of an electrode [16–18]. However, the electrochemical polymerization has a number of advantages. Particularly, there is no need for added oxidants, and the electrodeposited CPs are naturally integrated as a continuous uniform film on the electrode, saving the use of a binder. Therefore, electrodeposited films are ideal for the study of the electrochemical properties of these composites in sensors [19–21], electro-catalysts [22], and supercapacitors [23]. Presently, many reports have focused on the combination of CPs and CNTs by electrochemical polymerization method including polyaniline/CNTs [24–26], polypyrrole/CNTs [27, 28], and poly(3,4-ethylenedioxythiophene)/CNTs [29–31]. These composite films exhibit excellent charge storage and transfer capabilities due to their high surface areas, conductivities, and electrolyte accessibilities of the nanoporous structure. As one of the polyaniline derivatives, poly(*o*-methoxyaniline) (POMA) has been extensively investigated due to its good solubility [32, 33], electroactivity [34, 35], electrochromism [36, 37], and thermal stability

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[38, 39]. POMA has been applied to different fields such as battery [40], optical fiber [41, 42], corrosion inhibition [43, 44], capacitor [45], resistor [46], field effect transistor [47], and nano-biocomposite [48–50]. For many of the applications, it is necessary to develop the composites of POMA and CNTs.

In this article, POMA/CNTs composites were prepared successfully by electrochemical co-deposition method. The thermal stability, spectroscopic properties, and morphology of as-prepared composites were investigated in detail.

Experimental

Materials

o-Methoxyaniline (99%) is purchased from the Johnson Matthey Company. Multi-walled CNTs are purchased from Shenzhen Nano-Technologies Port Co. Ltd., and the acid-treated CNTs are obtained according to a previously described acid treatment process [51]. Sulfuric acid (H_2SO_4, AR grade) was purchased from Nanjing Chemical Reagent Industries Ltd. All the solutions were freshly prepared with distilled-deionised water.

Preparation of POMA and POMA/CNTs composite films

The electrochemical experiments were carried out using a CHI660B potentiodynamic synthesis (Shanghai Chenhua Instrumental Co., Ltd., China). For the electrochemical examination, Glassy carbon electrode (GC, 3 mm diameter) was used as the working electrode. The counter electrode and the reference used were platinum wire (0.5 mm diameter) and saturated calomel electrode (SCE), respectively. The solutions were deaerated by a dry nitrogen stream, and a slight nitrogen overpressure was maintained during experiments. POMA and POMA/CNTs composites films were prepared by cyclic voltammograms (CVs) in 0.5 M H_2SO_4 solution containing 0.1 M *o*-methoxyaniline and absence/presence of the acid-treated CNTs (0.5 wt%).

Characterization

The conductivity measurements of the pressed-pellet POMA/CNTs samples were carried out on an insulator substrate by a conventional four-probe technique [52]. The thermogravimetric analysis (TGA) was performed with a thermal analyzer of DTA6300. A scanning electron microscope (SEM, S-4700, Japan) was used to determine the morphology. Transmission electron microscopy (TEM) investigations were performed on a Tecnai G220, equipped with a Schottky emitter operating at 200 kV.

Results and discussion

Electrochemical deposition of POMA and POMA/CNTs composite films

Figure 1 shows the photographs of untreated CNTs (a) and treated CNTs (b) dispersed in 0.5 M H_2SO_4 solution containing *o*-methoxyaniline monomer. The two CNTs samples were prepared with sonication for several minutes and placed undisturbedly for 24 h. From the comparison we can see that a complete dissolution of treated CNTs in 0.5 M H_2SO_4 solution forms a homogeneous dark solution and is very stable at room temperature without precipitation for 24 h. The possible reason for the stability of the treated CNTs in such acidic solution is that the surface negative charges on CNTs are not protonated completely due to the presence of the substantive SO_4^{2-} in the solution. However, it is found that the untreated CNTs are unstable and get deposited fast to the bottom of the bottle.

Figure 2 shows the anodic polarization curves of 0.1 M *o*-methoxyaniline + 0.5 M sulfuric acid (a) and 0.1 M *o*-methoxyaniline + 0.5 M sulfuric acid + 0.5 wt% CNTs (b). As seen in Fig. 2, the onset oxidation potential of *o*-methoxyaniline decreases from 0.62 to 0.60 V and the oxidation current increases significantly when 0.5 wt% CNTs is added into the *o*-methoxyaniline sulfuric acid solution. The explanation of the effect of CNTs on the process of electro-deposition of POMA should be ascribed to two aspects, (1) The negatively charged CNTs act as a supporting electrolyte during polymerization, which increases the conductivity of *o*-methoxyaniline solution; (2) The negatively charged CNTs act as a dopant during the process of POMA electro-deposition, which may enhance

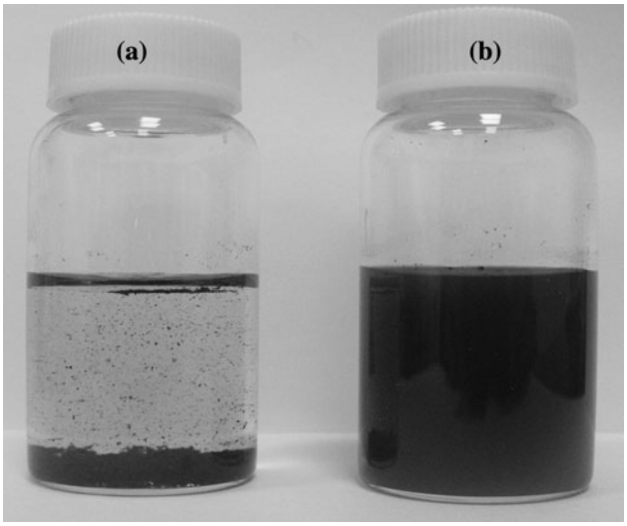


Fig. 1 Photographs showing the stability of untreated CNTs (**a**) and treated CNTs (**b**) dispersions in 0.5 M H_2SO_4 solution containing *o*-methoxyaniline monomer

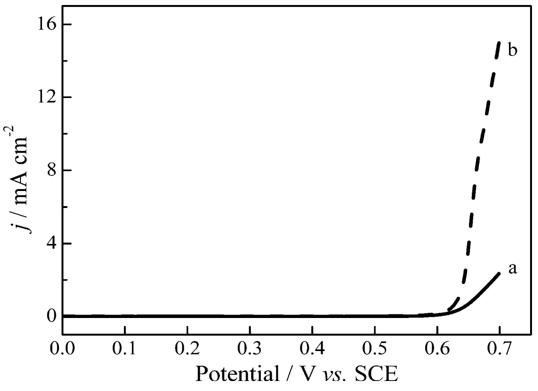


Fig. 2 Anodic polarization curves of 0.1 M *o*-methoxyaniline + 0.5 M sulfuric acid (*a*) and 0.1 M *o*-methoxyaniline + 0.5 M sulfuric acid + 0.5 wt% CNTs (*b*) at 50 mV s^{-1}

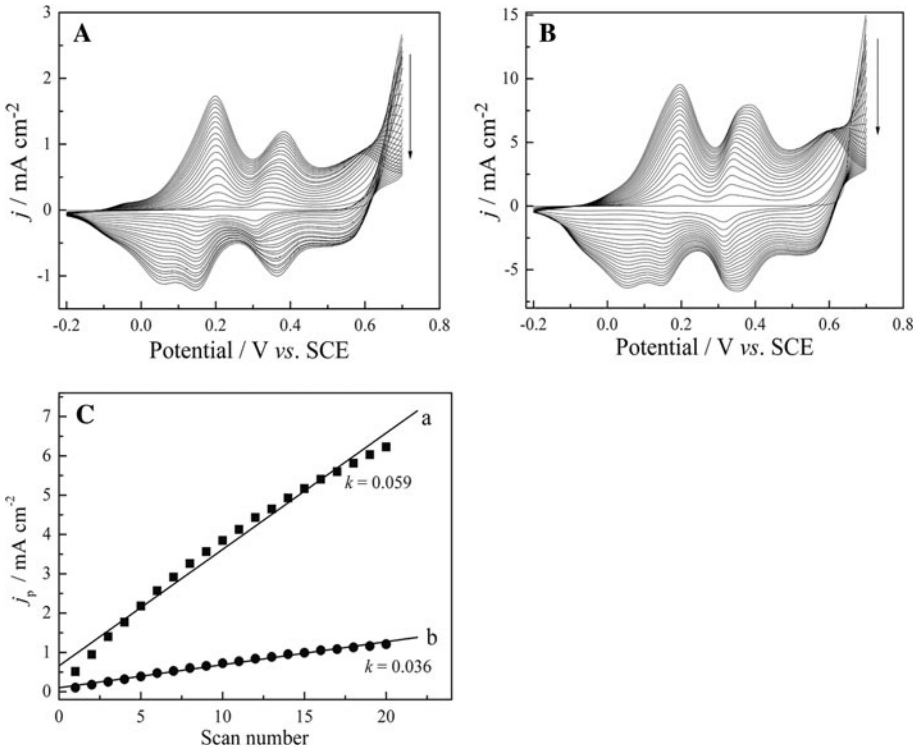
the conductivity and capacitance of POMA [51]. Therefore, the addition of small amounts of CNTs is useful for the deposition of POMA.

The successive CVs of 0.1 M *o*-methoxyaniline + 0.5 M sulfuric acid (A) and 0.1 M *o*-methoxyaniline + 0.5 M sulfuric acid + 0.5 wt% CNTs (B) at 50 mV s^{-1} are shown in Fig. 3. The CVs show the typical growth of POMA and POMA/CNTs films. For POMA homopolymers, there are three pairs of redox current peaks, which are similar to the polyaniline. The first peak at about 0.20 V can be ascribed to the oxidation of POMA in the leukoemeraldine oxidation state to the emeraldine oxidation state. The second at about 0.38 V corresponds to the oxidation of head-to-tail dimer. The peak with the highest potential at about 0.61 V corresponds to the conversion from emeraldine to pernigraniline structure [53, 54]. As the CV scan continues, the intensity of three pairs of redox peaks increases, indicating a continuous deposition of POMA on the GC electrode. Compared with POMA homopolymers, however, the peak current densities of POMA/CNTs are higher and the oxidation potentials of three pairs of redox peaks are shifted negatively to 0.18, 0.33, and 0.59 V, respectively (Fig. 3B). This may be because the CNT is a good electron acceptor, *o*-methoxyaniline is a fairly good electron donor, and CNTs and *o*-methoxyaniline may form a charge-transfer complex in their ground state when CNTs are dissolved in the *o*-methoxyaniline solution [55]. On the other hand, the increase rate of the current densities of POMA/CNTs is faster than that of POMA homopolymers (Fig. 3C). This is because CNTs doped or coated into the films can provide more sites for the polymerization of *o*-methoxyaniline.

Electrochemistry of POMA and POMA/CNTs composite films

Figure 4 shows CVs of POMA (a) and POMA/CNTs (b) in 0.5 M sulfuric acid at potential scan rate of 50 mV s^{-1}. The CVs indicate several important differences between POMA and POMA/CNTs. The first is that the output current of POMA/CNTs is about three times of that of the pure POMA. Since capacitance can be estimated from the output

Fig. 3 Cyclic voltammograms of 0.1 M *o*-methoxyaniline + 0.5 M H_2SO_4 (**A**) and 0.1 M *o*-methoxyaniline + 0.5 M H_2SO_4 + 0.5 wt% CNTs (**B**) at 50 mV s^{-1}. **C** the plot of cathodal peak current density at 0.15 V against scan numbers, (*a*) and (*b*) corresponding to (**B**) and (**A**), respectively



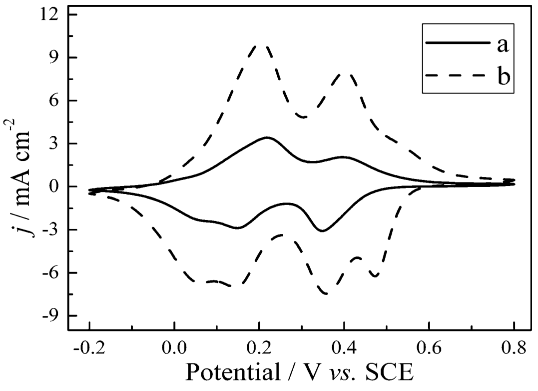


Fig. 4 CVs of POMA (*a*) and POMA/CNTs (*b*) films in 0.5 M sulfuric acid at potential scan rates of 50 mV s^{-1}

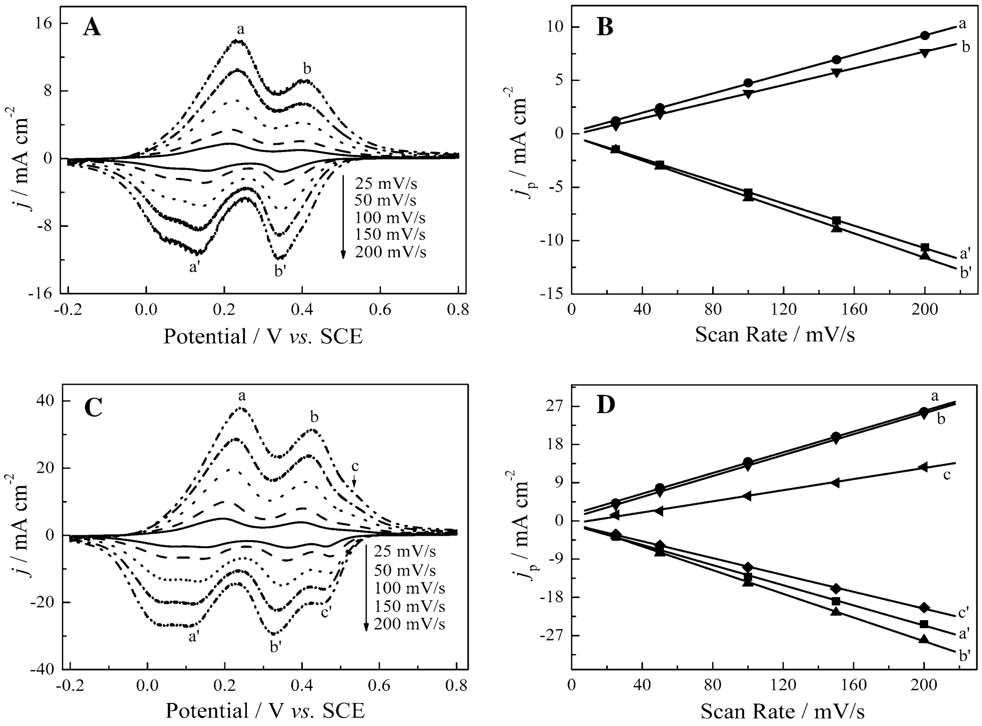
current divided by the scan rate, this implies that the capacitance of the composite films is about three times of that of the pure polymer [23, 56]. The second point worth noting is that new redox peaks are observed at 0.47 V (cathodic peak potential) and at 0.52 V (anodic peak potential) for POMA/CNTs films, confirming the presence of anionic dopant of the CNTs in the composite films [51].

The electrochemical behavior of the POMA (A, B) and POMA/CNTs composite films (C, D) via varying the scan rates was studied in 0.5 M sulfuric acid (Fig. 5). The steady-state CVs represented broad anodic and cathodic peaks. Similar to the results of homopolymers (Fig. 5A, B), the peak current densities were proportional to the scan rates (Fig. 5C, D), indicating the good redox activity of POMA/CNTs composite. Furthermore, these polymer films could be cycled repeatedly between the conducting (oxidized) and insulating (neutral) states without significant decomposition of the materials, indicating high structural stability of the polymer. Additionally, at high scan rate, for example, at 200 mV s^{-1}, the potentials of the reduction peaks of POMA/CNTs shift negatively relative to those of POMA, which is similar to that of polyaniline/CNTs [57]. Interestingly, the output currents of as-formed POMA/CNTs have been enhanced greatly in comparison with POMA, which are significantly different from those between polyaniline and polyaniline/CNTs [57] and from those between polypyrrole and a polypyrrole/MWNT [51]. Therefore, as-formed POMA/CNTs are expected to find applications in supercapacitors and secondary batteries.

Thermal analysis

The thermal stability of a conducting polymer is very important for its potential application. Thermogravimetry (TG) is a significant and useful dynamic way to detect the degradation behavior in which the weight loss of a polymer sample is measured continuously while the temperature is changed at a constant rate. In order to investigate the thermal stability of the POMA and POMA/CNTs composites, the thermal analyses of POMA and POMA/CNTs composites were tested, yielding the results shown in Fig. 6. It can be clearly seen from Fig. 6 that the weight loss of POMA and POMA/CNTs at about 380 K is mainly because of the evaporation of water in polymer. Note that the degradation of POMA/CNTs is slower than that of

Fig. 5 CVs of POMA (**A**, **B**) and POMA/CNTs (**C**, **D**) films in 0.5 M sulfuric acid at potential scan rates of 25, 50, 100, 150, and 200 mV s^{-1}. j_p is defined as the peak current density



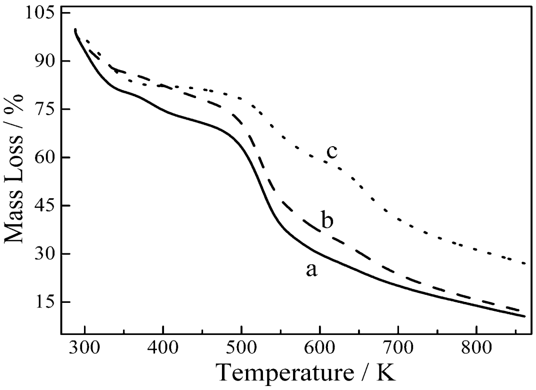


Fig. 6 TGA thermograms of POMA (*a*) and POMA/CNTs [0.2 wt% CNTs (*b*) and 0.5 wt% CNTs (*c*)]

POMA with the temperature increase, and the thermal stability of POMA/CNTs containing 0.5 wt% CNTs is higher than that of POMA/CNTs containing 0.2 wt% CNTs. The results implied that the incorporation of CNTs into POMA resulted in the improvement of the thermal stability of POMA.

Electrical conductivity and morphology

The SEM of POMA films (a) and POMA/CNTs composites (b–d) is recorded, as shown in Fig. 7. Macroscopically, POMA films that formed on the electrode were flat and compact and metallic black in color. Microscopically, POMA has a rough surface consisting of grains (Fig. 7a). It can be seen from Fig. 7b–d that POMA/CNTs composites

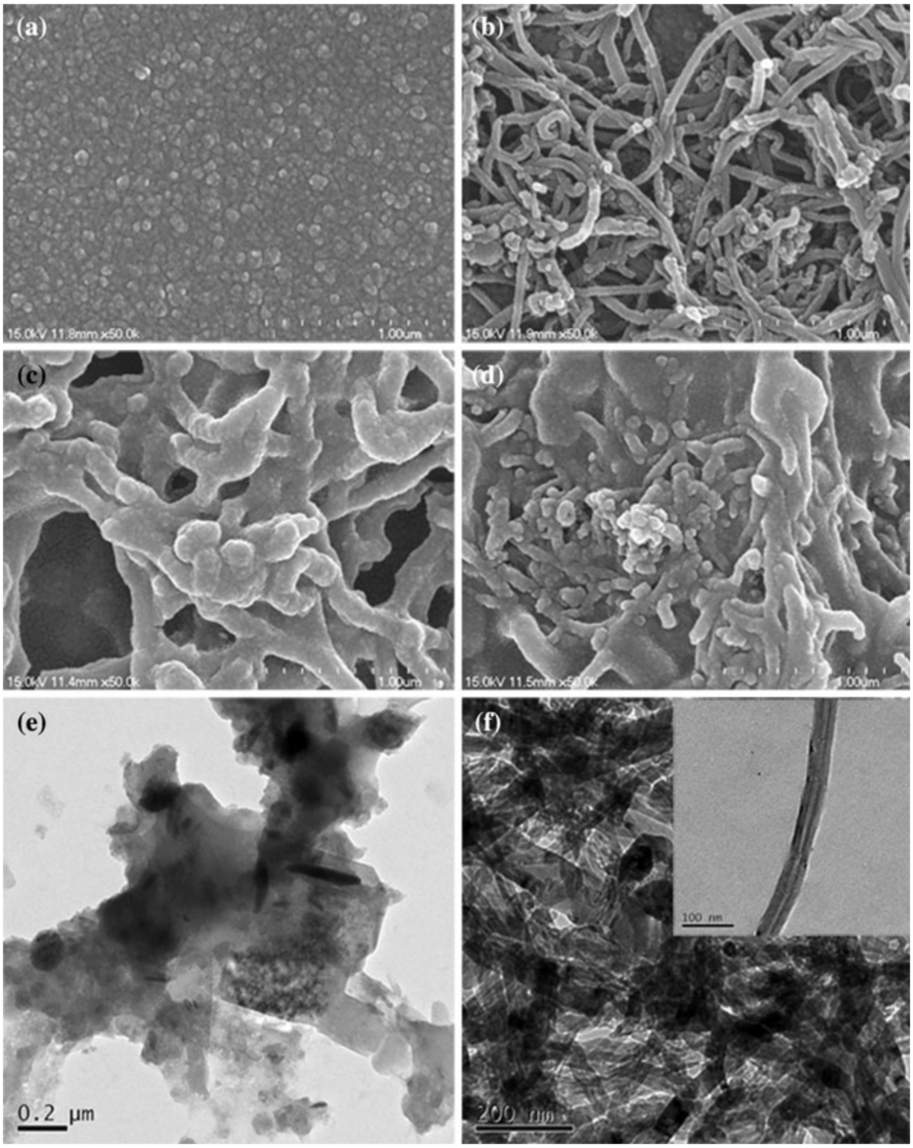


Fig. 7 SEM of POMA films (**a**) and POMA/CNTs composites (0.06 C cm^{-2} (**b**), 1.12 C cm^{-2} (**c**), 10.2 C cm^{-2} (**d**)), TEM of POMA films (**e**) and POMA/CNTs composites (**f**), inseted TEM of CNTs

are successfully prepared, in which CNTs and POMA are attached to each other and tightly fixed onto the working electrode. To further confirm the structure of composites, the TEM images of POMA films and POMA/CNTs composites are shown in Fig. 7e, f. For POMA/CNTs composites, it is clear that a layer of uniform POMA film is presented on CNTs' surface relative to the TEM of CNTs (inset of Fig. 7f).

The conductivity of POMA/CNTs containing 0.5 wt% CNTs is 3.12 S/cm, which is higher than that of POMA (about 0.22 S/cm). This indicates that the coating/doping of CNTs into POMA films is helpful to improve the conductivity of POMA, which may be beneficial to extend the application of POMA.

Conclusions

Composite films with conductivity of 3.12 S/cm are prepared via electrochemical co-deposition from the aqueous solutions containing *o*-methoxyaniline and acid-treated CNTs. The addition of small amounts of CNTs to *o*-methoxyaniline can accelerate significantly the electrochemical polymerization rate of the monomer. Thermal stability of composite films is higher than that of POMA. SEM and TEM reveal that CNTs have been uniformly coated with POMA, forming dense nanoporous networks composite films. The capacitance of the composite films is about three times of that of the pure POMA, which holds great promise for supercapacitors and secondary batteries.

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