Polaranine/Carbon nanotube Electrochromic Films: Electrochemical Polymerization and characterization

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Abstract: Polyaniline/Carbon nanotube (PANI/CNT) composite films doped with dodecyl-benzene sulfonic acid were synthesized by cyclic voltammetry on an ITO-coated glass substrate. FTIR, XRD and electrochemical analyzer were used to characterize the micro-morphology, chemical structure, crystallinity and electrochromic behavior of the films, respectively. The effect of CNT content on the properties of the films was investigated. Results show that the introducing CNTs make aniline polymerize easier than before. Within a range, the conductivity and crystallinity of PANI/CNT composites improves with CNT content increasing. The electrochromic device made from the PAN/CNT film with a CNT content of 2.5wt% presents a reflectance contrast of 38.8%, a mean response time of 2.3s and a coloration efficiency of 386.4cm²/C at 540nm. The PAN/CNT film shows better electrochromic behaviors due to some interaction between CNTs and the PANI backbones than PANI film.

1. Introduction

Polyaniline (PANI) with metal-like conductivity and electrochromic behavior can be obtained from inexpensive aniline and some doping agents by electrochemical polymerization or chemical oxidation. It has diverse potential applications such as electrochromic devices (ECDs), super capacitors and electromagnetic shielding, etc. However, as a versatile conducting polymer, PANI has some unavoidable shortcomings, such as lower charge transferring capacity and shorter life cycles of duty-cycle operation, which need to be improved by acid-doping or compounding with other materials [1].

Carbon nanotubes (CNTs) have recently attracted much attention owing to their unique spiral structure, quantum effect, surface action, electronic properties and so on [2]. Some studies indicate that the electric conductivity and mechanical properties of polymers can improve by introducing CNTs into a polymer matrix [3]. Therefore, nano-composites that combine CNTs and conducting polymers have recently attracted considerable interest. As PANI has high affinity for the surface of CNTs, PANI-CNT composites have been synthesized in situ by chemical or electrochemical oxidation of aniline in the presence of CNTs. The composites show enhanced electrical, thermal or mechanical properties by comparison to PANI or CNTs alone, and exhibit potential applications including of cells, sensor, micro/nano electronic components and optoelectronic devices [4].

At present, PANI/CNT composites are mainly prepared in situ by chemical oxidation, and the powdered product limits their further application. In this paper, PANI/CNT composite films were synthesized by electrochemical polymerization, and their behaviors were characterized.
2. Material and Methods

2.1. Materials

Aniline (≥99.5%) was distilled twice before used for polymerization. Carbon nanotubes (96%) with a diameter of 20-40nm and a length of 10-30μm were received from Beijing Boyu Technology Co. Ltd. Dodecylbenzene sulfonic acid (DBSA, ≥96%); alcohol (C₂H₅OH, ≥99.7%) and deionized water were all needed. A 1.0cm×3.0cm ITO-coated glass with a resistivity of 6-8Ω/sq was used as a substrate.

2.2. Electrochemical polymerization of PANI/CNT film

PANI/CNT films were synthesized in a three-component cell, and the potential was scanned between -0.2 and 1.0V at a rate of 50mV/s, where an ITO-coated glass slide, platinum strip and saturated calomel electrode were used as working electrode, counter and reference electrodes.

The electrolyte for polymerization was prepared as follows: The mixture of 0.25mol·L⁻¹ aniline, 0.8mol·L⁻¹ DBSA and 5mol·L⁻¹ C₂H₅OH was ready, and then, the suspension of various weight percent of CNTs by ultrasonic dispersion was added to the mixture, respectively. Finally, PANI/CNT composite films with various CNT content were prepared by electrochemical polymerization as mentioned above.

2.3. Measurements

An ECD in which the PANI/CNT film with 2.5wt% CNTs acted as electrochromic layers was made, and its electrochemical and electrochromic behaviors were performed by a CHI760 electrochemical analyzer. IR spectra were recorded by VER TEX 80+HYPERION 2000 FTIR spectrometer. XRD patterns were obtained on an X’Pert Pro X-ray diffractometer (Cu Kα radiation). The conductivity was measured by four-point probe technique with a 1934 Conductivity Meter of China. HATCHI U-4100 Spectrophotometer was used to measure the reflectivity of films.

3. Results and Discussion

3.1. Cyclic voltammetric analysis

The electrochemical polymerization of PANI/CNT films can be described by cyclic voltammograms (CVs). The CVs for sample CP-3 are showed in Fig 1. Compared with pristine PANI [5], a pair of redox peaks appears and the current density rises obviously at 0.2V and 0.9V at the first cycle, which implies higher electroactivity. The interaction between CNTs and PANI through π-stacking can enhance the delocalization of electrons [6]. And meanwhile, we can see the film color change cyclically among light yellow, yellow green, green and dark green.

![Fig 1 CVs of PANI/CNT films](image-url)

3.2. FTIR spectra
FTIR spectra of PANI/CNT composites and PANI are showed in Fig 2. All samples present similar peaks, such as aromatic ring stretching at 1555\text{cm}^{-1}, quinoid ring stretching at 1470 \text{cm}^{-1}, C-N stretching of aromatic amines at 1300\text{cm}^{-1}, C-N stretching of benzenoid ring at 1238\text{cm}^{-1}, a vibration mode of N=Q=N at 1108 \text{cm}^{-1}, an out-of-plane stretching vibration of C-H of aromatic ring at 790 \text{cm}^{-1}, etc. Remarkably, the wide and strong band at 1108 \text{cm}^{-1} is described as “electronic-like band” and is considered a measure of electron delocalization degree \cite{7}. Thus, this peak can be used to characterize the conductivity of PANI. It is clear that increasing CNT content results in a distinct increase of the band intensity at 1108 \text{cm}^{-1}, which indicates that PANI/CNT composites have a better conductivity than PANI alone. This result is in good agreement with the conductivity test data (Table 1) and indicates that CNTs are well mixed with PANI in the composite films.

\begin{figure}
\centering
\includegraphics[width=0.4\textwidth]{Fig2.png}
\caption{FT-IR spectra of PANI/CNT films with various CNT contents}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.4\textwidth]{Fig3.png}
\caption{XRD patterns of PANI/CNT composites with various CNT contents}
\end{figure}

3.3. XRD patterns
Fig 3 shows XRD patterns of PANI/CNT composites. The peak at 2\theta=20.7^\circ is attributed to the period structure of PANI chains, and that at 25.2^\circ is for the amorphous state of PANI. As for CP-1 and CP-6, the peaks at 2\theta=20.7^\circ, 25.2^\circ are stronger than those of sample P-0, which implies that PANI crystallinity in PANI/CNT composites improves obviously while the formation of PANI side chains is inhibited by introducing CNTs. Meanwhile, the introduction of CNTs leads to two peaks at 2\theta=25.9^\circ (002) and 43^\circ (100) corresponding to a graphite-like CNT structure \cite{8}.

3.4. Electrical conductivity
Table 1 shows the electrical conductivity of PANI/CNT films with various CNT content. The conductivity rises sharply as the CNT content increases from 0.5 to 2.5wt\%, and then does slowly and approaches to a certain value. As CNTs are good electron acceptor owing to their large length-diameter ratio and specific surface, they can serve as conductive bridges to connect conducting domains of PANI and improve charge transfer. A proper content CNT can offer enough conductive bridges to form some conductive paths and result in a high conductivity.

\begin{table}
\centering
\caption{Conductivity of PANI/CNT films with various CNT contents}
\begin{tabular}{|c|c|c|}
\hline
Samples & CNT content (wt\%) & Conductivity(S.cm^{-1}) \\
\hline
P-0 & 0 & 1.123 \\
CP-1 & 0.5 & 1.927 \\
CP-2 & 1.5 & 9.224 \\
CP-3 & 2.5 & 19.465 \\
CP-4 & 3.5 & 24.653 \\
\hline
\end{tabular}
\end{table}
3.5. Electrochromic behaviors

Fig 4 shows Vis-NIR reflectance spectra for CP-3 film when applied potentials step between -0.4V and 0.8V with a step of 0.1V. With the potential increasing, the reflectivity at 500-600nm reduces gradually until the peak disappears, and a maximal color contrast of 38.8% appears at 540nm. Meanwhile, we can see the film color change from dark green to yellow green.

![Vis-NIR reflectance spectra of PANI/CNT films at -0.4~0.8V](image)

Coloration efficiency (CE) is a key parameter to characterize the electrochromic behavior of materials and devices [9], which can be derived from the slope of optical density~current density curve as showed in Fig 5. Therefore, the CE at 540nm for CP-3 film is 368.4 cm²/C. The film color becomes darker at 0.8V with the drop of reflectivity at 540nm, and lighter at -0.4V with reflectivity rising.

As showed in Fig 6(a), applied potentials step between 0.8V and -0.4V with a residence time of 5s. Fig 6(b) shows the reflectivity changes at 540nm for CP-3 film after several cycles. It reveals that the average response time is about 2.3s both for coloring state and bleaching one, which means a fast response of PANI/CNT electrochromic film. The reflectivity contrast nearly keeps unchangeable after four cycles, which means a good memory effect and stability of the film.

![Optical density and charge density of PANI/CNT films at 540nm](image)

![Charge time (a) and response time (b) profiles of PANI/CNT composites at 540nm](image)
4. Conclusion

DBSA-doped PANI/CNT composite films were synthesized by cyclic voltammetry. The introduction of CNTs promotes the polymerization of aniline. A reflectance contrast of 38.8% and a coloration efficiency of 386.4 cm$^2$/C at 540nm occurs in PANI/CNT film with CNT content of 2.5 wt%. Compared with the pristine PANI film, the PANI/CNT composite film shows a higher conductivity, a shorter response time, a higher electrochromic efficiency and better stability due to some interaction between CNTs and the PANI backbones.

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