

Electrochemical fabrication of polyaniline/multi-walled carbon nanotube composite films for electrooxidation of methanol

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Abstract Polyaniline (PANI)/multi-walled carbon nanotubes (MWNTs) composite films were fabricated by electropolymerization of aniline containing well-dissolved MWNTs. The films can be used as catalyst supports for electro-oxidation of methanol. Cyclic voltammogram and Chronoamperogram results show that platinum particles deposited on PANI/MWNT composite films exhibit higher electrocatalytic activity towards methanol oxidation than that deposited on pure PANI films. The porous structure and electrical conductivity of PANI films has been significantly changed by introduction of MWNTs, higher surface areas of PANI/MWNT composites has been achieved therefore. It favors for platinum particles to be highly dispersed on the PANI/MWNT composite films and the better electrocatalytic activity of Pt/PANI/MWNT electrode is induced consequently.

Introduction

The direct methanol fuel cell (DMFC) has attracted a great interest as power sources for many advantages, such as high energy density of methanol, low negative impact on the environment and ease of maintenance [1]. To improve the performance of DMFC, considerable

efforts have been devoted to the studying of electrode materials [2–4]. Platinum has been recognized as the most powerful electrocatalyst among noble metals for methanol electrooxidation [5, 6]. Today, to reduce the amount of platinum required and improve the electrooxidation efficiency, the design of catalyst supports has attracted great interesting [7]. The support material also influences catalytic activity [1].

Conducting polymers have been widely used as porous catalyst supports for electrooxidation of methanol [11]. Among these conducting polymers, polyaniline has many advantages over other conducting polymers due to its relatively facile process ability, high electrical conductivity and environmental stability [12–14].

Carbon nanotubes are unique nanostructured materials with remarkable physical and mechanical properties [15, 16]. These properties have inspired interest in using CNTs as the nano-fillers in polymer composite systems to obtain composite structural materials with enhanced electrical, mechanical and optical characteristics [17, 18].

Recent studies have shown that carbon nanotubes can be dissolved in aniline via formation of donor–acceptor complex [19]. In this work, we have prepared Polyaniline/multi-walled carbon nanotubes (PANI/MWNT) composite by electropolymerization of aniline containing well-dissolved MWNTs. Platinum particles were electrodeposited on the composite films subsequently. The primary focus of these studies is to compare the methanol oxidation activity on the Pt/MWNT/PANI and Pt/PANI electrode. To our knowledge, little work has been done to study the electrocatalytic activity at the Pt/MWNT/PANI electrode towards methanol electrooxidation.

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Experimental sections

MWNTs were produced via the chemical vapor deposition method as reported previously [20]. As shown in Fig. 1, the average diameter of MWNTs was about 10–20 nm and the length 5–15 μm .

Aniline was purified by distillation under reduced pressure and stored under nitrogen atmosphere at 4 °C. All other reagents were of analytical grade and were used as received. All the solutions were prepared with twice distilled water.

0.8 g MWNTs were added to 25 ml aniline and the mixture was heated at reflux for 3 h in the dark. Dissolution of MWNTs in aniline can be observed by color change of the solution with continuous heating. The original colorless aniline solution first become brownish and then turned dark red. After has been cooled to room temperature and settled for 24 h, a small quantity of unresolved MWNTs were precipitated from MWNT-aniline solution.

Electrochemical experiments were performed on CHI660A electrochemical working-station (Covarda) in a three electrodes system and controlled by CH instrument electrochemical software. A platinum sheet (geometric surface area = 1 cm^2) was used as substrate-working electrode. Another platinum sheet and a saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. The two platinum sheets were polished mechanically using emery paper (grade 1200) to a mirror surface and then cleaned by potential cycling between -0.2 V and 1.2 V at 50 mV s^{-1} in 0.5 M H_2SO_4 until a stable cyclic voltammogram was obtained.

The PANI/MWNT composite films were electrodeposited on the platinum substrate-working electrode by

using the cyclic voltammetry (CV) technique (at 50 mV s^{-1} between -0.1 V and 0.9 V for 15 cycles at 20 °C, in 0.5 M H_2SO_4 + 0.1 M aniline containing well dissolved MWNTs). The thickness of the composite film, varied by changing the number of potential cycles and calculated by the height of the first peak in the redox process, reaches to 0.86 μm [21, 22]. Platinum particles were deposited on the presynthesized MWNT/PANI composite film from 0.5 M H_2SO_4 solutions containing 1 mM H_2PtCl_6 at constant potential of -0.1 V [23]. Prior to the dispersion of the platinum, the MWNT/PANI coated electrode was soaked in 1 mM H_2PtCl_6 + 0.5 M H_2SO_4 solution for 15 min. The amount of platinum deposited, calculated from the integral of the cathodic charge passed during the deposition process and estimated by assuming that reduction of Pt^{4+} to Pt^0 is 100% efficient, is 126 $\mu\text{g cm}^{-2}$ [22, 24].

Pt modified pure PANI electrode free of MWNTs was fabricated following the identical method as the Pt modified MWNT/PANI electrode. The thickness of films is 0.86 μm and platinum loading is 126 $\mu\text{g cm}^{-2}$ also.

Measurements

X-ray diffraction (XRD) data of the samples were collected using a Rigaku D/MAX 24000 diffract meter with Cu-K_α radiation. SEM studies were performed using a JSM-6700F (JEOL) instrument. FTIR spectra were collected using a Nicolet Nexus 670 Fourier transform infrared spectrometer. The morphology of PANI/MWNT/Pt films was characterized by transmission electron microscopy (TEM Hitachi 600), operating at an accelerating voltage of 100 keV.

Results and discussion

Transmission electron microscopy and thermogravimetric analysis

Figure 2a shows the typical TEM image of the MWNT-aniline solution. It gives direct evidence that MWNTs have been resolved in aniline successfully. Thermogravimetric analysis (TGA) has been used to investigate the concentration of MWNTs in aniline. As shown in Fig. 2b, The sudden of the weight loss occurs at temperatures about 90 °C is corresponds to solvent evaporation and the residues remained is pristine MWNTs. A total weight loss of 98.7% was observed and the solubility of MWNTs in aniline can be calculated up to 1.3 wt%.

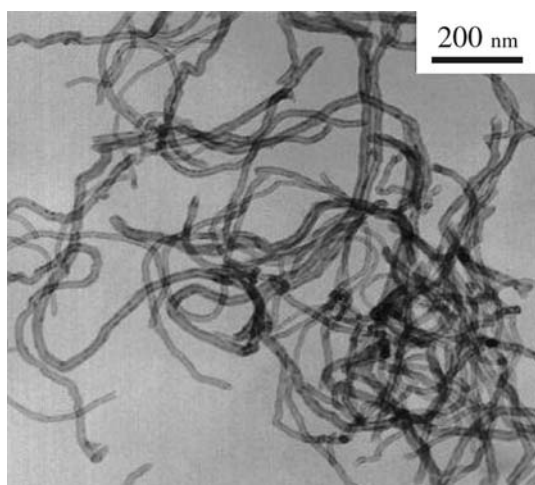
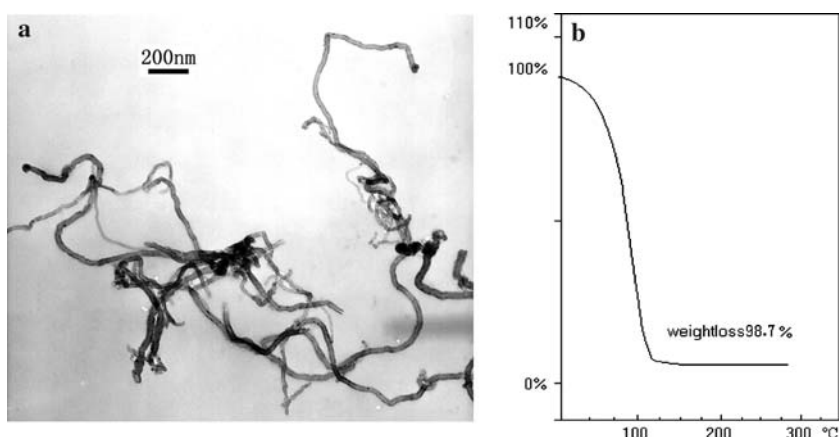


Fig. 1 TEM image of multi walled carbon nanotubes

Fig. 2 (a) TEM image of MWNTs resolved in aniline; (b) Thermogravimetric analysis data of MWNT-aniline solution (conducted in argon, heating rate: 5 °C min⁻¹)



XRD and FTIR investigation

XRD investigation gives the evidence that MWNTs have been dispersed in PANI matrix successfully. The bottom spectrum in Fig. 3 shows the typical XRD pattern for MWNTs. The peaks at 26.22° and 42.53° are assigned to MWNT (002) and (100), respectively [25–30]. In PANI/MWNT spectra, The peaks at 26.22°, labeled as 1, is assigned to MWNT (002). The broad peak at 42.53°, labeled as 2, should be assigned to MWNT (100).

The electrical conductivity of PANI and PANI/MWNT composites was measured by the four-point probe technique. The conductivity for each is 8.743 S cm⁻¹ and 89.276 S cm⁻¹, respectively. An order of magnitude increase of PANI/MWNT over that of pure PANI was measured. It indicates that incorporation of MWNTs into PANI films influence the electric properties of the polymer.

The FTIR spectra of pure PANI and PANI/MWNT composites are presented in Fig. 4. The bands situated 1490 cm⁻¹ and 1580 cm⁻¹ are attributed to benzoid and

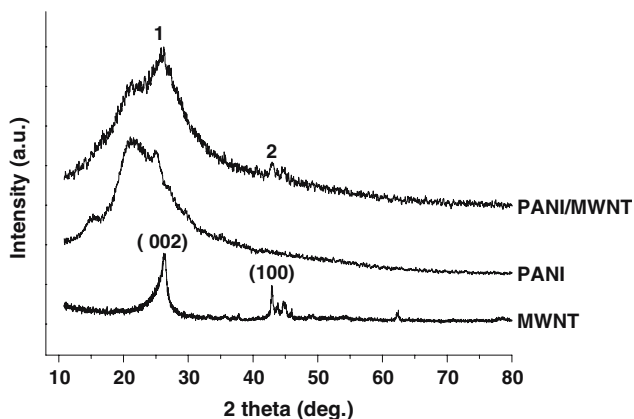


Fig. 3 XRD patterns for MWNTs and PANI/MWNT composite films

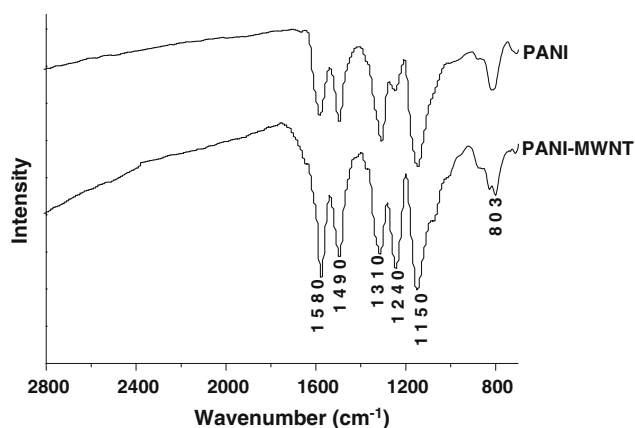
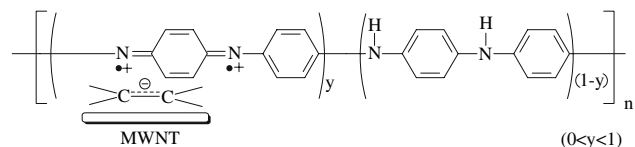


Fig. 4 FTIR spectra for PANI and PANI/MWNT composites

quinoid ring vibrations, respectively [31, 32]. It’s commonly observed for PANI that the quinoid band at 1580 cm⁻¹ is less intense than that of the benzenoid band at 1490 cm⁻¹. As shown in spectrum of PANI/MWNT composites, an inverse 1580/1490 cm⁻¹ intensity ratios was exhibited. These data reveal that PANI in the composite is richer in quinoid units than the pure PANI. This fact may suggest that PANI–MWNTs interactions promote and stabilize the quinoid ring structure. As shown in Scheme 1, the interaction between polyaniline and MWNTs may result in “charge transfer” [33–35]. The π-bonded surface of the carbon nanotubes might interact strongly with the conjugated structure of polyaniline, especially through the quinoid ring [34–37]. Such



Scheme 1 Illustration of the interaction between polyaniline and multi-walled carbon nanotube

selective interaction of the carbon nanotubes with the quinoid ring of PANI has been reported in previous literature [34, 35, 37, 38]. The peak at 1240 cm^{-1} is attributed to C–N stretching + ring deformation + C–H bending vibration mode [31, 35, 39]. Detected as a weak band in the spectrum of pure PANI, its enhancement in PANI/MWNT composites indicates more vibrational units associated to C–N bonds. The new covalent C–N bonds are mainly formed between the imine nitrogen atoms of the repeating units of PANI and the carbon atoms of carbon nanotubes. An appropriate microscopic picture for these composites is that of a carbon nanotube wrapped with the polymer [31, 35, 40].

The strong band at 1150 cm^{-1} is considered to be a measure of the degree of delocalization of electrons and thus it is characteristic peak of PANI conductivity [31, 34]. The increase of the signal at 1150 cm^{-1} is in good agreement with our increased conductivity measurements. It appears that the interaction between PANI and MWNTs increases the effective degree of electron delocalization, and thus enhances the conductivity of the polymer chains.

The other bands at 803 cm^{-1} and 1310 cm^{-1} attributed to C–H out-of-plane bending vibration in paradisubstituted benzene and stretching of aromatic C–N [35].

SEM analysis

The surface morphology of the pure PANI and PANI/MWNT composite films were examined by SEM. From Fig. 5a, the pure PANI films show typical spherical grain morphology. It made the surface rough with no uniformity. The porosity of PANI film has been significantly changed by the introduction of MWNTs. The PANI/MWNT composite films show a considerable quantity of fibers of diameter about 100 nm together with a small quantity of spherical grains. The fibers entangled to form a relatively uniform web and made the film more highly porous. During the growth process, MWNTs are uniformly dispersed in

PANI matrix and may serve as condensation nuclei. Therefore, they were coated with a considerable amount of PANI to form such a fibrous material.

Figure 6 shows the surface morphology of platinum modified PANI and PANI/MWNT composite electrode. The white grains in the micrographs should be attributed to platinum micro-particles. Owing to PANI/MWNT composite material possessing more highly degree of porosity and higher electrical conductivity than PANI, it favors for platinum particles to be highly dispersed on the composite films.

Transmission electron microscope (TEM) technique was used to investigate the structure of PANI/MWNT/Pt composite films deposited on the working substrate electrode. To prepare the samples, the PANI/MWNT/Pt composites were peeled off from working electrode and dispersed in ethanol under ultrasonication. Drops of the suspension were then deposited on a TEM copper grid and the ethanol was evaporated before measurement. The TEM photographs (Fig. 7a) clearly show that Pt particles (black aggregates) distributed on PANI/MWNT composite films. These aggregates generally have a diameter of about 20–40 nm and are composed of fine particles (about 4–6 nm of size). MWNT/PANI composite fibers have been observed in Fig. 7b. It gives more evidence for the presence of MWNTs in the composite films.

Electrocatalytic activity towards methanol oxidation

Figure 8 shows the cyclic voltammogram (CV) of methanol oxidation at Pt modified pure PANI electrode and Pt modified PANI/MWNT electrode in $0.5\text{ M CH}_3\text{OH} + 0.5\text{ M H}_2\text{SO}_4$. It's clearly to be observed that the platinum modified MWNT/PANI electrode performs higher catalytic activity than platinum modified pure PANI electrode.

Figure 9 shows Chronoamperometric curve for methanol oxidation at (a) 0.54 V and (b) 0.64 V at Pt

Fig. 5 SEM images of (a) pure PANI and (b) PANI/MWNT composites

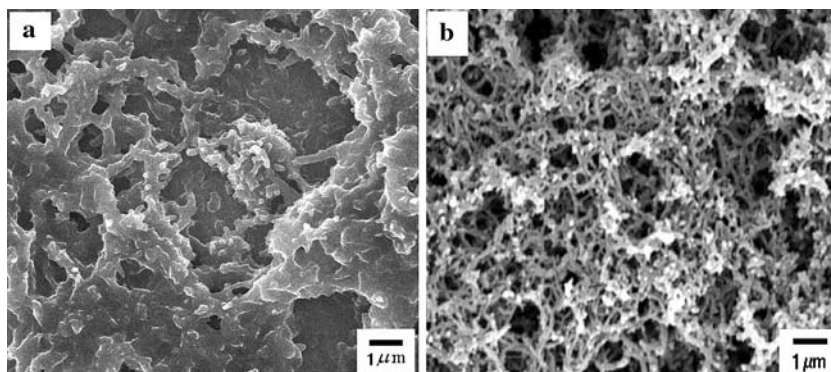


Fig. 6 SEM images of the platinum modified PANI (a) and PANI/MWNT electrode (b)

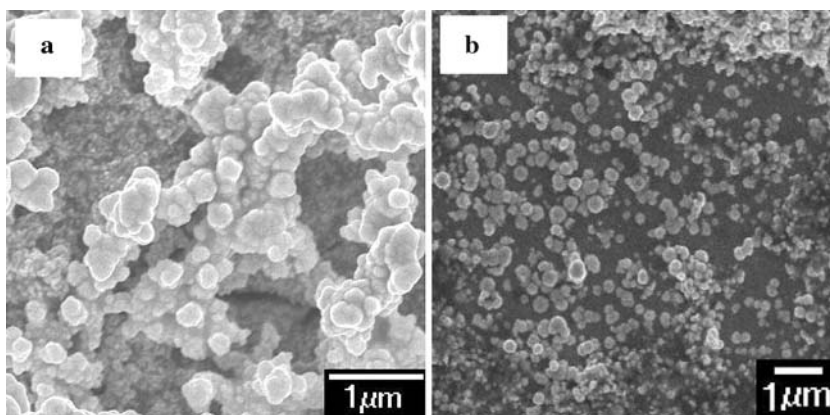
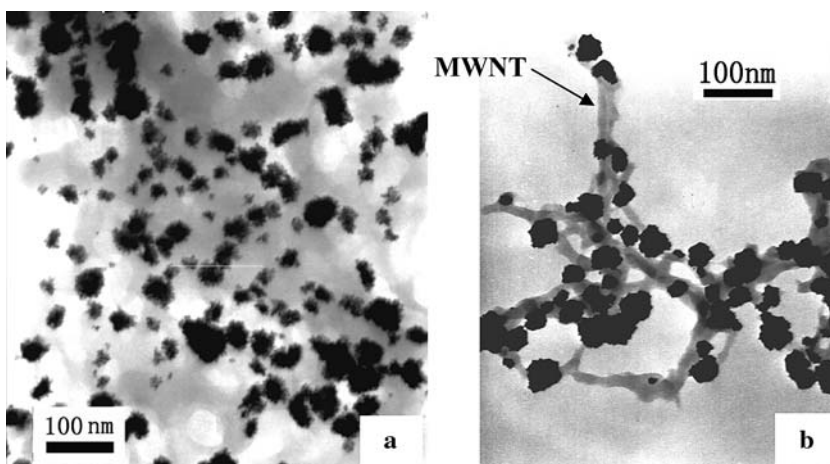


Fig. 7 Typical TEM images of the PANI/MWNT/Pt composite films. (a) Magnified at 120,000 and (b) 80,000



modified pure PANI electrode and Pt modified MWNT/PANI electrode, respectively. After 1200 s electrolysis, the current density on these two electrodes reached to stability state and the current density on Pt

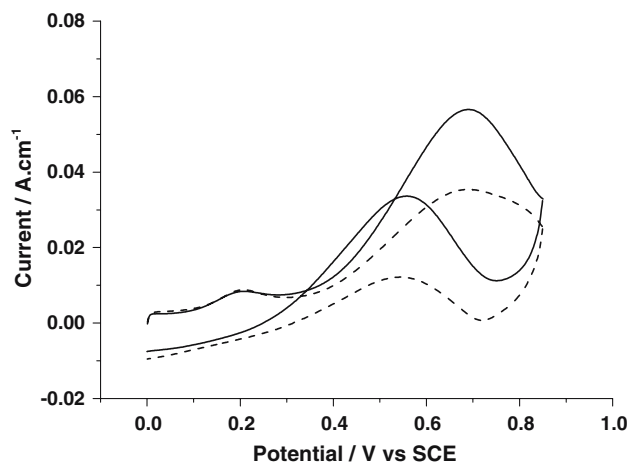


Fig. 8 The cyclic voltammogram of methanol electrooxidation at Pt modified PANI (bottom) and Pt modified PANI/MWNT (top) electrode in 0.5 M CH₃OH + 0.5 M H₂SO₄

modified SWNT/PANI electrode is well above that of Pt modified PANI electrode. Figure 9 gives more evidence to conclude that Pt modified SWNT/PANI electrode exhibits higher catalytic activity toward methanol oxidation.

Comparing the two electrodes, since the substrate electrode is the same one, the thickness of PANI/MWNT and PANI films and the magnitude of platinum loading are the identical too. So the higher electrocatalytic activity of Pt modified PANI/SWNT electrode should be attributed to the MWNTs incorporated into PANI.

Conclusions

We have prepared PANI/MWNT composite films using electropolymerization technique based on that MWNTs can be well dissolved in aniline. The obtained PANI/MWNT composites can be used as porous catalyst supports for direct methanol fuel cell. Cyclic voltammogram and Chronoamperogram results show that

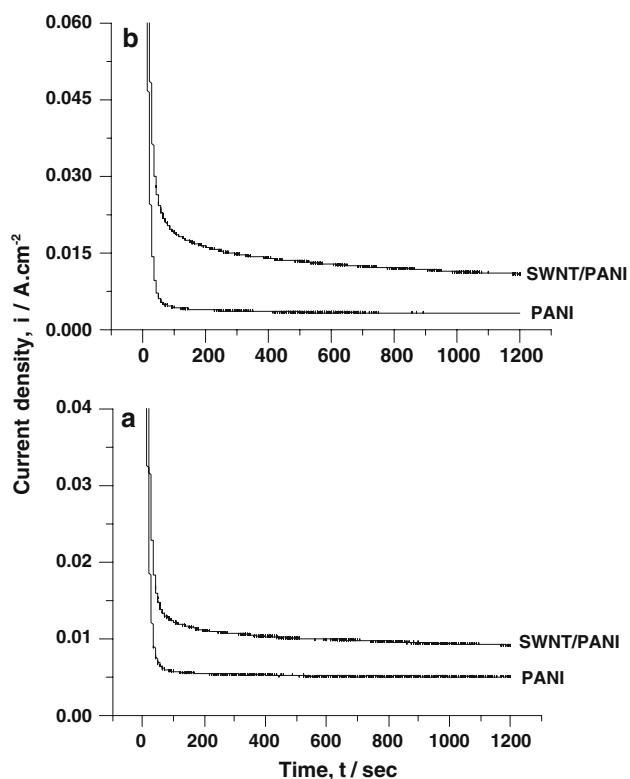


Fig. 9 Chronoamperograms for the electrooxidation of methanol on Pt modified pure polyaniline electrode and Pt modified MWNT/PANI electrode at potential of (a) 0.54V and (b) 0.64 V in 0.5 M CH₃OH + 0.5 M H₂SO₄ (vs SCE)

platinum modified PANI/MWNT electrode exhibits higher catalytic activity on methanol electrooxidation than that of platinum modified PANI electrode. Owing to the introduction of the MWNTs in PANI, the porous structure and electrical conductivity of the polymer have been significantly changed. The increased porosity and the enhanced electrical conductivity of PANI/MWNT composites allow for platinum particles to be highly dispersed and give high surface area for electrooxidation of methanol, which induce the improvement of electrocatalytic activity of platinum modified PANI/MWNT composite electrode. The platinum modified PANI/MWNT composite electrode exhibits a promising application in direct methanol fuel cell.

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