

Incorporation of 4-Aminobenzene Functionalized Multi-Walled Carbon Nanotubes in Polyaniline for Application in Formic Acid Electrooxidation

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ABSTRACT: Incorporation of carbon nanotubes (CNTs) in conducting polymer can lead to new composites with enhanced electrical and mechanical properties. However, the development of such composites has been hampered by the inability to disperse CNTs in polymer matrix due to the lack of chemical compatibility between polymers and CNTs. Covalent sidewall functionalization of carbon nanotube provides a feasible route to incorporate carbon nanotube in polymer. In this work, 4-aminobenzene groups were grafted onto the surface of multi-walled carbon nanotube (MWNT) via C–C covalent bond. Polyaniline (PANI)/MWNT composites were fabricated by electrochemical polymerization

of aniline containing well-dissolved functionalized MWNTs. The obtained composites can be used as catalyst supports for electrooxidation of formic acid. Cyclic voltammogram results show that platinum particles deposited in PANI/MWNT composite films exhibit higher electrocatalytic activity and better long-term stability towards formic acid oxidation than that deposited in pure PANI films. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1815–1820, 2010

Key words: multi-walled carbon nanotubes; polyaniline; formic acid; electrooxidation; cyclic voltammogram; fuel cell

INTRODUCTION

Direct formic acid fuel cells (DFAFC) have been widely investigated in recent years because that DFAFC are generally considered as attractive portable power devices.^{1,2} Formic acid electrooxidation catalyst is crucial for the development of DFAFC.³ Platinum is recognized as the most active metal for formic acid electrooxidation.^{4,5} Owing to platinum is too expensive for practical application, it is necessary to decrease platinum loading as far as possible.⁶ Catalyst support plays a very important role in determining catalyst particle size, dispersion degree, catalytic performance, cost reduction, and stability.⁷ Therefore, in recent years, considerable efforts have

been devoted to investigate novel catalyst supports for formic acid electrooxidation.⁸ Due to the attractive features of high accessible surface area, low resistance, high stability, and low cost, conducting polymers are commonly used as a matrix to incorporate precious metal catalyst for small organic molecules electrooxidation.⁸ Among the various conducting polymers, polyaniline has become the most attractive one because of its facile preparation, high conductivity, and good environmental stability.⁹ Many literature surveys indicate that platinum micro-particles dispersed in polyaniline matrix exhibit high activity toward formic acid electrooxidation.⁸

Carbon nanotubes (CNTs) are unique nanostructured materials with remarkable physical and mechanical properties.¹⁰ These properties have inspired interest in using CNTs as the nano-fillers in polymer composite systems to obtain composite structural materials with enhanced electrical and mechanical characteristics.^{11,12} However, because CNTs are relatively inert, the development of such composites has been hampered by the inability to incorporate CNTs in the polymer matrix due to the lack of chemical compatibility between the polymers and CNTs. Covalent sidewall functionalization of CNTs provides an excellent route to incorporated carbon nanotube in polymer.^{13,14} In this work, Multi-walled carbon nanotubes (MWNTs) were functionalized with 4-aminobenzene groups in liquid ammonia.

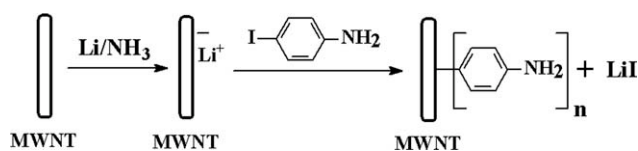
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Scheme 1 Chemical modification of MWNTs with 4-aminobenzene group.

PANI/MWNTs composite films were fabricated by electropolymerization of aniline containing well-dissolved functionalized MWNTs. Platinum particles were electrodeposited in the PANI/MWNT composite matrix subsequently. The purpose of the present work is to study the electrocatalytic oxidation efficiency of formic acid at Pt-modified MWNT/PANI composite electrode. To our knowledge, little work has been done to fabricate PANI/MWNT composites via incorporation of MWNTs in PANI matrix by chemical modification of MWNTs with 4-aminobenzene.

EXPERIMENTAL SECTIONS

Chemicals

MWNTs were purchased from Shenzhen Nanotech Port Company (China). The average diameter of MWNTs was about 5–15 nm and the length 5–20 μm . All of the reagents were of analytical grade and were used as received. All the solutions were prepared with twice distilled water.

Chemical modification of MWNTs with 4-aminobenzene groups

Scheme 1 illustrates the reaction of covalent modification of MWNT with p-iodoaniline.¹³ The covalent side wall modification reactions of MWNT were carried out by adding the MWNTs (40 mg) under the atmosphere of argon to a dry 100 mL, three-neck, round-bottomed flask fitted with a dry ice condenser. Ammonia (60 mL) was then condensed into the flask followed by the addition of lithium metal (0.12 g). The p-iodoaniline (6.4 mol) was then added and the mixture was stirred at -33°C for 12 h with the slow evaporation of ammonia. The reaction mixture was quenched by slow addition of ethanol followed by water. The mixture was acidified (10% HCl), filtered through a 0.2 μm PTFE membrane, and washed successively with water and ethanol. The functionalized MWNTs were dried overnight in vacuum at 80°C .

Preparation of MWNTs-aniline solutions

Aniline was purified by distillation under reduced pressure. Functionalized MWNTs (20 mg) were

added to 5 mL aniline under sonication. The mixture was heated at reflux for 3 h in the dark. After has been cooled to room temperature and settled for 24 h, a small quantity of unresolved MWNTs was precipitated from MWNT-aniline solution.

Electrochemical experiments

Electrochemical experiments were performed on CHI760C electrochemical working-station in a three electrodes system and controlled by CHI instrument electrochemical software. A gold sheet (geometric surface area = 1 cm^2) was used as substrate-working electrode. Another gold sheet and a saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. The two gold sheets were polished mechanically using emery paper (grade 1200) to a mirror surface and then cleaned by potential cycling between 0 V and 1.5 V at 50 mVs^{-1} in 0.1 M H_2SO_4 (vs SCE) until a stable cyclic voltammogram was obtained.

The PANI/MWNT composite films were electrodeposited on the gold substrate-working electrode by using the cyclic voltammetry (CV) technique in the potential range -0.2 to $+0.9\text{ V}$ at scan rate of 50 mVs^{-1} at 20°C , in 0.5 M H_2SO_4 + 0.1 M aniline containing well dissolved 4-aminobenzene functionalized MWNTs. The thickness of the composite films, varied by changing the number of potential cycles and was calculated by the height of the first peak in the redox process, reaches to 0.86 μm .^{15,16} Platinum particles were deposited on the presynthesized PANI/MWNT composite films in 0.5 M H_2SO_4 solutions containing 1.5 mM K_2PtCl_6 at constant potential of -0.1 V .¹⁷ Prior to the dispersion of the platinum, PANI/MWNT coated electrode was soaked in 1.5 mM PtCl_6^{2-} + 0.5 M H_2SO_4 solutions 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 $\mu\text{g}/\text{cm}^2$.^{16,18}

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

Characterization

X-ray diffraction (XRD) data of the samples were collected using a Rigaku D/MAX 24,000 diffractometer with Cu- K_α radiation. SEM studies were performed using a XL 30 ESEM instrument. FTIR spectra were collected using a Nicolet Nexus 670 Fourier transform infrared spectrometer. The morphology of Pt/PANI/MWNT composites was characterized by

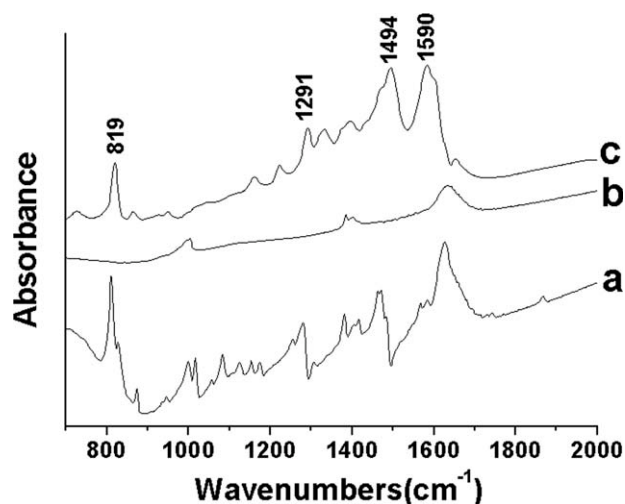


Figure 1 FTIR spectrum of (a) p-iodoaniline, (b) pristine MWNTs, and (c) MWNTs functionalized with 4-aminobenzene.

transmission electron microscopy (TEM Hitachi H7000).

RESULTS AND DISCUSSION

FTIR analysis

Figure 1 shows the FTIR spectra for the MWNTs functionalized with 4-aminobenzene groups (top curve). By comparing with infrared spectra of p-iodoaniline (bottom), and pristine MWNTs (middle), the peaks centered at 1590 cm^{-1} are due to C—C stretching vibration of the benzene rings that attached to the framework of individual MWNT. The peaks centered at 1494 cm^{-1} are related to the mixed C—C stretching and C—H bending vibration of benzene rings. The peak at 1291 cm^{-1} is

attributed to stretching vibration of aromatic C—N. The peak centered at 819 cm^{-1} is the well-known C—H out-of-plane bending vibration in para-substituted benzene. All mentioned peaks suggest that 4-aminobenzene groups have been covalently grafted onto the surface of MWNTs, successfully.

Thermogravimetric investigation

Figure 2(a) shows the typical TEM image of the MWNT-aniline solutions. It gives direct evidence that functionalized MWNTs have been resolved in aniline successfully. Thermogravimetric analysis (TGA) has been used to investigate the concentration of MWNTs in aniline. As shown in Figure 2(b), the sudden weight loss occurs at temperature range of $60\text{--}135^\circ\text{C}$ correspond to solvent evaporation, and the residues remained is MWNTs. A total weight loss of 96.9% was recorded and the solubility of MWNTs in aniline can be calculated up to 3.1 wt %. The phenylated nanotubes exhibit high solubility or dispersability in aniline.

XRD analysis

Figure 3 shows XRD patterns for MWNTs, pure PANI, and MWNT/PANI composites. The bottom spectrum shows the typical XRD pattern for MWNTs. The peaks at 26.22° and 42.53° are assigned to MWNT (002) and (100), respectively. In PANI/MWNT spectra, The peak 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).^{19,20} XRD investigation gives the evidence that MWNTs have been incorporated in PANI matrix successfully.

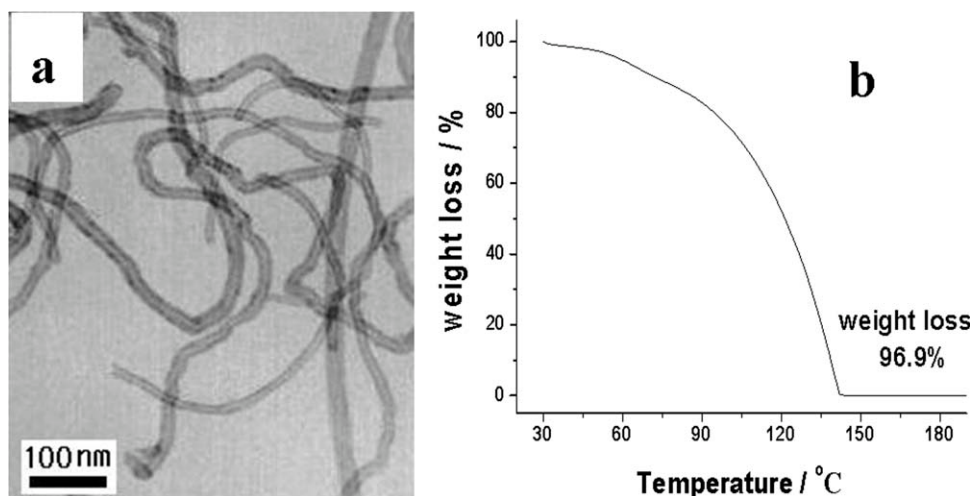


Figure 2 (a) TEM image of MWNTs-aniline solution and (b) thermogravimetric analysis data of MWNT-aniline solution (conducted in argon, heating rate: 5°C min^{-1}).

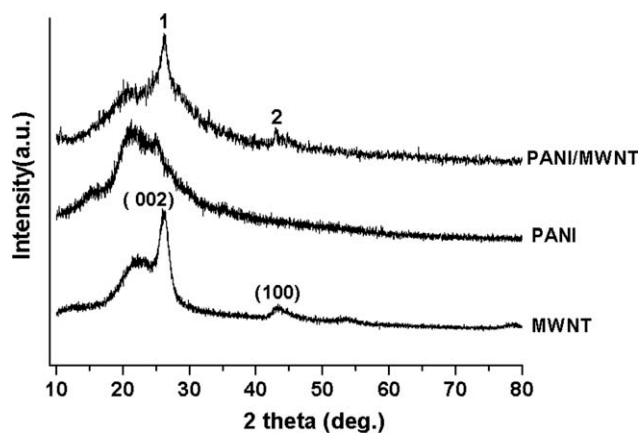


Figure 3 XRD patterns for MWNTs, pure PANI, and PANI/MWNT composites.

Four-point probe investigation

Electrical conductivities of pure PANI and PANI/MWNT composites were measured according to the standard four-point probe technique. The conductivity for each one was calculated to be 8.043 S cm^{-1} and 91.276 S cm^{-1} , respectively. The room-temperature conductivity of the composites is increased by 11 times in comparison to pure PANI. This enhanced conductivity is perhaps due to the dopant effect or charge transfer from polyaniline to CNTs. MWNTs serve as “conducting bridge” connecting PANI conducting domains. The enhanced conductivity of MWNT/PANI composites may be due to the strong interaction between functionalized MWNTs and PANI, which facilitates the effective degree of electron delocalization on polymer chains in MWNT/PANI composites and therefore facilitate the charge transfer between PANI and MWNT.

SEM characteristics

The surface morphology of the pure PANI and PANI/MWNT composite films were examined by

SEM. From Figure 4(a), the pure PANI films show typical spherical grain morphology. It made the surface rough with no uniformity. As shown in Figure 4(b), the porosity of PANI film has been significantly changed by the introduction of MWNTs in PANI. The PANI/MWNT composite film shows a considerable quantity of fibers of diameter about 100 nm. The fibers entangled to form a relatively uniform web and made the film more highly porous. Such a porous structure is desirable because it enables the polymer with high penetrability. 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 5 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 high degree of porosity and higher electrical conductivity than PANI, it favors for platinum particles to be highly dispersed in composite. Therefore, it can be observed that Pt particles have been highly dispersed in PANI/MWNT composites.

TEM observation

Transmission electron microscope (TEM) technique was used to investigate the morphology of Pt/PANI and Pt/PANI/MWNT composite deposited on the working substrate electrode. To prepare sample, Pt/PANI and Pt/PANI/MWNT composites were peeled off from working electrode and dispersed in ethanol under ultrasonication. A drop of the suspension was deposited on a TEM copper grid. After ethanol was evaporated, the sample can be observed on TEM instrument.

Figure 6(a) shows the TEM image of Pt/PANI composites. Platinum exists in the form of very fine microparticles which aggregate in groups three-

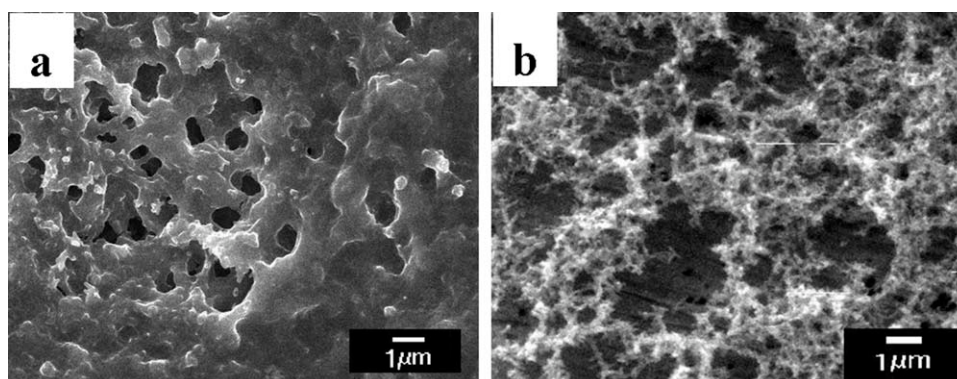


Figure 4 SEM images of (a) pure PANI and (b) PANI/MWNT composites.

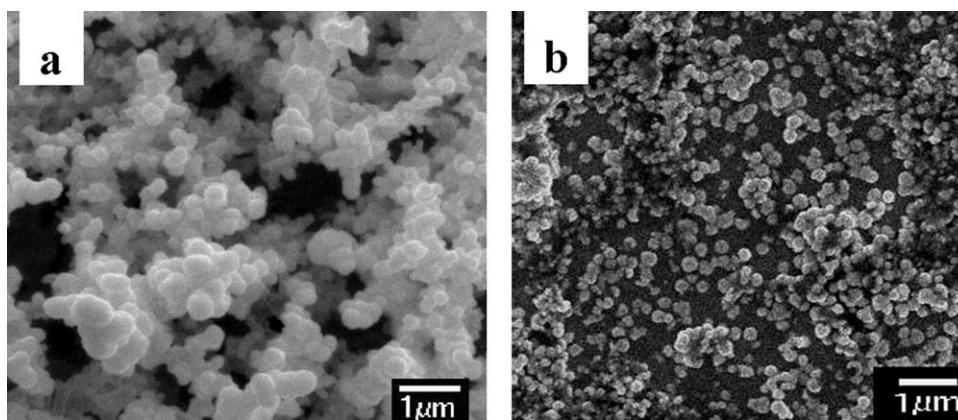


Figure 5 SEM images of platinum modified (a) PANI and (b) PANI/MWNT electrode.

dimensionally and are almost homogeneously dispersed over the polyaniline matrix.^{21,22} Figure 6(b) shows the TEM image of Pt/PANI/MWNTs composites. Abundant fiber-like PANI/MWNTs composites can be observed. Such fibrous structure is desirable because it facilitates the diffusion of formic acid in solution to the reaction zone, where the electrocatalytic conversion occurs. Pt aggregates are highly distributed on the surface of fibrous PANI/MWNT composites and generally have a diameter of 10–30 nm. It is worth noting that closer inspection reveals these platinum aggregates comprise of 4–6 nm diameter particles.

Figure 7 shows the cyclic voltammogram (CV) of formic acid oxidation at Pt-modified pure PANI electrode and Pt-modified PANI/MWNT composite electrode in 0.5 M CHOOH + 0.5 M H₂SO₄ solution, at scan rate 50 mV s⁻¹ and in the potential range -0.2V to 1.0V. As shown in Figure 4, during the positive scan, the peak at 0.21 V is attributed to oxidation of weakly bounded species and the one at 0.73 V to oxidation of the strongly chemisorbed species. During the negative scan, the peak at 0.49 V is

attributed to direct oxidation of formic acid to form CO₂ without forming carbon monoxide intermediate.^{4,23} It is clearly to be observed that the platinum modified PANI/MWNT electrode exhibits higher catalytic activity than platinum modified pure PANI electrode.

The long-term stability of the Pt-modified PANI/MWNT composite electrode and the Pt-modified PANI film electrode was also investigated in 0.5 M HCOOH + 0.5 M H₂SO₄ solutions. The results are shown in Figure 8. Comparing the two curves, Pt/PANI/MWNT composite films exhibit better long-term stability in acidic solution. It can be observed that the peak current of Pt/PANI electrode and Pt-modified PANI/MWNT composite electrode decrease gradually with the successive scans. The loss of catalytic activity may be resulted from the consumption of formic acid during the CV scan. It also may be due to poisoning and the structure change of the platinum nanoparticles during the scanning in aqueous solutions, especially in presence of the organic compound.²⁴ After the long-term CV experiments, the Pt/MWNT/PANI composite

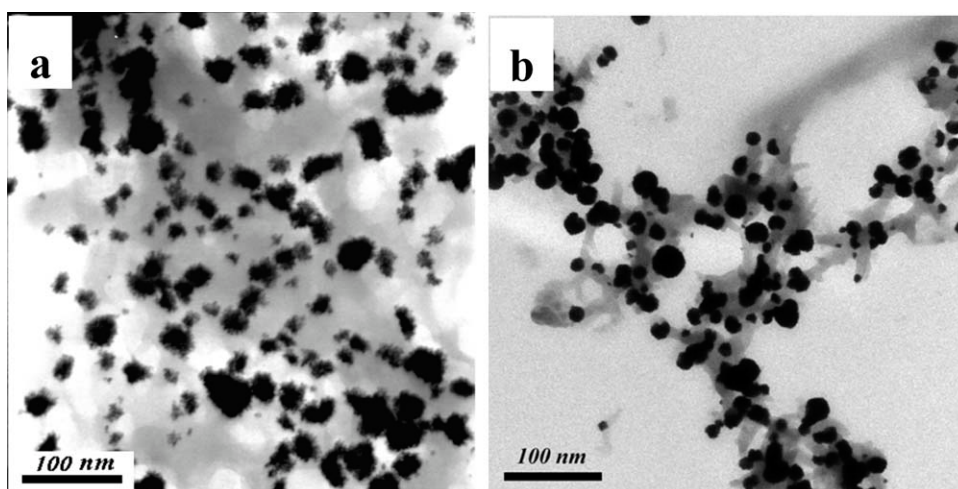


Figure 6 Typical TEM images of (a) Pt/PANI and (b) Pt/PANI/MWNT composites.

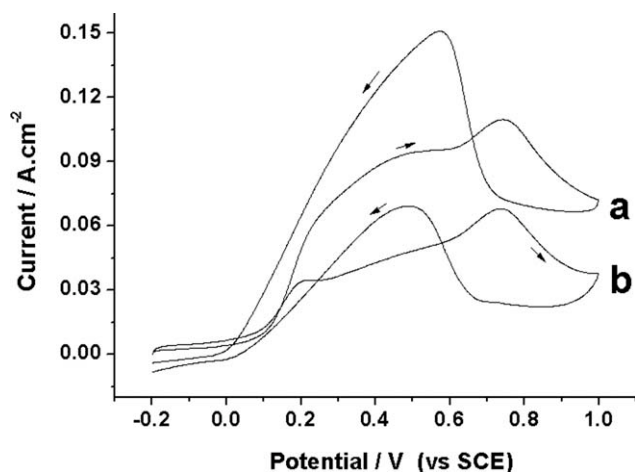


Figure 7 Cyclic voltammogram of formic acid electrooxidation at (a) Pt-modified PANI electrode and (b) Pt-modified PANI/MWNT electrode in 0.5 M HCOOH + 0.5 M H₂SO₄ (Vs SCE).

electrode were stored in water for a week, then formic acid oxidation was carried out again by CV, and excellent catalytic activity towards formic acid oxidation was still observed.

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

CONCLUSIONS

MWNTs were covalently functionalized with 4-aminobenzene groups and the resulting phenylated MWNTs exhibit high solubility or dispersability in aniline. PANI/MWNTs composites were fabricated by electrochemical polymerization of aniline contain-

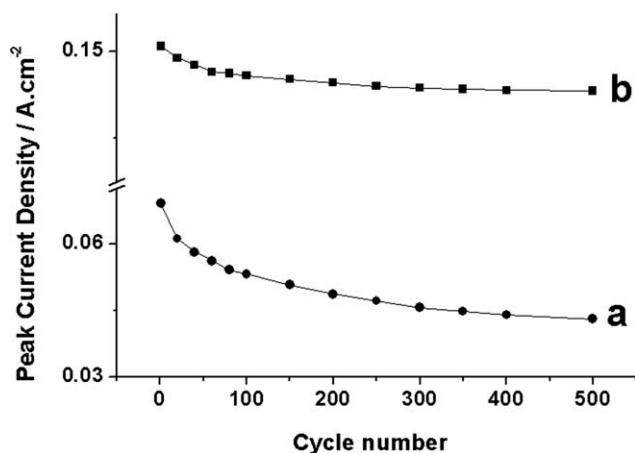


Figure 8 Long-term stability of (a) Pt-modified PANI electrode and (b) Pt-modified PANI/MWNT electrode in 0.5 M HCOOH + 0.5 M H₂SO₄ (scan rate: 50 mVs⁻¹, Vs SCE).

ing well-dissolved functionalized MWNTs. The obtained composites can be used as porous catalyst supports for formic acid electro oxidation. Cyclic voltammogram results show that platinum modified PANI/MWNT electrode exhibits higher catalytic activity and better long-term stability for formic acid electrooxidation than platinum modified pure PANI electrode. Owing to introduction of MWNTs in PANI matrix, the porous structure and electrical conductivity of PANI has been significantly changed. The increased porosity and the enhanced electrical conductivity of PANI/MWNT composites favor for platinum particles to be highly dispersed in PANI/MWNT composites. Highly dispersed Pt nano-particles inside PANI/MWNT support leads to better Pt utilization and an improvement of catalytic activity for formic acid electrooxidation. The method described in this work is a simple and efficient process to incorporate MWNTs in polyaniline and could be of considerable importance in several applications.

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