A highly porous NiO/polyaniline composite film prepared by combining chemical bath deposition and electro-polymerization and its electrochromic performance

To cite this article: X H Xia et al 2008 Nanotechnology 19 465701

View the article online for updates and enhancements.

You may also like

- Flexible ammonia sensor integrated with polyaniline/zinc oxide/graphene composite membrane materials Chao-Yuan Ting, Ping-Lun Wu, Cheng-Chun Huang et al.
- Fabrication and Characterization of Graphene Oxide/Polyaniline Electrode Composite for High Performance Supercapacitors Yaoyao Wang, Yanxiang Wang, Yu Tian et al.
- <u>Understanding the interaction in</u> <u>functionalized multi-walled carbon</u> <u>nanotube/polyaniline composite by</u> <u>impedance study at low temperature</u> Krishna Prasad Maity, Ananya Patra and V Prasad





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 18.118.99.7 on 10/05/2024 at 13:39

Nanotechnology 19 (2008) 465701 (7pp)

A highly porous NiO/polyaniline composite film prepared by combining chemical bath deposition and electro-polymerization and its electrochromic performance

X H Xia¹, J P Tu¹, J Zhang¹, X L Wang¹, W K Zhang² and H Huang²

 ¹ Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China
 ² College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310032, People's Republic of China

E-mail: tujp@zju.edu.cn

Received 28 August 2008, in final form 19 September 2008 Published 22 October 2008 Online at stacks.iop.org/Nano/19/465701

Abstract

A highly porous NiO/polyaniline (PANI) composite film was prepared on ITO glass by combining the chemical bath deposition and electro-polymerization methods, successively. The porous NiO film acts as a template for the preferential growth of PANI along NiO flakes, and the NiO/PANI composite film has an intercrossing net-like morphology. The electrochromic performance of the NiO/PANI composite film was investigated in 1 M LiClO₄ + 1 mM HClO₄/propylene carbonate (PC) by means of transmittance, cyclic voltammetry (CV) and chronoamperometry (CA) measurements. The NiO/PANI thin film exhibits a noticeable electrochromism with reversible color changes from transparent yellow to purple and presents quite good transmittance modulation with a variation of transmittance up to 56% at 550 nm. The porous NiO/polyaniline (PANI) composite film also shows good reaction kinetics with fast switching speed, and the response time for oxidation and reduction is 90 and 110 ms, respectively.

1. Introduction

Electrochromic materials present a reversible change in optical properties when they are electrochemically oxidized or reduced [1]. These materials include transition oxides, inorganic coordination complexes, organic molecules, conducting conjugated polymers and so on [2]. Early studies of electrochromism mainly focus on inorganic and small-molecule organic electrochromes, which suffer from processing, compatibility and performance problems. More recently, electrochromic research has heavily focused on electrochromic conducting polymer films because of their high color contrast, multiple color possibilities, rapid response times and ease of processing [3–5]. A primary advantage that conducting

polymers hold over inorganic electrochromic materials is their fast electrochromic response, which is controlled by the diffusion of counter-ions into the electrochromic materials [5]. The ion-intercalation reaction is limited both by the diffusion coefficient and by the length of the diffusion path. The former depends on the molecular structure of the material, while the latter is determined by the microstructure of the material [6]. A molecular-level approach to improve response time is the rational design and synthesis of novel electrochromic polymers with fast electrochromic response [7]. Meanwhile, an alternative approach is to fabricate films with a highly porous structure, which can provide a very short diffusion pathway for the counter-ions as well as a large active surface. Some porous electrochromic films have been successfully prepared and exhibited improved electrochromic performance. For example, poly(3,4-ethylenedioxythiophene) (PEDOT) nanotubes were electrochemically synthesized on an ITO substrate in the AAO nanopores [8], which exhibited fast color changes with 50 and 70 ms response times for oxidation and reduction, respectively. Therefore, constructing a porous structure is an effective way to improve response time.

Polyaniline (PANI), a unique conjugated polymer, has been extensively studied as a promising polyelectrochromic material exhibiting three main stable oxidation states: the fully reduced leucoemeraldine (LE) form (transparent yellow), the 50% oxidized emeraldine salt (ES) form (green) and the fully oxidized pernigraniline form (purple) [9]. The PANI can be prepared by a chemical or an electrochemical oxidative polymerization, in which the electro-polymerization is believed to be the most simple and convenient method for preparation of the PANI film [10]. Nevertheless, the adherence of the PAN film on ITO glass is very weak and it can be easily rinsed out from the substrate. A lot of work has been devoted to improving the mechanical strength and flexibility of a PANI film on ITO glass. Several insulated polymers such as PVA and poly(4-styrenesulfonate) were selected to act as a template for electro-deposition of PANI films [11, 12]. The adherence was found to have dramatically improved. Nonetheless, these template materials are insulated polymers, which always decrease the response speed. To overcome this shortcoming, a porous conducting film will be a good candidate for the supporting matrix. It can act as a solid support without sacrificing response time due to the porous structure, which can provide good pathways for electron transfer and ion diffusion at the same time.

Template synthesis is one of the most commonly used methods to fabricate highly porous structures. A variety of porous conducting polymers including PANI, PEDOT and polypyrrole have been synthesized using porous AAO and track-etched polycarbonate membranes [8, 13–15]. The object materials could be deposited into nanosized template pores to form nanotubes or nanowires. However, to date, there are few reports on the electrochromic performance of porous PANI films. Recently, we have pioneered the electrochromics of highly porous NiO with pore diameters ranging from 50 to 250 nm [16]. The porous NiO film has high transparency and electrochromic performance, which is important for electrochromic devices. These results provide the impetus for the application of the highly porous NiO as a template to synthesize porous materials. Up to now, there are only a few reports on the synthesis of NiO/PANI composites. NiO/PANI nanobelt and NiO/PANI rectangular tube powders have been successfully synthesized via chemical polymerization by the Additionally, Peng et al [19] group of Guo [17, 18]. reported that a NiO_x /PANI composite film, used as a catalyst towards electro-oxidation of polyhydroxyl compounds, could be prepared by electro-deposition in a neutral aqueous solution. Actually, the composite film prepared by Peng et al [19] is Ni(OH)₂/PANI, not NiO/PANI. In a recent study, our group reported a porous NiO/PANI composite on a foam nickel substrate for Li-ion anode material, but the possible formation mechanism was not discussed [20]. Combining the

electrochromic capabilities of PANI and highly porous NiO in a composite film is an attractive goal and has not been explored. In this present work, the highly porous NiO film was used as a template to prepare highly porous net-like NiO/PANI composite films on an ITO substrate by combining chemical bath deposition and electro-polymerization, successively. The microstructure, formation mechanism and electrochromic performances of this porous NiO/PANI composite film were also investigated.

2. Experimental details

2.1. Chemical materials

All chemical reagents were AnalaR (AR) grade. Nickel sulfate (NiSO₄·6H₂O), aqueous ammonia (25–28%), potassium persulfate (K₂S₂O₈), perchloric acid (HClO₄), lithium perchlorate (LiClO₄) and propylene carbonate (99.9%) were obtained from Shanghai Chemical Reagent Co. All aqueous solutions were freshly prepared using high purity water (18 M Ω cm resistance).

2.2. Preparation of highly porous NiO film

The synthesis routes for highly porous NiO films have already been described in detail in our previous work [16] and thus will only be briefly described here. Clean ITO glass substrates $2.5 \times 2.5 \text{ cm}^2$ in size were placed vertically in the freshly deposition solution containing 80 ml of 1 M nickel sulfate, 60 ml of 0.25 M potassium persulfate and 20 ml of aqueous ammonia (25–28%). After stirring for 20 min, the substrate was removed from the solution and washed with distilled water. Finally, the as-prepared sample was annealed at 300 °C for 1.5 h. The thickness of the NiO film was approximately 480 nm, determined with Alpha-step 200 profilometry.

2.3. Preparation of highly porous NiO/PANI composite film

Aniline was distilled under reduced pressure and stored in the sealed state at 4 °C. The electrolyte for the electropolymerization of PANI was obtained by dissolving 1 ml aniline in 100 ml of 0.01 M H₂SO₄ solution. The electro-polymerization of PANI was carried out in a threecompartment system, with the above porous NiO thin film electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a Pt foil as the counter-electrode. The PANI film was deposited by cyclic voltammetry as follows: the first cycle was conducted in the potential range of -0.2-1.3 V with a sweep rate of 50 mV s⁻¹. The subsequent 10 cycles were carried out in the potential range of -0.2-1.0 V with a sweep rate of 50 mV s⁻¹. Calculated from the weight increment, the content of PANI in the composite film was 20 wt%.

2.4. Characterization

The morphology and microstructure of samples were characterized by a field emission scanning electron microscope (FESEM, Hitachi S-4700), a transmission electron microscope



Figure 1. Cyclic voltammetric curves of electro-polymerization of PANI on the NiO film.

(TEM, JEM-2010), x-ray diffraction (XRD, Philips PC-APD with Cu K α radiation) and Fourier-transform infrared (FTIR) measurements (Perkin-Elmer System 2000 FTIR interferometer). The cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) measurements of the NiO/PANI film were carried out in a three-compartment system containing 1 M LiClO₄ + 1 mM HClO₄/propylene carbonate (PC) as the electrolyte, a saturated calomel electrode (SCE) as the reference electrode and a Pt foil as the counter-electrode on a CHI760B Electrochemical Workstation (Chenhua, Shanghai). The CV measurements were carried out in the potential range of -0.2-1.0 V with a scanning rate of 50 mV s⁻¹ at room temperature (25 ± 1 °C). The film electrodes, $0.5 \times 1.0 \text{ cm}^2$ in size, were used for electrochemical impedance spectroscopy (EIS) measurements, which were made with a superimposed 5 mV sinusoidal voltage in the frequency range of 100 kHz-0.01 Hz. The transmission spectra of NiO/PANI films in different redox states were measured over the range from 200 to 900 nm with a Shimadzu UV-240 spectrophotometer. Each spectrum was recorded ex situ (after the samples were taken out of the three-compartment system, instantly rinsed and wiped to remove the remaining persistent solution). N2 adsorption was determined by BET (Brunauer-Emmett-Teller) measurements using a NOVA-1000e surface area analyzer.

3. Results and discussion

3.1. Electro-deposition and structure characterization

Figure 1 shows the cyclic voltammograms (CVs) of electrodeposition of PANI films on the porous NiO film. The CVs exhibits three pairs of redox peaks, which are similar to those reported by other authors [21, 22]. The increasing current with each cycle reflects the growth of the polymer film. The first redox couple A_1/C_1 is ascribed to the oxidation of leucoemeraldine to emeraldine salt [23]. The second redox couple A_2/C_2 is due to the degradation of radicals to benzoquinone during polymerization and has been assigned to the branched structure of PANI [24, 25]. The third redox couple A_3/C_3 corresponds to the conversion from emeraldine



Figure 2. XRD patterns of (a) NiO film and (b) NiO/PANI composite film on ITO glass.



Figure 3. FTIR spectra of powders from (a) NiO film and (b) NiO/PANI composite film.

base to pernigraniline structure. The A_4 peak is attributed to the nucleation of aniline, which is similar to the previous report [26]. The XRD patterns of NiO and NiO/PANI composite films on ITO substrates are presented in figure 2. The diffraction peaks of both samples can be indexed as cubic NiO phase (JCPDS 4-0835). No obvious diffraction peaks of PANI are observed, indicating the amorphous nature of PANI deposited by the CVs.

Figure 3 shows the FTIR absorption spectra of powders from the films on ITO substrates. For the NiO film, a strong band centered at 418 cm^{-1} [27] corresponding to the stretching vibration of NiO is presented in spectrum a. A broad OH band centered at 3420 cm⁻¹ is indicative of hydrogen-bonded water within the film structure. The bands in the spectral region of 900–1150 cm⁻¹ belong to sulfate groups (SO_4^{2-}) [28]. The band at 587 cm⁻¹ corresponds to δ (OH). For the NiO/PANI film, a broad band at 3180-3480 cm⁻¹ is observed, which is assigned to the stretching vibration NH of an aromatic amine as well as the stretching vibration of absorbed water. The bands centered at 1578 and 1487 cm^{-1} are due to the C=C stretching vibrations of a quinoid (Q) ring and benzenoid ring, respectively [29]. The band centered at 1306 cm^{-1} is assigned to the C-N stretching band of an aromatic amine. The characteristic band of the PANI base is the N=Q=N stretching



Figure 4. SEM and TEM micrographs of (a), (b) NiO film and (c), (d) NiO/PANI composite film.

band at 1130 cm^{-1} and a 820 cm^{-1} band to an aromatic CH out-of-plane bending [30]. The band at 587 cm⁻¹ corresponds to the bending vibration of OH. A strong band characteristic of NiO at 418 cm⁻¹ is also observed. Therefore, both FTIR and XRD results are in complete agreement and show an effective formation of the NiO/PANI film.

The SEM and TEM images of NiO and NiO/PANI composite films are shown in figure 4. The NiO film has a structure with huge porosity. The diameters of the pores range from 50 to 250 nm. The interconnecting network is made up of flaky nickel oxides with thicknesses of 30–50 nm, which



Figure 5. BET measurements of (a) NiO film and (b) NiO/PANI composite film.

is similar to that reported by Wu et al [31]. The NiO/PANI composite film maintains the highly porous net-like structure, but the thickness of the flakes becomes thicker, ranging from 70 to 90 nm. In addition, the diameter of pores of the NiO/PANI film is much smaller than that of the NiO film, ranging from 25 to 110 nm. BET measurements (figure 5) show that the surface area of porous NiO and NiO/PANI films is 350 and 485 m² g⁻¹, respectively. The pore size distributions of both films show peaks at 150 and 70 nm, respectively. The porous NiO template has a porosity of about 86%. After electro-polymerization, the porosity of the NiO/PANI film decreases but is still high up to 60%. From the TEM images of flakes of NiO and NiO/PANI composite films, it is noticed that these two flakes have distinct surface morphology. The flake before electro-polymerization is thin and flat with low roughness, while the flake after electropolymerization is much thicker with a very rough appearance. It is inferred that the NiO flake is enwrapped by the PANI, which means that the composite flake is composed of two parts: the inner layer is NiO and the outer layer is PANI. Based on the above results, a plausible formation mechanism of an NiO/PANI composite film could be described as follows: the porous NiO film acts as a template for PANI growth during the electro-polymerization, leading to the preferential growth of PANI along NiO flakes. The electro-polymerization of



Figure 6. Schematic diagram of fabricating porous NiO/PANI composite films on an ITO substrate.

PANI first occurs along the NiO flakes and protects them from dissolving in an acid solution. The schematic for the synthesis of porous NiO/PANI composite films on ITO glass is illustrated in figure 6. The reason that the PANI preferentially nucleates and grows along NiO flakes may be due to the solvophobic and electrostatic interactions [14, 15]. On the one hand, the aniline is soluble, but the PANI is completely insoluble. Hence, there is a solvophobic component to the interaction between the PANI and the NiO flake. On the other hand, there is also an electrostatic component to the interaction between the PANI and the NiO flake. This is because the PANI is cathodic, and there are anionic sites on the NiO flakes. As a result, the two factors contribute to the PANI preferentially nucleating and growing along NiO flakes and the formation of porous NiO/PANI films.

3.2. Electrochromic and electrochemical properties

The electrochromism of PANI is closely related to its unique redox doping/dedoping processes, which can be easily controlled by applying electrical potentials. The transmittance spectra of the NiO/PANI composite film under six different applied potentials are shown in figure 7, and the photographs of a sample on the corresponding states are shown in figure 8. It is clearly seen that the NiO/PANI film presents a noticeable electrochromism with reversible color changes from transparent pale yellow to purple when the potential is varied from -0.2 to 1.0 V. It is observed that the transmittance decreases and the transmittance edges show a blueshift to the ultraviolet region as the applied potential increases from -0.2 to 0.7 V. While the PANI is oxidized into the totally pernigraniline structure (purple), the transmittance increases in the near-infrared region. This phenomenon is in accordance with the result in the literature [32]. The transmittance variation between leucoemeraldine and pernigraniline states is up to 56% at 550 nm. This value is comparable with the result obtained by Wang et al [33].

The electrochromic response is an important criterion for selecting an electrochromic material. In this case, the porous NiO/PANI composite film was switched from an oxidized state to a reduced state by applying alternating square potentials between 0.8 and -0.2 V (versus SCE). Figure 9 shows the resultant current-time response. The response times for oxidation and reduction are 90 and 110 ms, respectively. The



Figure 7. Optical transmittance spectra of NiO/PANI composite film s under six different applied potentials.



Figure 8. Photographs of a sample with a size of 2.5×2.5 cm² under different applied potentials.

switching speeds are much slower than those obtained by Lacroix et al (100 μ s) [34], but better than the result of Ram et al (205 ms) [35]. The response time is dependent on several factors such as applied potential, film thickness and electrolyte conductivity. The PANI film obtained by Lacroix et al is much thinner (120 nm) and tested in 2 M The thin film prepared by Ram et al is about H_2SO_4 . 400 nm and tested in 1 M HCl. Our sample is about 480 nm and tested in 1 M LiClO₄ + 1 mM HClO₄/PC, which has lower electrolyte conductivity. Nevertheless, the NiO/PANI film still exhibits a much faster electrochromic response than the conventional PANI film (>500 ms) [36] and inorganic electrochromic materials (>1 s). This is mainly due to the highly porous structure. The electrochromic processes involve double injection (extraction) of ions and electrons into (from) the film. The processes are believed to first occur at grain boundaries and on grain surfaces. The highly porous structure of the NiO/PANI composite film provides a large reaction surface and inner space, which facilitate electrolyte penetration into the film and shorten diffusion pathways for the counterions. Meanwhile, the intercrossing network provides much more paths for the double injection (extraction) of ions and electrons into (from) the film. All these contribute to the improvement of response speed.



Figure 9. Chronoamperometric curve of the porous NiO/PANI composite film.

The electrochemical stability of the NiO/PANI film in 1 M LiClO₄ + 1 mM HClO₄/PC was typically characterized by cyclic voltammetry in the potential range of -0.2–0.8 V, at a sweep rate of 50 mV s⁻¹. The evolution of CVs of the NiO/PANI film is shown in figure 10. There is a significant shift in the shape of the recorded curves. The CV curve at the first cycle shows three typical redox couples. The first redox couple P₁/C₁ corresponds to the change between leucoemeraldine base (LB) and emeraldine salt (ES) with anion doping upon oxidation and dedoping upon reduction, which can be simply expressed as follows [33, 37]:

$$\begin{array}{l} \text{PANI} + n\text{ClO}_4^{-1} \Leftrightarrow (\text{PANI}^{n+})(\text{ClO}_4^{-1})_n + n\text{e}^{-1} \\ \text{(LB, yellow)} \qquad (\text{ES, green}) \end{array}$$
(1)

The second redox couple P_2/C_2 has been attributed to the redox reactions of degradation products of PANI, including benzoquinone and quinoneimines [24, 25, 38, 39]. The redox couple P_3/C_3 is due to the conversion between emeraldine base (EB) and pernigraniline salt (PS) with doping/dedoping of the anion processes, represented by the following reaction [33, 37]:

$$EB + mClO_4^{-1} \Leftrightarrow (EB^{m+})(ClO_4^{-1})_m + me^{-1}.$$
(EB, blue) (PS, purple) (2)

The conversion between ES and EB is due to protonation/deprotonation processes illustrated as follows:

$$\begin{array}{l}
\text{ES} \Leftrightarrow \text{EB} + n\text{ClO}_4^{-1} + n\text{H}^+. \\
\text{(Green)} \qquad \text{(Blue)}
\end{array}$$
(3)

No electrochemical current peaks of NiO are observed in this potential range. It indicates that the PANI plays a leading role in this potential range for electrochromism, and the NiO mainly plays the role of support. From CV results, an obvious degradation has been observed. After 200 cycles, the peak P_2 starts to merge with the peak P_3 . The peaks C_2 and C_3 merge together at the 800th cycle. Up to the 10³th cycle, only one redox couple can be seen. The current decreases dramatically and presents a fading of about 60% at the 10³ cycle. Similar phenomena for PANI electrochemical degradation have also



Figure 10. Cyclic voltammogram of NiO/PANI composite film in 1 M LiClO₄ + 1 mM HClO₄/PC at a sweep rate of 50 mV s⁻¹.

been observed by others [24, 25]. The cycling stability of the NiO/PANI film in the present system has been found to be less than 10^3 cycles on going from the reduced state to the oxidized state in the potential range of -0.2-0.8 V. The result is much lower than the value of 10^6 cycles, as observed by Kobayashi et al [40] for a 1.0 μ m PANI thin film on switching between leucoemeraldine and emeraldine salt. The shorter lifetime is due to the degradation of the pernigraniline and NiO chemical instability in the electrolyte solution for a prolonged time. It is believed that the pernigraniline is not stable as a result of benzoquinone formation by hydrolysis during cycling, especially under a potential higher than 0.7 V (versus SCE). On the other hand, these degradation products are soluble in the electrolyte and peel off from the film electrode during cycling. As mentioned above (figure 4), the NiO flake is enwrapped by PANI. When the PANI degrades and peels off, the NiO will be exposed to the acid electrolyte and dissolve. This leads to the breakdown of the NiO backbone and results in worse stability.

Figure 11 shows EIS plots of NiO and NiO/PANI composite films and an equivalent circuit model. Both Nyquist plots are recorded in 1 M LiClO₄ + 1 mM HClO₄/PC after both samples have been subjected to a step voltage of 0.6 V for 5 s. The impedances of both film electrodes consist of a depressed arc in high frequency regions and a straight line in low frequency regions. Generally, the semicircle reflects the electrochemical reaction impedance (Rct) of the film electrode and the straight line represents the diffusion of electroactive species (Rw). Compared to the NiO film, the NiO/PANI film exhibits a much smaller capacitive arc and slower slope. According to previous reports [41-43], a larger semicircle means a larger charge transfer resistance and smaller electrochemical capacitance (Qc), and a higher slope signifies a lower diffusion rate. It is concluded that the NiO/PANI film has much lower charge transfer resistance and ion diffusion resistance as well as larger electrochemical capacitance than the NiO film, indicating the composite film is favorable for charge transfer and ion diffusion. This is due to the porous conductive network formed by the PANI. It is well known that the PANI exhibits high electrical conductivity



Figure 11. EIS plots of both film electrodes.

in the partially oxidized state. In our experiment, a uniform PANI film is deposited on the NiO film after electrochemical polymerization, which provides a good conductive network for the whole composite film. On the other hand, the highly porous structure of the NiO/PANI film provides a large reaction surface and inner space, facilitating ion diffusion.

4. Conclusion

The highly porous NiO/PANI composite film was successfully prepared by combining the chemical bath deposition and electro-polymerization methods, successively. It is expected that this synthetic method may be applicable for the synthesis of other inorganic material-conducting polymer composite films. The as-prepared NiO/PANI composite film has a net-like structure with huge porosity. The NiO film acts as a template for the preferential growth of PANI along NiO flakes. The NiO flakes are coated by PANI and protected from dissolving in an acidic environment. The NiO/PANI composite film exhibits a noticeable electrochromism with reversible color changes from pale yellow to purple. The NiO/PANI composite film presents quite a good transmittance modulation with a variation of transmittance up to 56% at 550 nm. In addition, the NiO/PANI composite film electrode exhibits quite good reaction kinetics with fast switching speed due to its highly porous structure. The response time for oxidation and reduction is 90 and 110 ms, respectively.

References

- [1] Granqvist C G 2005 J. Eur. Ceram. Soc. 25 2907
- [2] Somani P R and Radhakrishnan S 2002 Mater. Chem. Phys. 77 117
- [3] Shim G H, Han M G, Sharp-Norton J C, Creager S E and Foulger S H 2008 *J. Mater. Chem.* **18** 594
- [4] Chang C W, Liou G S and Hsiao S H 2007 J. Mater. Chem. 17 1007

- [5] Berridge R, Wright S P, Skabara P J, Dyer A, Steckler T, Argun A A, Reynolds J R, Harrington R W and Clegg W 2007 J. Mater. Chem. 17 225
- [6] Lee S-H, Deshpande R, Parilla P A, Jones K M, To B, Mahan H and Dillon A C 2006 Adv. Mater. 18 763
- [7] Aubert P-H, Argun A A, Cirpan A, Tanner D B and Reynolds J R 2004 Chem. Mater. 16 2386
- [8] Cho S I, Xiao R and Lee S B 2007 Nanotechnology 18 405705
- [9] Stilwell D E and Park S M 1988 J. Electrochem. Soc. 135 2491
- [10] Huang M R, Tao T, Li X G and Gong Q C 2007 Am. J. Phys. 75 839
- [11] Gangopadhyay R, De A and Ghosh G 2001 Synth. Met. 123 21
- [12] Kimura K and Kumar J 2004 J. Printing Sci. Technol. 41 109
- [13] Martin C R, Van Dyke L S, Cai Z H and Liang W B 1990 J. Am. Chem. Soc. 112 8976
- [14] Martin C R 1996 Chem. Mater. 8 1739
- [15] Parthasarathy R V and Martin C R 1994 Chem. Mater. 6 1627
- [16] Xia X H, Tu J P, Zhang J, Wang X L, Zhang W K and Huang H 2008 Sol. Energy Mater. Sol. Cells 92 628
- [17] Song G P, Han J and Guo R 2007 Synth. Met. 157 170
- [18] Han J, Song G P and Guo R 2006 J. Polym. Sci. A 44 4229
- [19] Peng X Y, Li W, Liu X X and Hua P J 2007 J. Appl. Polym. Sci. 105 2260
- [20] Huang X H, Tu J P, Xia X H, Wang X L and Xiang J Y 2008 Electrochem. Commun. 10 1288
- [21] Genies E M and Tsintavis C 1985 J. Electroanal. Chem. 195 109
- [22] Genies E M, Lapkowski M and Penneau J F 1988 J. Electroanal. Chem. 249 97
- [23] Leon-Silva U, Nicho M E, Hu H L and Cruz-Silva R 2007 Sol. Energy Mater. Sol. Cells 91 1444
- [24] Kobayashi T, Yoneyama H and Tamura H 1984 J. Electroanal. Chem. 177 293
- [25] Stilwell D E and Park S-M 1988 J. Electrochem. Soc. 135 2497
- [26] Ou Yang L Y, Chang C, Liu S, Wu C and Yau S L 2007 J. Am. Chem. Soc. 129 8076
- [27] Cerc Korošec R, Bukovec P, Pihlar B and Padežnik Gomilšek J 2003 Thermochim. Acta 402 57
- [28] Surca A, Orel B, Pihlar B and Bukovec P 1996 J. Electroanal. Chem. 408 83
- [29] Ma X F, Li G, Wang M, Cheng Y, Bai R and Chen H Z 2006 *Chem. Eur. J.* 12 3254
- [30] Wang Y G, Li H Q and Xia Y Y 2006 Adv. Mater. 18 2619
- [31] Wu M S and Yang C H 2007 Appl. Phys. Lett. 91 033109
- [32] Shreepathi S and Holze R 2005 Chem. Mater. 17 4078
- [33] Wang J Y, Yu C M, Huang S C, Ho K C and Chen L C 2008 Sol. Energy Mater. Sol. Cells 92 112
- [34] Lacroix J C, Kanazawa K K and Diaz A 1989 J. Electrochem. Soc. 136 1308
- [35] Ram M K, Maccioni E and Nicolini C 1997 Thin Solid Films 303 27
- [36] Dhawan S K, Ram M K, Malhotra B D and Chandra S 1995 Synth. Met. 75 119
- [37] Lin T H and Ho K C 2006 Sol. Energy Mater. Sol. Cells 90 506
- [38] Yang H and Bard A J 1992 J. Electroanal. Chem. 339 423
- [39] Shim Y-B, Wan M-S and Park S-M 1990 J. Electrochem. Soc. 137 538
- [40] Kobayashi T, Yoneyama H and Tamura H 1984 J. Electroanal. Chem. 161 419
- [41] Zimerman A H and Effa P K 1984 J. Electrochem. Soc. 131 709
- [42] Armstrong R D and Wang H 1991 Electrochim. Acta 36 759
- [43] Kostecki R, Ulmann M and Augustynski J 1993 J. Phys. Chem. 97 8113