Supplementary Information for

High efficient PANI/Pt nanofiber counter electrode used in dye-sensitized solar cell

Jihuai Wu*, Ziying Tang, Min Zheng, Qunwei Tang, Qin Liu, Jianming Lin and Jiangli Wang Institute of Materials Physical Chemistry, Huaqiao University, Quanzhou 362021, P.R. China.

1 Experimental section

1.1 Synthesis of PANI nanofiber film

PANI nanofiber electrode was prepared by an electrochemical deposition method in a three-electrode system on an electrochemical workstation (CHI660C, CH Instruments, Shanghai) according to the references. ^[S1,S2] An indium tin oxide (ITO) glass substrate was used as the working electrode $(1.5 \times 2 \text{ cm}^2)$, a platinum wire as the counter-electrode and a saturated Ag/AgCl as reference. Anodic deposition was controlled in a solution containing 1.0 M HClO₄ and 0.2 M aniline (ANI) monomer. PANI nanofiber film was fabricated by controlling the number of sweep segments and with initial E = -0.2 V, high E = 0.9 V, low E = -0.2 V, final E = 0.4 V, scan rate = 50 mV·s⁻¹, segment = 71. The resultant PANI nanofiber films were washed with ethanol and distilled water followed by drying in a vacuum at 60 °C for 24 h.

1.2 Deposition of PANI/Pt and Pt electrode:

The platinum nanoparticle was deposited onto PANI nanofiber by modifing the references. ^[S3,S4] PANI/Pt was prepared in 0.5 M HCl, 0.002 M H₂PtCl₆ solution by using the

PANI nanofiber as working electrode, a platinum wire as the counter-electrode and a saturated Ag/AgCl as reference electrode at the potentials between -0.25 and 0.25 V for 80 cycles with initial E = -0.25 V, high E = 0.25 V, low E = -0.25 V, final E = 0.25 V, scan rate = $50 \text{ mV} \cdot \text{s}^{-1}$. The platinum electrode was prepared by using ITO glass as working electrode under the same conditions as the preparation of PANI/Pt.

1.3 Preparation of TiO₂ film and fabrication of DSSCs

A TiO₂ film with a thickness of about 10 μ m was prepared by using doctor blade as the method we previously reported ^[S5-S7]. The TiO₂ photoanode was obtained by loading TiO₂ film in 0.3 mM dye N719 ethanol solution and soaking for 24 h. The dye-sensitized solar cells (DSSCs) were assembled by injecting the liquid electrolyte (containing of 0.6 M tetrabutylammonium iodide, 0.1M LiI, 0.06 M I₂, and 0.5 M TBP, solution: acetonitrile) into the aperture between the TiO₂ photoanodes and counter electrodes. The detailed procedure for DSSCs were described by us elsewhere. ^[S5-S7]

1.4 Measurement and characterization

SEM images of the sample were recorded with a S-4800 instrument (Japan) at an acceleration voltage of 5 kV. EDS measurements were conducted with an INCA 7201 EDS (England). The FTIR measurements were performed on a Nicolet Impact 410 FTIR spectrophotometer using KBr pellets.

The cyclic voltammetry (CV) of PANI, Pt, PANI/Pt electrodes were carried out ^{S8} in a three-electrode system on an electrochemical workstation (CHI660C, CH Instruments, Shanghai) by using the prepared electrode as working electrode, a Pt-foiled as counter electrode and a saturated Ag/AgCl as reference electrode dipped in an acetonitrile solution of

100 mM LiClO₄, 10 mM LiI and 1 mM I₂, at a scan rate of 10 mV \cdot s⁻¹.

EIS tests ^{S9} were performed using a sandwich cell configuration with symmetric films in an acetonitrile electrolyte containing 0.05 M I₂, 0.1 M LiI, 0.6 M tetrabutylammonium iodide and 0.5 M TBP. A 50 μ m Surlyn film was used to separate the films and to seal the cells. The magnitude of the alternating signal was 5 mV, and the frequency range was 100 kHz to 0.1 Hz, the active area of the electrodes about 0.5 cm². Unless otherwise noted, All measurements were carried out at a temperature of 20 °C.

The photovoltaic test of DSSC was carried out by measuring the J-V characteristic curves under simulated solar illumination with intensity of 100 mW·cm⁻² (AM 1.5) from a 100 W xenon arc lamp (XQ-500W, Shanghai Photoelectricity Device Company, China) in ambient atmosphere. The fill factor (FF) and light-to-electric energy conversion efficiency (η) of the cell were calculated according to the following equations: ^{S5}

$$FF = \frac{V_{\max} \times J_{\max}}{V_{oc} \times J_{sc}}$$
(S1)

$$\eta(\%) = \frac{V_{\max} \times J_{\max}}{P_{in}} \times 100\% = \frac{V_{oc} \times J_{sc}}{P_{in}} \times 100\%$$
(S2)

Where J_{SC} is the short-circuit current density (mA·cm⁻²), V_{OC} is the open-circuit voltage (V), P_{in} is the incident light power, and J_{max} (mA·cm⁻²) and V_{max} (V) are the current density and voltage in the *J*–*V* curves at the point of maximum power output, respectively.

2 Result and discussion

2.1 PANI films

Figure S1 presents the SEMs of PANI film. Figure S1a and 1b show the top view of PANI film, it can be seen that PANI nanofibers twist and uniformly grow with a diameter

around 100 nm. It can also be seen that the PANI nanofiber film is microporous and the pores interconnected with each other, which provides a high effective surface area of PANI film.^{S10} Figure S1c and S1d give the SEM images of the cross-section of the PANI films, it can be seen that the two PANI layers deposit on ITO glass under this condition. The first layer is a compact underlayer, the second layer is a nanofiber structure layer, which coincides with the previous reports of electrodeposited PANI film.^{S2,S10} Figure S1e shows the surface morphology of the first PANI underlayer, the underlayer is microspheroid and compact, which is beneficial for the growth of PANI fibers on substrates. Figure S1f presents the back-side SEM images of PANI films. It is very compact and smooth, indicating the excellent interface contact between PANI with ITO substrate.^{S11}





images of PANI films, (e) top and (f) cross-section images of the compact underlayer of PANI.

2.2 PANI/Pt hybride nanofibers



Figure S2 EDS of the PANI nanofibers (a) and PANI/Pt hybride nanofibers (b).



Figure S3 FTIR spectra of PANI nanofibers and PANI/Pt hybrid nanofibers.

Figure S3 shows the FTIR spectra of PANI and PANI/Pt. For PANI, the peak at 3440 cm^{-1} is belonged to the N–H stretching, the peak at 1660 cm^{-1} is for C=N stretching, the peak at 1580 cm^{-1} is due to the C–C stretching mode for the quinoid ring, the peak at 1490 cm^{-1} is for the benzenoid rings vibration, the peaks at 1380 and 1300 cm^{-1} comes from the aromatic C–N stretching mode, the peak at 1240 cm^{-1} is for the C–N⁺ stretching vibration, the peak at 1120 cm^{-1} is due to the C–H in-plane deformation, and the peak at 795 cm^{-1} is ascribed to the out-of-plane bending vibration of C–H, which are coincided with the previous reports^{S12,S13} and confirm the formation of PANI. On the other hand, when Pt nanoparticles are deposited

onto the PANI nanofibers, no obvious other absorption peaks appear in PANI/Pt sample except for some red or blue shifts. The FIIR spectra also further confirms that the PANI structure remains unchanged during the deposition of Pt nanoparticles on the surface of PANI fibers.

2.3 Cyclic voltammogram for PANI fiber and PANI/Pt hybride fiber.



Figure S4 Cyclic voltammogram for PANI fiber and PANI/Pt hybride fiber. (A) CV of PANI fiber film deposited using 71-sweep-segments, itial E = -0.2 V, high E = 0.9V, low E = -0.2 V, scan rate = 50 mV·s⁻¹, (B) CV of Pt deposited onto PANI fiber film, sweep segment = 81, itial E = -0.25 V, high E = 0.25V, low E = -0.25 V, scan rate = 50 mV·s⁻¹.

During the electrodeposition of PANI process, it can be seen that the homogeneous green-colour film deposited on the ITO substrate and when the applied potential varies from -0.2 to +0.9 V, its colour changes from transparent leucoemeraldine to yellow/green emeraldine and eventually to blue/black pernigraniline. There are three redox pairs, with oxidation peaks at (a) 0.25 V, (b) 0.50 V and (c) 0.77 V (vs. Ag/AgCl), (a') 0 V, (b') 0.40 V and (c') 0.60 V (vs. Ag/AgCl) are the corresponding reduction peaks. The first peak (a)

corresponds to the first step of oxidation of neutral PANI, and the third peak (c) corresponds to the further oxidation of PANI, from emeraldine to nigraniline, the middle pair bb' attributes either to the presence of ortho-coupled polymers or to the degradation of PANI (soluble species such as benzoquinone and hydroquinone).^{S3,S14} Subsequent potential cyclings indicate a regular growth of the polymeric deposit as previously described.^{S1,S13} From the Cyclic voltammogram of PANI, we can see that the current density is much low and increases slowly at the initial polymerization process, while at the final polymerization process, the current density is much larger and increases faster, this may because of that at the initial polymerization progress distributed nucleation sites and short chain PANI nanoparticles slowly and homogeneously grow on the ITO substrate, which leads to the formation of a compact layer or enrichment at local sites. However, in the final polymerization process, long chain PANI or ever PANI fibers have formed on ITO glass and the nucleation sites are much more, which is benefit for the overgrowth of PANI nanofibers, besides, the formed PANI at the early age may have a catalytic action on the followed growth of PANI fibers.

The cyclic voltammogram for the deposition of Pt NPs onto PANI fibers is shown in Figure S 4B. From the figure, we can see that only one peak corresponding to the reduction of Pt NPs can be observed (Corresponding to the reduction of Pt: $PtCl_6^{2^-} + 4e^- = Pt + 6Cl^-$). Additionally, the current density shows little changes, which demonstrates that the PANI or PANI/Pt hybrid nanofibers is well stable, and the second deposition of Pt NPs procedure will not destroy the structure of formed PANI fibers.

References

- S1 J. Zhang, T. Hreid, X. Li, W. Guo, L. Wang, X. Shi, H. Su, Z. Yuan, *Electrochim. Acta*, 2010, 55, 3664.
- S2 X. Yu, Y. Li, N. Zhu, Q. Yang, K. Kalantar-zadeh, Nanotechnology, 2007, 18, 1.
- S3 K. Ka, D. Bartak, Anal. Chem., 1988, 60, 2379.
- S4 A. Kitani, T. Akashi, K. Sugimoto, S. Ito, Synth. Met., 2001, 121, 1301.
- S5 J. Wu, Z. Lan, J. Lin, M. Huang, S. Hao, T. Sato, S. Yin, Adv. Mater., 2007, 19, 4006.
- S6 J. Wu, S. Hao, Z. Lan, J. Lin, M. Huang, Y. Huang, P. Li, S. Yin, T. Satot, J. Am. Chem. Soc., 2008, 130, 11568.
- S7 J. Wu, S. Hao, J. Lin, M. Huang, Y. Huang, Z. Lan, P. Li, *Crystal Growth & Design*, 2008, 8, 247.
- S8 Y. Saito, W. Kubo, T. Kitamura, Y. Wada, S. Yanagida, J. Photoch. Photobio. A., 2004, 164, 153.
- S9 H. Tian, Z. Yu, A. Hagfeldt, L. Kloo and L. Sun, J. Am. Chem. Soc., 2011, 20, 9413.
- S10 W. Huang, B. Humphrey, A. MacDiarmid, J. Chem. Soc., Faraday Trans. 1986, 82, 2385.
- S11 M. Chang, X. Cao, H. Zeng, J. Phys. Chem. C, 2009, 113, 15544.
- S12 J. Chiang, A. MacDiarmid, Synth. Met., 1986, 13, 193.
- S13 Q. Tang, J. Wu, X. Sun, Q. Li, J. Lin, *Langmuir*, 2009, 25, 5253.
- S14 S. Pruneanu, E. Veress, I. Marian, L. Oniciu, J. Mater. Sci., 1999, 34, 2733.