Electronic Supporting Information

In situ synthesis of platinum/polyaniline composite counter electrodes for flexible dye-sensitized solar cells

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Experiment Section

1. Fabrication of Pt/PANI, PANI and Pt films on ITO/PET substrates

The Pt/PANI composite film was fabricated as follows.[1] Firstly, a formic acid solution of PANI (EB, half-oxidized form) (1 wt%) and a formic acid solution of K_2PtCl_4 (10 mM) were mixed in equal volumes and sonicated for 1 h. The treatment of the EB form with acid produced the doped conducting form (ES, half-oxidised, protonated form). Then a film on a ITO/PET substrate (14 $\Omega\ \square^{-1}$, Solaronix) was obtained by a spin-coating method from the Pt/PANI solution at 2000 rpm for 30 s. Finally, the formed Pt/PANI film was immersed into a neutral aqueous solution of K_2PtCl_4 (10 mM) for 30 min. This treatment step could cause a leveling of the surface topography and further enhance Pt loading. For comparison, the pristine PANI film was obtained by spin-coating and conventional Pt was prepared by sputtering Pt on ITO/PET substrates for 30 s under sputter current of 20 mA.

2. Fabrication of TiO_2 films on ITO/PET substrates

TiO_2 paste for the flexible ITO/PET substrates contains a mixture of 10 wt% TiO_2 nanoparticles and water solvent.[2] The TiO_2 mixture is combined by 20 nm and 100 nm TiO_2 nanocrystalline. Titanium tetraisopropoxide (TTIP) was added to water (Ti : H_2O = 1 : 50) slowly and stirred for 1 h. The obtained white precipitate was washed three times with water. It was then transferred to a tetramethylammonium hydroxide (TMAH) solution and refluxed at 100 ºC for 4 h under stirring. The resultant colloids were heated at 270 ºC for 4 h in a titanium autoclave under stirring. TiO_2 particles with 20 nm and 100 nm were obtained when the molar ratio of TMAH to Ti was varied. These 20 and 100 nm TiO_2 nanoparticles with weight ratio of 7:3 were then mixed with water to form homogeneous paste. Then the TiO_2 paste was printed on ITO/PET substrates by a doctor-blade method, and the thickness could be controlled by the by selection of screen mesh size and repetition of printing. After air drying at 150 ºC for 10 min and then followed a mechanical compression at 100 MPa, the TiO_2 film was obtained.

1. A. P. O'Mullane, S. E. Dale, J.V. Macpherson and P. R. Unwin, *Chem. Commun.,* 2004, **40,** 1606.

2. T. Yamaguchi, N. Tobe, D. Matsumoto, T. Nagai and H. Arakawa, *Sol. Energy Mater. Sol. Cells,* 2010, **94,** 812.

3. Assembly Characterization of DSCs

The obtained TiO_2 photoelectrode with an area of 0.16 cm^2 was then soaked into an ethanol solution of the Ru complex dye N719 for 24 h at room temperature. The dye-sensitized samples were then washed in ethanol to remove unanchored dye and dried under vacuum. A mixture of I_2 (0.05 M), LiI (0.1M), 1,2-dimethyl-3-propylimi-dazolium iodide (0.6 M), and 4-tert-butylpyridine (0.5 M) in dehydrated acetonitrile solvent was used as an electrolyte. Solar cells were made by sealing the electrolyte (a mixture of 0.6 M DMPImI, 0.1 M LiI, 0.05 M I_2, acetonitrile as a solvent) between the photoanodes (the dye-deposited TiO2 film) and the different counter electrodes.

4. Characterization and measurements

The morphology of the as-obtained films was investigated by using scanning electron microscopy (SEM, JEOL JSM-6701F), operated at 10 kV. High resolution transmission electronic microscope (HRTEM) images were performed with a Philips Tecnai F20 microscope with an accelerating voltage of 200 kV. The elemental compositions of the films were analyzed by energy-dispersive X-ray spectroscopy (EDS), which was attached to the SEM. The determination of the Pt loading on the FTO conductive glass was performed by ICP AES (Thermo Jarrell Ash Corp.). The transmittance spectra of the Pt, PANI, and Pt/PANI films were recorded at room temperature on a Jasco V-550 UV–vis spectrophotometer. Atomic force microscopy (AFM) characterization of the films was carried out by using a Nanoscope III (Digital Instruments, Inc., Santa Barbara, CA, USA) in tapping mode in air. Electrochemical impedance spectroscopy (EIS) of the counter electrodes was investigated by using the Autolab PGSTAT30 from 40 Hz to 1 M Hz with signal amplitude of 10 mV to determine their catalytic performance. For the EIS measurement, a symmetric cell configuration with two identical counter electrodes was assembled with the injection of the same electrolyte for the DSCs, and the active area of the cells is 0.25 cm^2. EIS spectra were obtained at zero bias potential and 10 mV amplitude over the frequency range 0.01–10^5 Hz. Cyclic voltammetry (CV) measurements were carried out in a N_2-purged acetonitrile solution at a scan rate of 100 mV/s. The prepared Pt/PANI film on the FTO glass substrate, a Pt coil and a Ag/Ag^+ electrode were used as the photocathode, the working electrode, and the reference electrode, respectively. The electrolyte was acetonitrile containing 0.1 mol/L $LiClO_4$ as the supporting electrolyte and 10 mmol/L LiI +1 mmol/L I_2 as the redox couple. The current density–voltage ($J-V$) curves of the assembled DSCs were performed

using a solar simulator (San Ei, Japan) under 1 sun and at AM1.5G condition. The level of standard irradiance (1 Sun conditions, 100 mW cm^{-2}) was set with a calibrated c-Si reference solar cell.

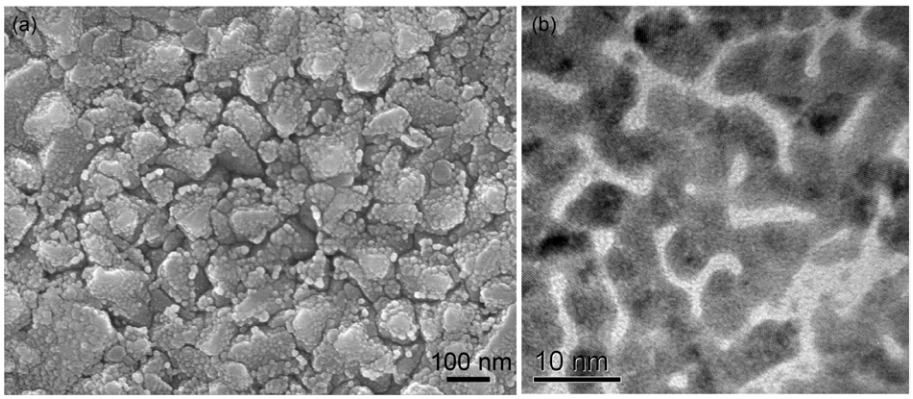

Fig. S1 SEM and TEM images of the sputtered Pt film.

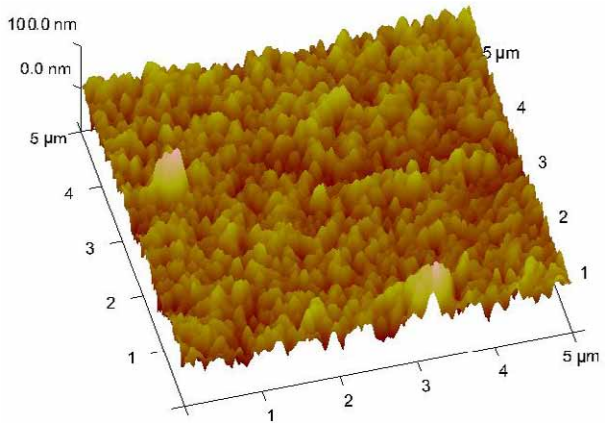

Fig. S2 Three-dimensional AFM image of the sputtered Pt film.