

Supporting Information

Novel PtO decorated MWCNTs as Highly Efficient Counter Electrode for Dye-Sensitized Solar Cells†

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Preparation of PtO-MWCNTs nanocomposites

The PMAA-PTTM polymer ligands were synthesized according to the literature¹. For the synthesis of PtO-MWCNTs nanocomposites, 100 mg of MWCNTs and 20 mg of PMAA-PTTM polymer ligands were added into a screw-neck glass bottle (25 mL) containing H₂PtCl₆/H₂O solution (10 mL, 0.2 mg/mL). After the solution becoming uniform by sonication, 1 mL of freshly prepared sodium borohydride (NaBH₄) aqueous solution (2 mg/mL) was rapidly injected into the solution under vigorously stirring (2000 r/min). After stirring for 2~3 h, another 1 mL of freshly prepared NaBH₄ solution was injected into the solution again. The stirring speed of the solution was kept to be 2000 r/min for 12 h. When the reaction was finished, the product can be obtained by filtration, washed with deionized water and ethanol separately for 5 times, dried in air at 333 K. In order to eliminate the effect in the preparation of counter electrodes, the synthesized PtO-MWCNTs nanocomposites were further annealed at 723 K under nitrogen atmosphere for 30 min and used for characterization.

Preparation of counter electrodes

The PtO-MWCNTs coated counter electrodes were prepared on F-doped tin oxide (FTO) conducting glass substrate (NSG, 8 Ω/square) using a paste that made from the obtained PtO-MWCNTs power by screen-printing technology. The paste was made by mixing 50 mg PtO-MWCNTs nanocomposites powder with 400 mg anhydrous terpineol, 560 mg ethyl celluloses in ethanol (10 wt%) and 5 mL ethanol followed by stirring, sonication and concentration. Then the formed films were annealed at 723 K for 30 min under nitrogen atmosphere.

The Pt electrode was prepared by drop-casting 0.5 mM H₂PtCl₆/ethanol solution on the clean FTO conductive glass. Subsequently, the formed films were annealed at 723 K for 30 min at ambient condition.

Fabrication of DSCs

The procedure of preparing the TiO₂ photoanode was described in detail as follow. Firstly, the FTO substrate was dipped into 40 mM TiCl₄ for 30 min at 343 K (TiCl₄ treatment). Then a 12 μm-thick layer of 20 nm-sized TiO₂ particles was loaded on the FTO by screen printer technique with an area of about 0.25 cm². After sintering at 398 K, the obtained layer was further coated with a 4 μm-thick scattering layer of 200 nm-sized TiO₂ particles (HEPTACHROMA, DHS-NanoT200) followed by sintering at 773 K. Another TiCl₄ treatment was carried followed by sintering at 773 K for 30 min. After cooling to 353 K, the photoanodes (TiO₂ films) were immersed in a 5×10⁻⁴

M solution of N719 dye (Solaronix SA, Switzerland) in acetonitrile/tert-butyl alcohol (V/V=1/1) for 24 h. DSCs were assembled together with the dye-sensitized TiO₂ electrode and the PtO-MWCNTs CE by a 25 μm-thick hot-melt film (Surlyn 1702, DuPont) and sealed up by heating. The cell internal space was filled with typical liquid electrolytes using a vacuum pump. The liquid electrolyte was composed of 0.60 M 1-butyl-3-methylimidazolium iodide, 0.03 M I₂, 0.50 M 4-tert-butyl pyridine, and 0.10 M guanidinium thiocyanate with acetonitrile as the solvent. The assembled DSCs were used for the photocurrent-voltage test with an active area of 0.25 cm². For electrochemical impedance spectroscopy (EIS) measurement, the symmetrical dummy cells were assembled by two identical CEs clipping the above liquid electrolyte.

Characterization

The PtO-MWCNTs composites were observed by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F, F20, 200 kV) and field emission scanning electron microscopy (FESEM, HITACHI S4800) with energy dispersive spectroscopy (EDS). Pt L₃-edge extended X-ray absorption fine structure (EXAFS) were performed on the 1W2B beamline of the Beijing Synchrotron Radiation Facility, China, operated at ~ 200 mA and ~ 2.5 GeV. Pt foil and PtO₂ were used as reference samples and measured in the transmission mode, and the PtO-MWCNTs were measured in fluorescence mode. We used IFEFFIT software to calibrate the energy scale, to correct the background signal and to normalize the intensity. The chemical states of Pt in PtO-MWCNTs were studied by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD), and the binding energy of the C 1s peak at 284.8 eV was taken as an internal reference. The current-voltage tests of DSCs were performed under one sun condition using a solar light simulator (Oriel, 91160, AM 1.5 globe). The power of the simulated light was calibrated to 100 mW·cm⁻² using a Newport Oriel PV reference cell system (model 91150 V). The EIS experiments were conducted with dummy cells in the dark by using an electrochemical workstation (Parstat 2273, Princeton). The frequency range of EIS experiments was from 100 mHz to 1 MHz with an AC modulation signal of 10 mV and bias DC voltage of 0.60 V. The curves were fitted by the Zview software. Cyclic voltammetry (CV) was conducted in a three-electrode system in an acetonitrile solution of 0.1 M LiClO₄, 10 mM LiI, and 1 mM I₂ at a scanning rate of 20 mV s⁻¹ by using a BAS 100 B/W electrochemical analyzer. Platinum served as a CE and the Ag/Ag⁺ couple was used as a reference electrode. Tafel polarization curves were measured with dummy cells in the dark using an electrochemical workstation (Parstat 2273, Princeton).

References:

1. Z. Li, B. Tan, M. Allix, A. I. Cooper and M. J. Rosseinsky, *Small*, 2008, **4**, 231–239.

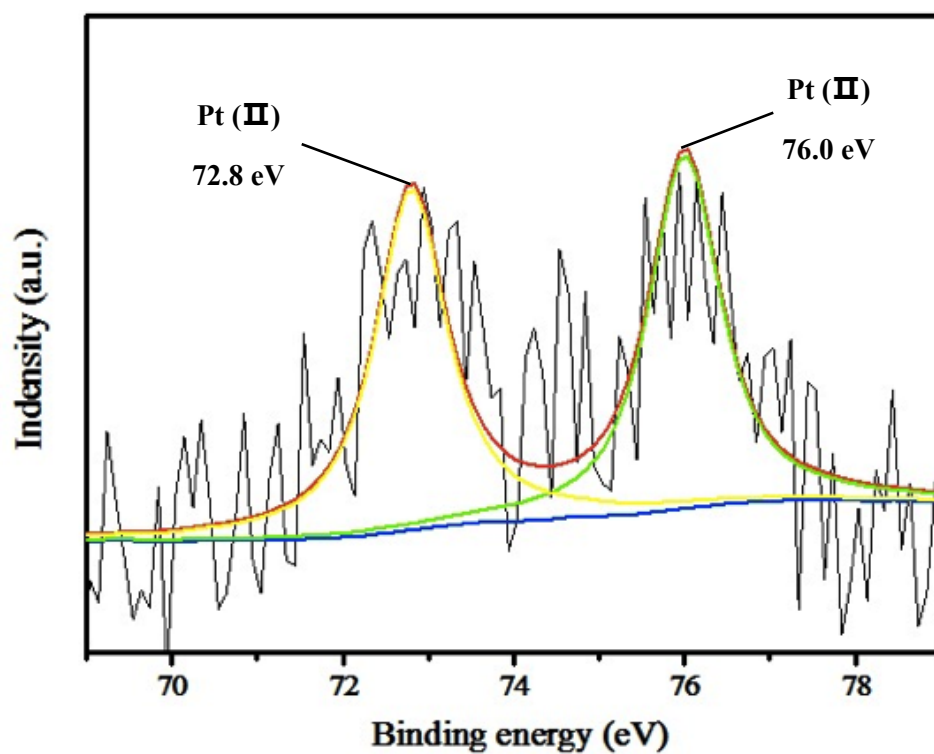


Fig. S1 The Pt4f peaks in the XPS spectra of PtO-MWCNTs nanocomposites.

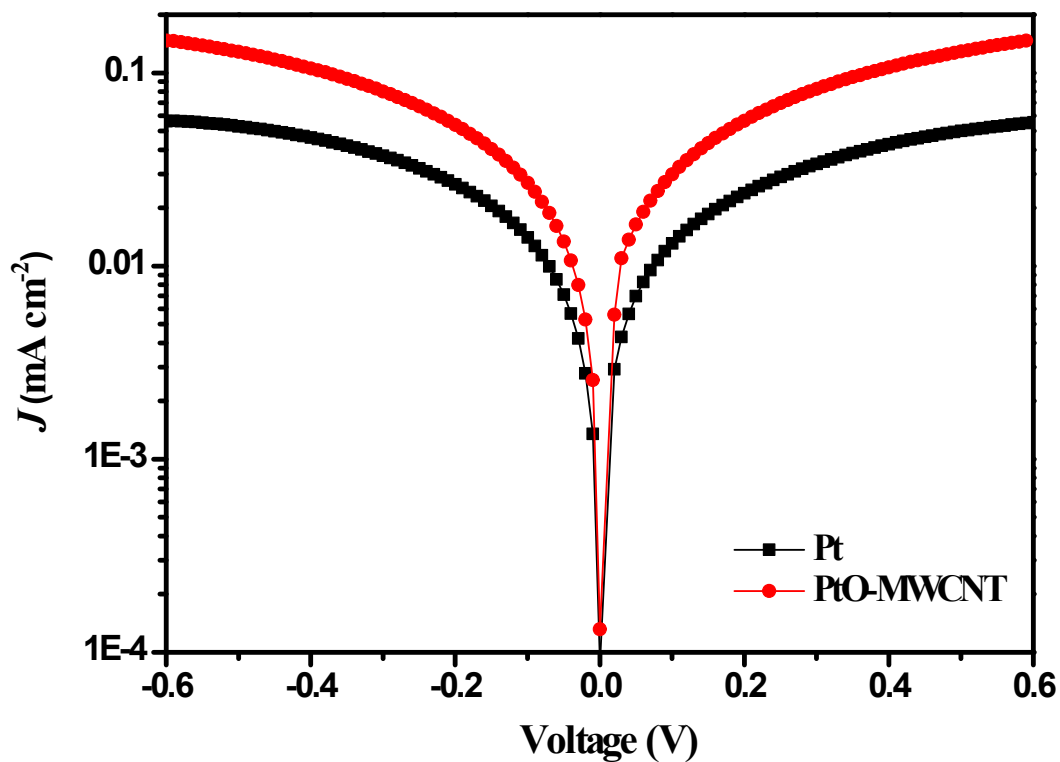


Fig. S2 Tafel curves of the symmetrical cells fabricated with two identical counter

electrodes of PtO-MWCNTs and Pt, respectively.

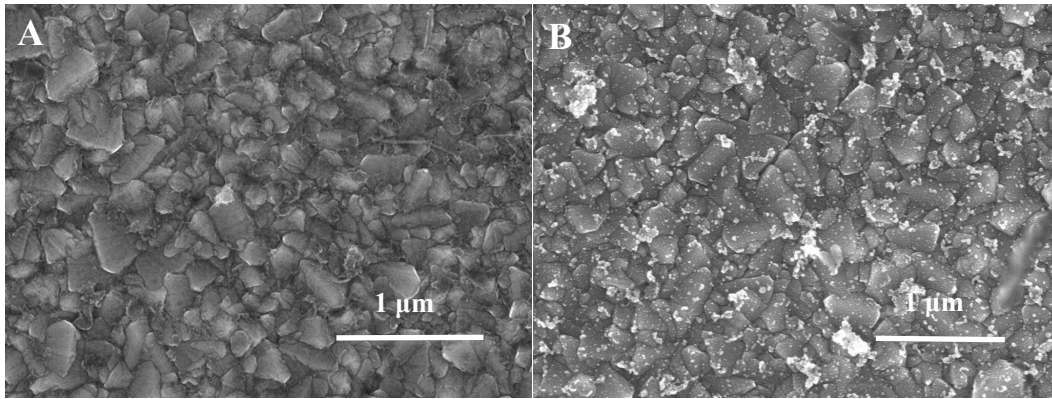


Fig. S3 (A) SEM images of PtO-MWCNTs CE on FTO. (B) SEM images of Pt CE on FTO.