Supporting Information

Efficient sinter-free nano-structure Pt counter electrode for dye-sensitized solar cells

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1. Experimental

1.1 Materials

The FTO conducting glass (fluorine doped tin oxide over-layer, transmission >85% in the visible, sheet resistance 7±1.5 Ω square⁻¹, Japan), 1-Butyl-3methyleimidazolium iodide (BMII), hydrochloroplatinic acid Di--bis(2,2'-bipyridyl-4,4'tetrabutylammonium cis-bis(isothiocyanato) dicarboxylato) ruthenium(II) (N719) obtained were from the Yingkou Youxuan Trade Co. Ltd. of China. Titania pastes of DSL 18NRT were purchased from Dyesol. Lithium iodide was from Fluka and iodine, 99.999%, was from Alfa Aesar.

1.2 Synthesis of platinum hydrosol precursor and the preparation of sinter-freePt electrodes

In the nano platinum hydrosol precursor, citrate salt was used as the reducing agent as well as stabilizer and dispersant during the formation of nanoparticles ^[S1, S2]. Compared with the polymer stabilizer, it exhibited good electrochemical and catalytic activity. The reaction mechanism is described as equations (1) and (2), respectively.

$$H_2PtCl_6 + 2RCH_2OH \longrightarrow Pt^0 + 2RCHO + 6HCl$$
 (1)

 $9PtCl_6^{2-} + 2H_2Cyt^{-} + 10H_2O \longrightarrow 9Pt^0 + 12CO_2 + 38H^+ + 54Cl^-$ (2)

4 mL of 5% H_2PtCl_6 (aq) was added to 340 mL of redistilled water and heated

to 80°C under stirring. Then 60 mL of 1% sodium dihydrogen citrate (aq) was dropped into the solution with holding temperature for 1h. Nano platinum hydrosol was obtained after refluxing for 30 min with tiny amount of sodium borohydride or 1 mL of methanol and the reaction was quenched through immersing the vessel into cold water. The color changed from orange to light yellow. The nano-structure sinter-free Pt (NPt) electrodes were formed under cyclic sweep in the range of 200-2000 mV for a period of time with fluorine-doped tin oxide (FTO) glass as substrate in the precursor solution using electrochemical workstation. In the following text, the NPt-5, NPt-10, NPt-15, NPt-20 and Pt represent the nano-structure sinter-free electrodes prepared by electrodeposition for 5, 10, 15, 20 min and the electrode made with conventional sinter method, respectively.

1.3 Preparation of dye-sensitized TiO₂ photoanode and Pt CEs

Dyes anchored photoanode and Pt CEs were prepared according to a published procedure ^[S3]. The electrodes coated with TiO₂ pastes were gradually heated under an air flow at 325 °C for 5min, 375 °C for 5 min, 450 °C for 15 min and 500 °C for 15 min before immersion in the solution of dye N719. And the Pt CEs were prepared with thermal decomposition by spin coating of H_2PtCl_6 solution. 1.4 Photovoltaic performance measurements

The current-density voltage (J-V) characteristics of the DSSCs with NPts and Pts were measured by recording J-V curves using a Keithley 2400 source meter under the illumination of AM 1.5 G simulated solar light (Newport-91160 equipped with a 300 W Xe lamp and an AM 1.5 G filter). The incident light intensity was calibrated to 100 mW cm⁻² with a standard silicon solar cell (Newport 91150V). Action spectra of the incident monochromatic photontoelectron conversion efficiency (IPCE) for the solar cells were obtained with a Newport-74125 system (Newport Instruments). The intensity of monochromatic light was measured with a Si detector (Newport-71640). The electrochemical impedance spectroscopy (EIS) measurements of all the DSSCs and the electrochemical deposition were performed using a Zahner IM6e Impedance Analyzer (Zahner Elektrik Gmbh & Cokg, Kronach, Germany). For EIS, The frequency range is 0.10 Hz-100 kHz. The applied voltage bias is -0.70 V with a magnitude of the alternative signal of 10 mV.

2. Test result

As shown in Figure S1, Photocurrent action spectrum (incident photon to current conversion efficiency, IPCE) is used to estimate J_{sc} and defined as the number of photogenerated charge carriers contributing to the photocurrent per incident photon.



Fig. S1 Photocurrent action spectra of the DSSCs with NPts and Pt counter electrode.

The photovoltaic properties and impedance data of DSSCs based on different CEs were listed in the Table S1.

CE	$J_{\rm sc}/{\rm mAcm}^{-2}$	$V_{\rm oc}/{ m mV}$	ff	PCE	R_S/Ω	$R_{ct}\!/\Omega$	Z_N / Ω	CPE/µF
NPt-5	16.8	731	0.68	8.4	22.1	3.48	2.16	6.3
NPt-10	16.7	730	0.70	8.5	20.8	3.30	1.60	7.4
NPt-15	20.0	742	0.68	10.1	22.8	1.57	0.96	10.0
NPt-20	16.7	741	0.71	8.8	16.4	1.91	2.10	13.0
Pt	19.5	740	0.67	9.7	23.8	5.06	4.25	4.6

Table S1. The Photovoltaic performances of the DSSCs with CEs of NPts and Pt CEs.

- S1 K. Aika, L. L. Ban, I. Okura, S. Namba, J. Turkevich, J. Res. Natl. Inst. Stan. 1976, 24, 54.
- S2 D. N. Furlong, A. Launikonis, W. H. F. Sasse and J. V. Sanders, J. Chem. Soc., Faraday Trans. 1, 1984, 80, 571.
- S3 W. J. Wu, J. Zhang, H. B. Yang, B. Jin, Y. Hu, J. L. Hua, C. Jing, Y. T. Long ,H. Tian, J. Mater. Chem. 2012, 22, 5382.