Supplementary Information

A new type of low-cost counter electrode catalyst based on platinum nanoparticles loaded on to silicon carbide (Pt/SiC) for high-efficiency dye-sensitized solar cells

Sining Yun,\textsuperscript{a} Liang Wang,\textsuperscript{b} Chunyu Zhao,\textsuperscript{b} Yanxiang Wang,\textsuperscript{c} Tingli Ma\textsuperscript{a\textsuperscript{b}}

\textsuperscript{a} School of Materials & Mineral Resources, Xi’an University of Architecture and Technology, Xi’an 710055, China.

E-mail: alexyun1974@yahoo.com.cn; Fax: +86-29-85535724; Tel: +86-29-82202022

\textsuperscript{b} State Key laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian, 116024, China.

E-mail: tinglima@dlut.edu.cn; Fax: +86-0411-39893820; Tel: +86-0411-39893820

\textsuperscript{c} Jingdezhen ceramic institute, Jingdezhen 333403, China.

* Corresponding authors: Dr. Sining Yun and Prof. Tingli Ma

Microwave-assisted synthesis of low-cost Pt/SiC composites

Greater than 99% purity of low-cost SiC nanopowder was purchased from Hefei Kaier Nanometer Technology and Development Co., Ltd. in China, which is a cubic...
crystal structure with an average size of 40 nm and a surface area of 90 m²/g. 1 g dihydrogen hexachloroplatinic acid hydrate (H₂PtCl₆·6H₂O) was dissolved in 97 ml deionized water to obtain the H₂PtCl₆ solution (approximately 0.5 wt.% of Pt). Pt/SiC nanocomposite electrocatalyst with ~10 wt.% calculated Pt loading was prepared by a microwave-assisted modified ethylene glycol method. ~10 wt.% calculated Pt loading is the mass ratio of Pt to Pt/SiC in composite counter electrode (CE) materials. In details: 15 ml H₂PtCl₆ aqueous solution was firstly dissolved in 20 ml ethylene glycol. Then 500 mg commercial SiC was added slowly into the above-mentioned solution and sonicated for 30 min for homogeneous dispersion. Pt-loading calculated is ~10 wt.% in Pt/SiC composite CE materials. The pH value was adjusted to 9-11 by the addition of NaOH in ethylene glycol solution. The completely homogeneous precursor mixture was moved into a quartz-tube reactor. Next, the reactor was placed in a domestic microwave oven operating at 2.45 GHz with a power of 800 W, and the microwave irradiation time is 5-8 min. Finally, the resulting products were cooled to room temperature, rinsed several times using the ethanol solution to remove Na⁺ and Cl⁻, and dried in the under the inert atmosphere, the expected Pt/SiC product was obtained.

**Roughly estimate the cost of Pt/SiC CE**

Replacing Pt CE catalyst with Pt/SiC (10 wt.% Pt loading), Pt use in DSC devices can be substantially reduced, which will result in at least 90 % cost reduction based on the price of noble metal Pt (*Monthly Average Price $51.96 per gram for May 2012, Johnson Matthey Plc*) and low-cost commercial SiC (*about several*
thousands of dollar per metric ton). Rough estimate of the cost of the as-prepared Pt/SiC composite counter electrode (CE) film is ¥0.70 (RMB) per cm$^2$ based on the market price of 100% Pt CE (RMB: ¥7.0 per cm$^2$) from Yingkou Opvtech New Energy Co.Ltd (China), Global Poineer in Organic Photovoltaic Technology. Company website: [http://www.opvtech.com/](http://www.opvtech.com/). This price will further decreased in the commercial process of the DSCs in future.

**X-ray diffraction peak assignments of the SiC(β-SiC)**

Chemical composition, crystal structures, space groups and lattice parameters of the Silicon carbide were summarized in Table S1. The polytypes of SiC in the present work is 3C (β), that is, the beta modification (β-SiC), with a zinc blende crystal structure. In Fig.1, X-ray diffraction peak assignments of the 3C-SiC(β-SiC) were as follows: the diffraction peaks at 36.60°, 41.36°, 59.94°, 71.74° and 75.54° are assigned to the crystal planes (111), (200), (220), (311) and (222), respectively. The diffraction peaks at 39.76°, 46.24° and 67.46° for Pt are assigned to the crystal planes (111), (200) and (220), respectively. The corresponding JCPDS card data were listed in Table S1.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Crystal structures</th>
<th>Space groups</th>
<th>JCPDS Card*</th>
<th>a (Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3C-SiC(β-SiC)</td>
<td>Zinc blende (cubic)</td>
<td>F$\bar{4}$3m[216]</td>
<td>65-0360</td>
<td>4.358</td>
<td>4.358</td>
<td>4.358</td>
</tr>
<tr>
<td>Pt</td>
<td>Cubic</td>
<td>Fm$\bar{3}$m [225]</td>
<td>04-0802</td>
<td>3.923</td>
<td>3.923</td>
<td>3.923</td>
</tr>
</tbody>
</table>

* PDF-2 data base.

**Structure morphologies of the Pt/SiC nanocomposites**
Preparation of SiC, Pt/SiC and Pt CEs as well as TiO2 Photoanode

The preparation of SiC and Pt/SiC CEs can be described as follows: 300 mg of SiC and Pt/SiC powder and a definite mount ZrO2 pearl were dispersed in 6 mL isopropanol and milled for 4 h. The obtained solution was then sprayed on an FTO glass substrate (Asahi Glass, type-U, 14 Ω sq⁻¹ Japan) using an airbrush (TD-128, Tiandi Co., Ltd.). The FTO glass substrate coated with SiC and Pt/SiC film was then annealed under N₂ atmosphere at 400 °C for 30 min in a tube furnace. Pt CE, designated hereafter dipping Pt in the present work, was prepared using a two step dip-coating process ¹⁻³. The FTO glass was immersed into conditioner for 5 min followed by activation with PVP-capped Pt nanoclusters for 5 min. The FTO glass was rinsed with de-ionized water, and dried, then heated in furnace at 270 °C for 10
Finally, the dipping-Pt CE was prepared. A 12-μm-thick TiO₂ (P25, Degussa, Germany) film with a grain size of 20 nm was coated on an FTO glass substrate by screen printing technique. The obtained film was annealed at 500 °C for 30 min and then cooled to 80 °C. The resulting TiO₂ films were immersed in 0.5 mM solution of N719 dye (Solaronix SA, Switzerland) in ethanol solution for 20 h to the dye-sensitized TiO₂ photoanode.

**Fabrication of DSCs and symmetrical cells**

A sandwich DSC with a 0.16 cm² active area was assembled with a dye-sensitized TiO₂ photoanode, a SiC or Pt/SiC CE, and an electrolyte containing 0.06M of LiI, 0.03M I₂, 0.6M 1-butyl-3-methylimidazolium iodide, 0.5M 4-tert-butyl pyridine, and 0.1M guanidinium thiocyanate in the acetonitrile solution. The as-assembled cells were used for photovoltaic performance test. The symmetrical dummy cell was fabricated by two identical CEs, and then the electrolyte, similar to that used in assembled DSCs, was filled in the symmetrical dummy cell and sealed with double-faced insulated adhesive tapes. The as-fabricated symmetrical cells were used in the EIS and Tafel tests. The active area of symmetrical dummy cell is 0.49 cm².

**The parameter of Tafel polarization curves**

Theoretically, the Tafel curve can be divided into 3 zones. The curve at low potential curve (|U|<120 mV) is attributed to the polarization zone, where the potential (V) is a linear function of current density (J). The slope of this region is the charge transfer resistance (R_{ct}), which is inversely proportional to the exchange current density (J₀), an important indicator to assess the electrochemical reaction activity, based on Eq.1.
The curve at middle potential (with a sharp slope) is attributed to the Tafel zone, where the potential \( V \) is a linear function of the logarithmic current density \( \text{Lg}J \) according to Eq.2. The curve at high potential (horizontal part) arises from the limiting diffusion zone, which depends on the transport of triiodide and iodide in the electrolyte. In the latter two zones, we can obtain information on the exchange current density \( J_0 \) and the limiting diffusion current density \( J_{\text{lim}} \), which interconnects closely with the catalytic activity of the catalysts. In terms of Eq.2 in the Tafel zone \( J_0 \) can be obtained by extending the line to the voltage as zero, and the current density \( J \) received from there. The intersection of the cathodic branch and the equilibrium potential line can be regarded as \( J_0 \). Thus a steep slope of the Tafel zone to some extent holds a large \( J_0 \). As shown in Fig. S2, a steep slope of the curve indicates a high \( J_0 \) on the CE surface. By comparison \( J_0 \), we can know that which CE material has a relatively higher catalytic activity for the reduction of triiodide ions. A smaller \( J_0 \) indicates a poor catalytic activity for the reduction of triiodide ions. In the diffusion zone, \( J_{\text{lim}} \) is determined by the diffusion properties of the redox couple and the CE catalysts. The intersection of the cathodic branch with the Y axis can be regarded as \( J_{\text{lim}} \). A large \( J_{\text{lim}} \) indicates a large diffusion coefficient at the same potential, meaning a higher diffusion velocity for the redox couple in the electrolyte, which is one reason that results in the DSCs exhibiting a relatively high photovoltaic performance. From the Eq.1 and Eq.3, it is clear that \( J_0 \) changes inversely with \( R_{\text{ct}} \) whereas \( J_{\text{lim}} \) varies linearly with the diffusion coefficient \( D \).
Fig. S2 Annotations of the Tafel curves

$$J_0 = \frac{RT}{nFR_{cr}}$$  \hspace{1cm} (1)

$$V = \frac{2.3RT(\log J - \log J_0)}{\alpha nF}$$  \hspace{1cm} (2)

$$D = \frac{l}{2nFC}J_{\text{lim}}$$  \hspace{1cm} (3)

where $R$ is the gas constant, $T$ is the temperature, $D$ is the diffusion coefficient of the triiodide, $l$ is the spacer thickness, $C$ is the triiodide concentration, $F$ is the Faraday constant, $\alpha$ is the distribution coefficient and $n$ is the number of electrons exchanged in the reaction at the electrolyte-CE interface.

**Characterization of microstructure and electrochemistry for CEs materials**

X-ray powder diffraction (XRD) patterns at room temperature were obtained on an automated X-Ray powder diffractometer (D/Max 2400, RIGAKU) with a rotating anode using Cu K$_\alpha$ radiation. The surface morphologies of SiC and Pt/SiC were observed using scanning electron microscopy (SEM, FEI HITACHI S-4800). Transmission electron microscope (TEM) images, the selected area electron diffraction (SAED) patterns and high-resolution transmission electron microscopy
(HR-TEM) images were obtained using a JEOL JEM-3010 microscope (TEM, JEOL JEM-3010). Cyclic voltammetry was performed on a CHI 660 (SHANGHAI, CHEN HUA) electrochemical analyzer in a three-electrode system. The scan rate is 0.01 V/s. Pt electrode is used as CE and Ag/Ag⁺ works as reference electrode. Photocurrent-voltage performance of the DSCs was measured with a Keithley digital source meter (Keithley 2601, USA) under simulated sunlight illumination condition (Xe arc lamp, 1.5 AM, 1000 W/m², PEC-L15, Peccell, Japan). The electrochemistry properties of three binary tantalum compounds CEs at frequencies ranging from 100 mHz to 1 MHz were measured with a computer-controlled potentiostat (Zennium Zahner, Germany) at the bias potential (-0.75 V) and the AC amplitude (10 mV). The spectra of the obtained EIS were fitted by Zview software. The equivalent circuit of the symmetrical cells is shown in Fig. S3. Tafel-polarization measurement was carried out on an electrochemical workstation system (LK-9805, Tianjin Lanli Inc.).

References: