Supplementary Material (ESI) for Chemical Communications

Platinum-free tungsten carbides as an efficient counter electrode for dye sensitized solar cells

Jum Suk Jan[§], Dong Jin Ham[§], Easwaramoorthi Ramasamy[§], Jinwoo Lee*, Jae Sung Lee*

[§]These authors contributed equally to this work.

[*] Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang, Korea. Fax: 82 54 279 8299; Tel: 82 54 279 2266; E-mail:jlee@postech.ac.kr, jinwoo03@postech.ac.kr

Preparation of mesoporous tungsten carbide catalysts

Two mesoporous tungsten mono-carbides were fabricated by calcination process of polymer intermediate obtained from the mixture of resorcinol, formaldehyde, ammonium metatungstate (AMT) and cetyltrimethylammonium bromide (CTABr). Thus, 18 mmol of CTABr were dissolved in 20 ml water, and another solution containing 1.7 mmol of AMT, 1.1 mmol of resorcinol, and 2.2 mmol of formaldehyde was added to previous CTABr solution. The mixture underwent conventional hydrothermal reaction at 423 K for 48 h and microwave-assisted hydrothermal process at 423 K for 1.5 h to obtain Polymer Derived WC (WC-PD) and Microwave-assisted MW (WC-MW), respectively. And then, resulting gel was calcined at 1173 K for 1 h under Ar and for 2 h under H_2 with the same flow rate of 68 μmole/sec for each gas.

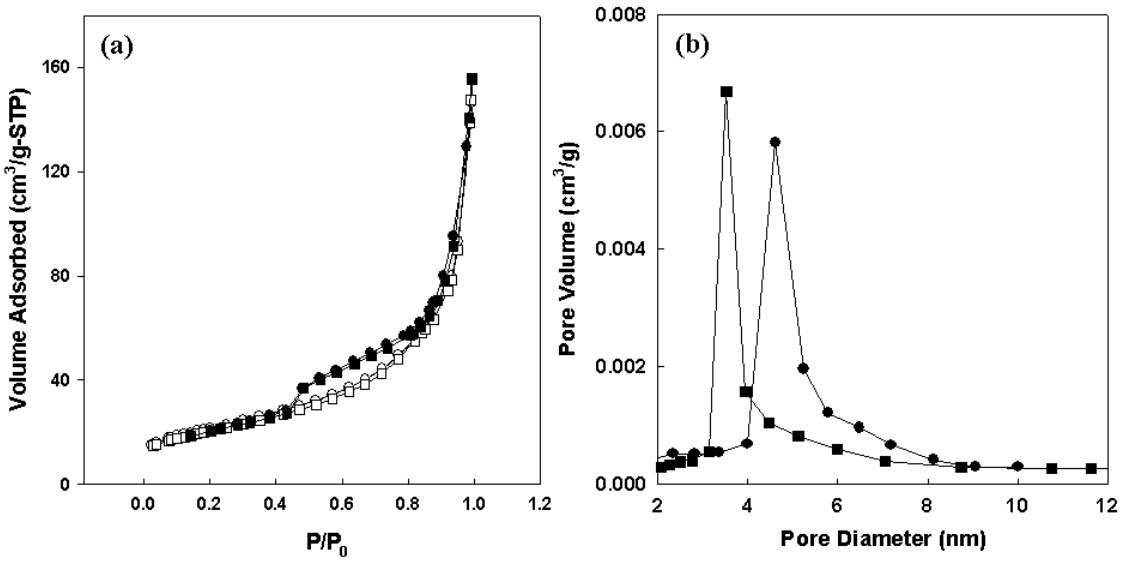

Figure S1. (a) N_2 adsorption-desorption isotherms for WC-PD (○,●), WC-MW (□,■). Filled and empty symbols denote adsorption and desorption branches of N_2 isotherms, respectively. (b) Pore-size distributions calculated by the BJH method from the desorption branch of the N_2 isotherm for WC-PD (●), WC-MW (■).

N_2 adsorption/desorption isotherms are shown in Figure S1(a) for WC-PD, WC-MW samples. The as-prepared mesoporous WC samples exhibit similar isotherm patterns corresponding to Type IV hysteresis. Pore size distribution curves of the samples are shown in Figure S1(b). The WC-PD has a slightly larger average pore diameter (ca. 4.5 nm) than that of the WC-MW (ca. 3.8 nm). The BET surface areas of the WC-PD, WC-MW samples are 64 and73 m^2g^{-1}, respectively.

WC counter electrode preparation

A 0.2 g of WC powders were finely ground in mortar and then mixed with 0.18 g of binder solution composed of ethyl cellulose (5 wt%)) in α-terpineol. The resultant homogenous WC paste was coated onto a FTO glass substrate (TEC-15, Hartford) by doctor blading method. After drying at room temperature, electrodes were heated at 250 ^{o}C for 1 h in air. The thickness of WC (a), WC-MW (b) films was ca. 10 μm, and they seemed to be well attached on FTO glass (Figure S2).

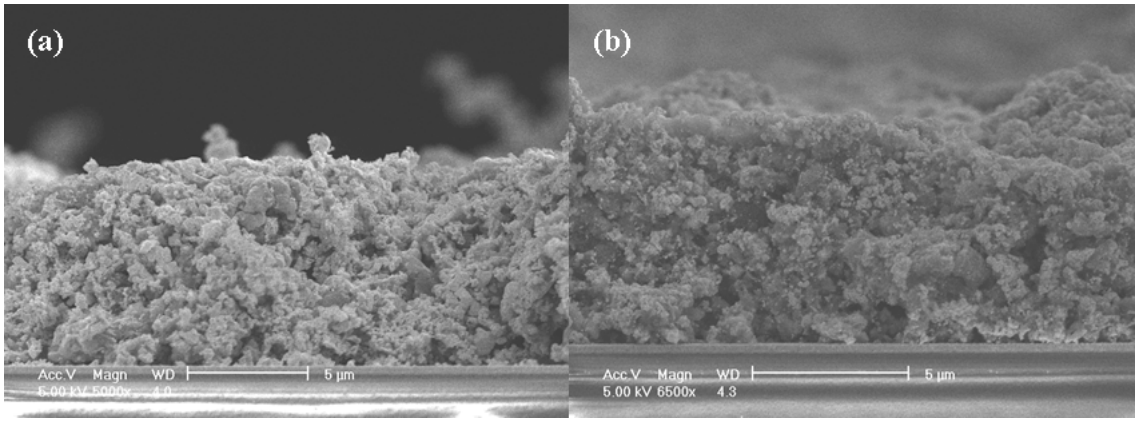

Figure S2. SEM images of cross section of WC-PD (a), WC-MW (b) film on FTO glass substrate.

TiO_2 working electrode and DSSC fabrication

The bilayer working electrodes comprised of ~15 μm thick nano-crystalline TiO_2 layer and 3 μm thick light scattering layer were prepared by screen printing method. After sintering at 500 ºC for 30 min in air, electrodes were soaked in a 0.5 mM solution of N719 dye in mixed solvent of acetonitrile and *tert*-butanol (volume ration 1:1) for 24 h. Dye sensitized TiO_2 electrodes were rinsed with anhydrous ethanol, dried in nitrogen flow, and assembled in a sandwich configuration with various WC counter electrodes. The liquid electrolyte with 0.5M 1-butyl-3-methylimidazolium iodide, 0.05M I_2 and

0.5M 4-*tert*-butylpyridine in acetonitrile was introduced into the cell via vacuum back filling method. The electrolyte injection hole was firmly sealed by Surlyn and microscope cover glass.

I-V characterization

Current-voltage characteristics of the DSSCs were measured both in the dark and under 1 sun illumination (100 $mW.cm^{-2}$, Air mass 1.5G) with Peccell (Model: PEL-L11) solar simulator. The intensity of incident solar light was adjusted to 1 sun condition using NREL calibrated silicon reference cell equipped with a KG-5 filter.

Cyclic voltammetry measurent

Cyclic voltammetry (CV) experiments were performed with Reference 600 potentiostat (Gamry Instruments) in a three-electrode configuration. WC or Pt coated FTO glass substrate was employed as a working electrode. Pt coil and Ag/AgCl electrode were used as counter and reference electrode, respectively. The electrolyte was 10 mM LiI, 1 mM I_2 and 0.1M $LiClO_4$ in acetonitrile.

Symmetric cell and EIS analysis

A thin layer symmetric cell was fabricated by stacking two similar WC or Pt electrodes on each other with surlyn polymer foil spacer and sealed by heating at hot plate. The liquid electrolyte composed of 0.5M 1-butyl-3-methylimidazolium iodide, 0.05M I_2 and 0.5M 4-*tert*-butylpyridine in acetonitrile was introduced into the cell gap through vacuum back filling method. Electrochemical impedance spectroscopy (EIS) analysis was carried out at 0 V over the frequency range of 0.1 Hz to 100 kHz.

Effect of WC counter electrode heat-treatment temperature

The WC counter electrodes were typically fabricated by coating the WC paste on FTO glass substrate followed by heat treatment at 250 ^{o}C for 1h in air. Therefore it is necessary to evaluate the effect of WC oxidation on the photoelectrochemical properties of DSSCs. As normally used organic binders (i.e, α-terpineol) burnout only at high temperature, new WC paste was prepared by mixing WC-MW powders in carboxymethyl cellulose (CMC) dissolved deionised water. The obtained paste was coated on FTO glass substrate and heat treated at 100 or 250 ^{o}C for 1h in air. As shown in Figure S3 and Table S1, heat treatment does not give rise to a large effect on the photovoltaic performance. This result confirming that WCs are fairly stable and retain the intrinsic electrocatalytic features during the course of counter electrode preparation.

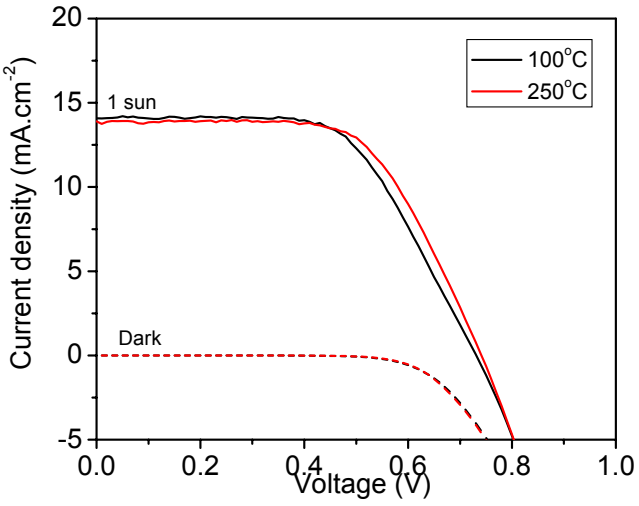

Figure S3. Current-voltage characteristics of DSSCs with WC-MW counter electrodes heat treated at 100 and 250 ^{o}C.

Table S1: Photovoltaic properties of DSSC with WC-MW counter electrodes heat treated at 100 and 250 ^{o}C, under 100mWcm^{-2}, AM 1.5G illumination.

Temperature	V_{OC} (V)	J_{SC} (mA.cm^{-2})	FF	η (%)
100^{o}C	0.731	14.11	0.61	6.29
250^{o}C	0.741	13.95	0.63	6.51