Supplementary Material (ESI) for Chemical Communications

Large pore sized mesoporous carbon electrocatalyst for efficient dye-sensitized solar cells

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Synthesis of ordered large pore size mesoporous carbon (MSU-F-C): A mesoporous silica template (MSU-F) exhibiting hexagonal structure was synthesized by following published procedures. Post-synthesis alumination was carried on MSU-F template to generate the acidic catalytic sites for the polymerization of furfuryl alcohol inside the mesopores. In a typical synthesis, 1 g of AlMSU-F was wetted with 1.5 ml of furfuryl alcohol using the incipient wetness technique and polymerized at 85^{o}C for 4 h. The composite was carbonized at 850^{o}C for 2 h under N_2 flow. Finally, the MSU-F-C was obtained by dissolution of silica template in HF solution. Fig.S1 shows the thermogravimetric analysis (TGA) of MSU-F-C carbon powder performed in air with a heating rate of 10 °C min^{-1}. The observed residual mass of 2.9% at 700 ^{o}C confirms that MSU-F-C is virtually silica free.

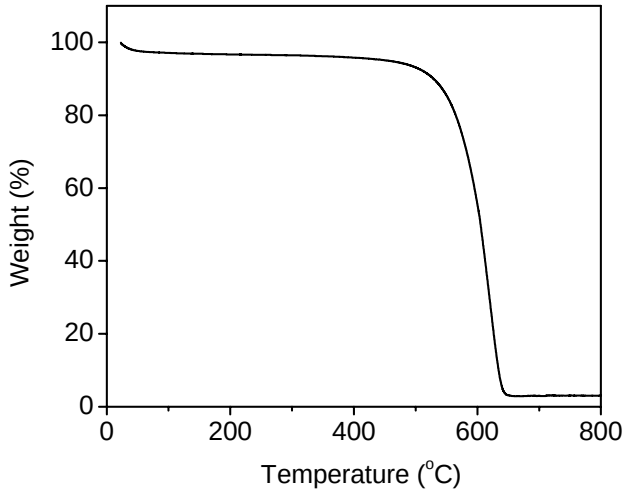

Fig.S1 TGA curve of MSU-F-C carbon powder performed in air with a heating rate of 10 °C min^{-1}.

Synthesis of CMK-3 carbon: The CMK-3 carbon was prepared through SBA-15 silica as a template and furfuryl alcohol as a carbon source. As synthesized SBA-15 silica was impregnated with $AlCl_3$ (Si / Al mole ratio = 20), to generate the catalytic sites for the polymerization of furfuryl alcohol inside the

mesoporous template. By following the similar carbonization and etching procedure of MSU-F-C, CMK-3 carbon with an average particle size of 1μm and BET surface area of 1400 m^2g^{-1} were obtained. Nitrogen adsorption-desorption isotherm in Fig.S2 indicates the nanoporous structure of the CMK-3 carbon with pore size distribution centred at 3 nm.

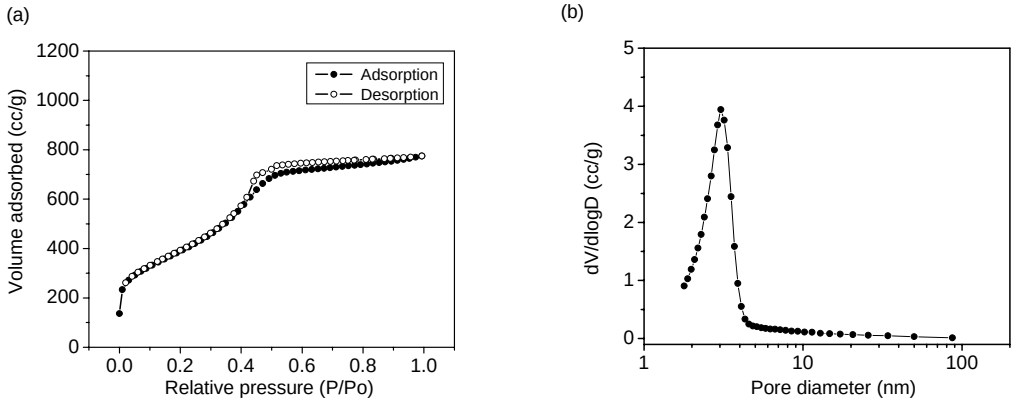

Fig.S2 (a) Nitrogen adsorption-desorption isotherm and, (b) Pore size distribution of CMK-3 carbon.

Symmetric cell and EIS analysis: A 12 mg of large pore sized mesoporous carbon powder (MSU-F-C) was ultrasonically dispersed in 12ml of anhydrous ethanol. The solution was transferred to a portable spray gun connected with N_2 carrier gas and deposited on F doped SnO_2 (FTO) glass substrate. The spray parameters such as solution flow rate, substrate temperature and the distance between spray nozzle and FTO glass substrate were optimized for uniform deposition of carbon film on FTO glass substrate. Fig. S3 shows the typical SEM images of MSU-F-C carbon powders spray deposited on FTO glass substrate at 100^{o}C. The average thickness of MSU-F-C film on FTO glass substrate was about 1.1 μm. In a similar way, CMK-3 and Vulcan XC-72 carbon electrodes were also prepared. A thin layer symmetric cell was fabricated by stacking two similar carbon 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. The schematic of completed thin symmetric cell was shown in Fig. S4. Electrochemical impedance spectroscopy measurements were carried out with Reference 600

Potentiostat/Galvanostat (Gamry instruments) in the frequency range of 0.1 Hz to 100 kHz. The magnitude of the alternative signal was 10 mV.

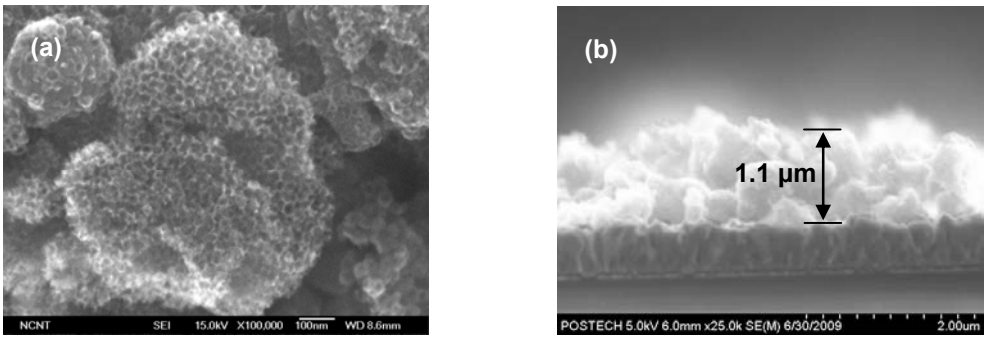

Fig.S3 SEM images of MSU-F-C carbon film on FTO glass substrate by spray deposition method, (a) Top-view and (b) Cross-sectional view.

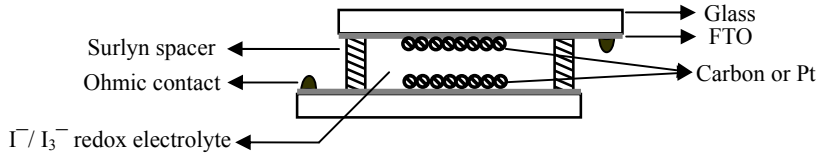

Fig.S4 Schematic illustration of thin layer symmetric cell with two similar carbon or Pt electrodes.

DSSC fabrication and I-V characterization: The bilayer working electrodes comprise 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 with the counter electrode made by spray deposition of MSU-F-C on FTO glass substrate. In order to have a good comparison with MSU-F-C counter electrodes, CMK-3, Vulcan and conventional Pt counter electrode DSSCs were also prepared as described above. 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.

Quasi-solid DSSCs were fabricated by using 9 μm thick nano-crystalline TiO_2 working electrode. A 5 wt% of poly (vinyldenefluoride-*co*-hexafluropropylene) (PVDF-HFP) was mixed with polymer electrolyte consisting of 0.5M 1-butyl-3-methylimidazolium iodide, 0.05M I_2, 0.5M 4-*tert*-butylpyridine in ethylene carbonate and propylene carbonate (volume ratio 1:1) and heated at 100 ^oC until PVDF-HFP was completely dissolved. The resultant hot and viscous solution was immediately introduced into the cell through an electrolyte injection hole, and firmly sealed by surlyn and microscope cover glass. After cooling down to the room temperature, motionless polymer gel electrolyte was observed inside the DSSC. 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). The intensity of incident solar light was adjusted to 1 sun condition using NREL calibrated silicon reference cell equipped with a KG-5 filter.