

# Soft-Template Simple Synthesis of Ordered Mesoporous Titanium Nitride-Carbon Nanocomposite for High Performance Dye-Sensitized Solar Cell Counter Electrodes

Easwaramoorthi Ramasamy,<sup>‡</sup> Changshin Jo,<sup>‡</sup> Arockiam Anthonysamy, Inyoung Jeong, Jin Kon Kim, and Jinwoo Lee\*

Department of Chemical Engineering, Pohang University of Science and Technology,  
Kyungbuk, 790-784, Korea

## 1. EXPERIMENTAL

### 1.1 Synthesis of the Organic Redox Couple

#### 5-mercapto-1-methyltetrazole N-tetramethylammonium salt (NMe<sub>4</sub><sup>+</sup>T<sup>-</sup>)

The organic redox couple was synthesized according to the literature.<sup>[1]</sup> 5-Mercapto-1-methyltetrazole (4.38 g, 37.8 mmol) (Aldrich, 98%) was neutralized with a 25-wt% solution of tetramethylammonium hydroxide in methanol (4.2 mL, 39.9 mmol) (Aldrich) added drop by drop under nitrogen atmosphere. The mixture was stirred at room temperature for 12 h. After the solvent's evaporation, the resulting white solid was dried under vacuum at 40°C for 48 h with P<sub>2</sub>O<sub>5</sub> (Aldrich, 98%).

Melting point = 171-173°C

<sup>1</sup>H-NMR (400 MHz, Bruker AMX400, DMSO-d<sub>6</sub>, ppm): δ = 3.61 (s, 3H, CH<sub>3</sub>), 3.10 (s, 12H, NMe<sub>4</sub><sup>+</sup>).

#### di-5-(1-methyltetrazole) disulfide (T<sub>2</sub>)

T<sub>2</sub> was prepared through the oxidation of 5-mercapto-1-methyltetrazole, using iodine (Aldrich, 99.8%) in water. Under sonication condition, 5-mercapto-1-methyltetrazole (4.0 g, 34.4 mmol) dissolved in the minimum amount of Millipore water and iodine (4.0 g, 15.8 mmol) was added very slowly to the reaction mixture, in 30 min. Then, the mixture was maintained under sonication for another hour until the iodine was consumed. After the reaction has completed, the reaction vessel was stored in the refrigerator for 5 h. The white precipitate was then collected by filtration under vacuum, washed thoroughly with cold Millipore water (4°C) and dried under vacuum at 40°C, for 48 h.

Melting point = 112°C (literature: 112°C)

<sup>1</sup>H-NMR (400 MHz, Bruker AMX400, DMSO-d<sub>6</sub>, ppm): δ = 4.04 (s, 6H, CH<sub>3</sub>).

## **1.2 Synthesis of Ordered Mesoporous Carbon (OMC)**

The ordered mesoporous carbon (OMC) was synthesized following the procedure described in literature.<sup>[2,3]</sup> Initially, 3.2 g of Pluronic F127 was dissolved in 16.0 g of ethanol with 2.0 g of 0.2 M HCl and stirred for 1 h at 40°C. Then, 4.16 g of tetraethyl orthosilicate and 10.0 g of 20 wt% resols' ethanolic solution were added. After stirring for 2 h, the solution was poured into a Petri dish, at room temperature for ethanol evaporation. After 8 h, the film was placed into an oven, at 100°C for 1 day for thermopolymerization. The as-synthesized products were scraped from the dishes and carbonized in nitrogen atmosphere at 350°C, for 3 h and, subsequently, in a tube furnace at 700°C for another hour.

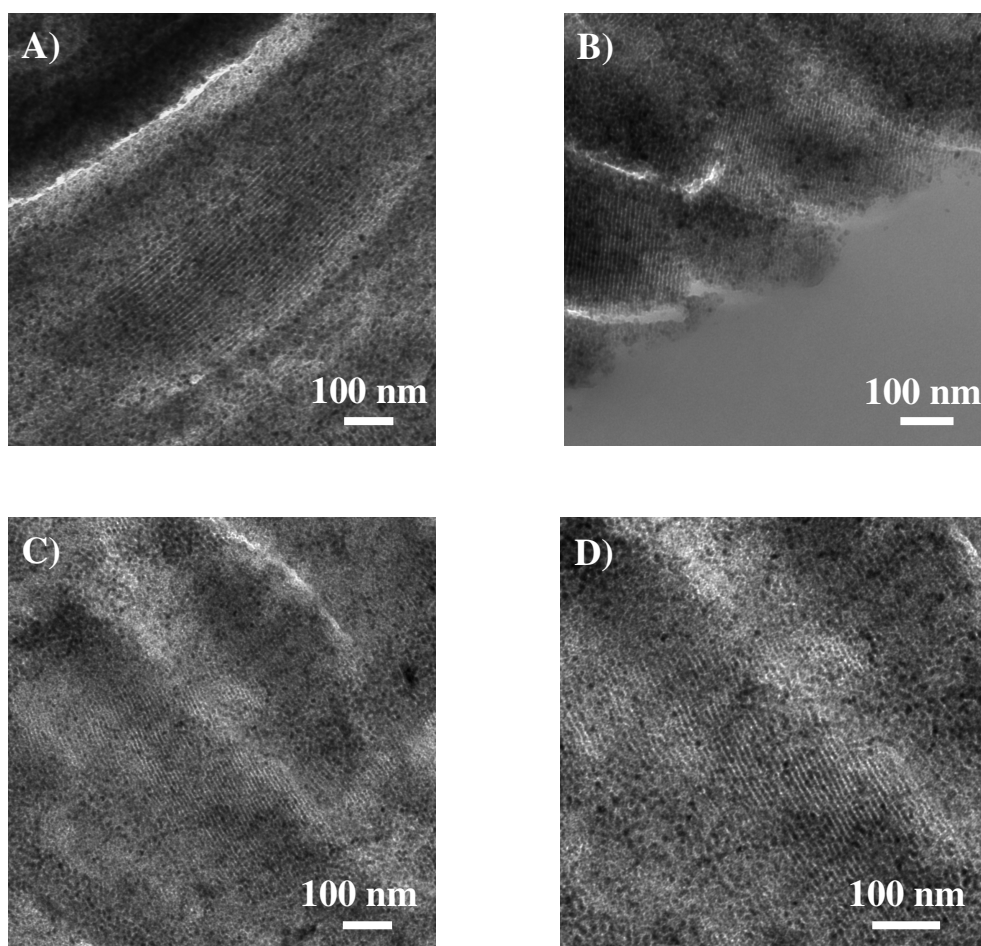
## **1.3 Synthesis of Titanium Nitride Nanoparticles (TiN NPs)**

The titanium nitride nanoparticles (TiN NPs) were synthesized by simply treating the TiO<sub>2</sub> nanoparticles with ammonia. The TiO<sub>2</sub> nanoparticles were synthesized through the sol-gel method<sup>[4]</sup> using titanium tetrachloride (TiCl<sub>4</sub>) and ethanol. In the custom method, 3.0 mL of

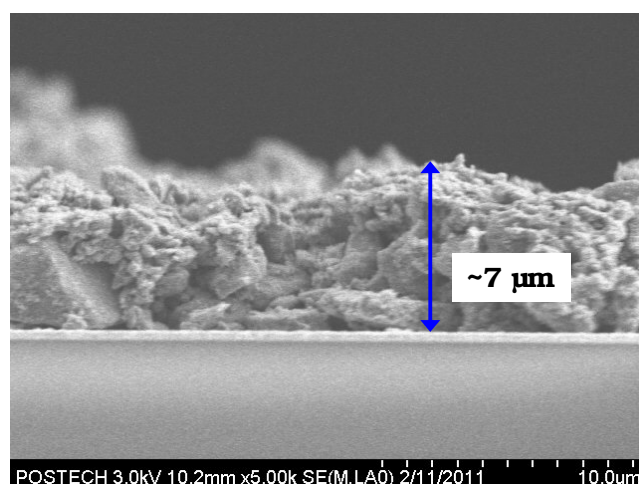
TiCl<sub>4</sub> was slowly mixed with 30.0 mL ethanol at room temperature. The mixture was stirred for several days to form sol-gel. After the colour turned to light yellow, the sol-gel solution was vaporized at 80°C until the dry-gel was obtained. Then, the powder was calcined at 700°C for 1 h in air. Finally, the calcined product was heat-treated at 700°C for 1 h in ammonia atmosphere.

## 2. RESULTS AND DISCUSSIONS

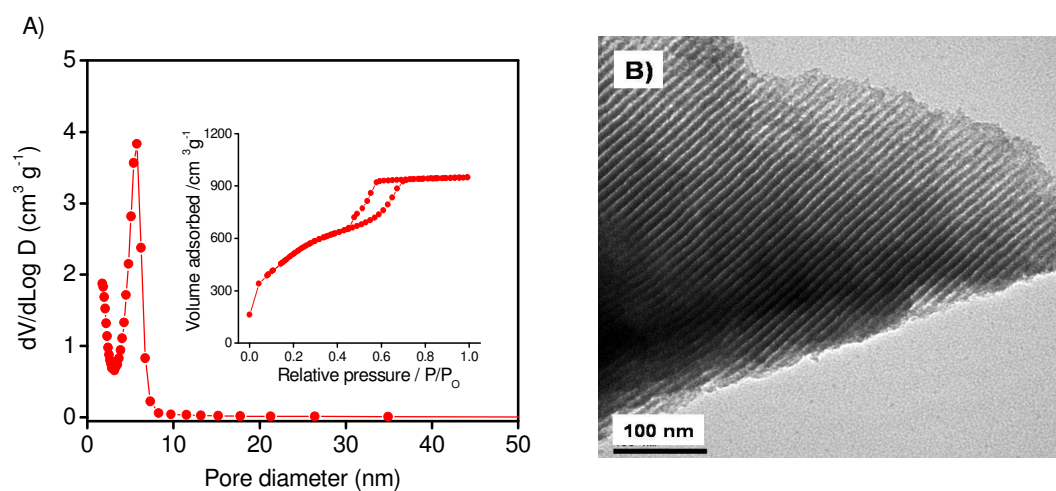
### 2.1 Structural Characterizations



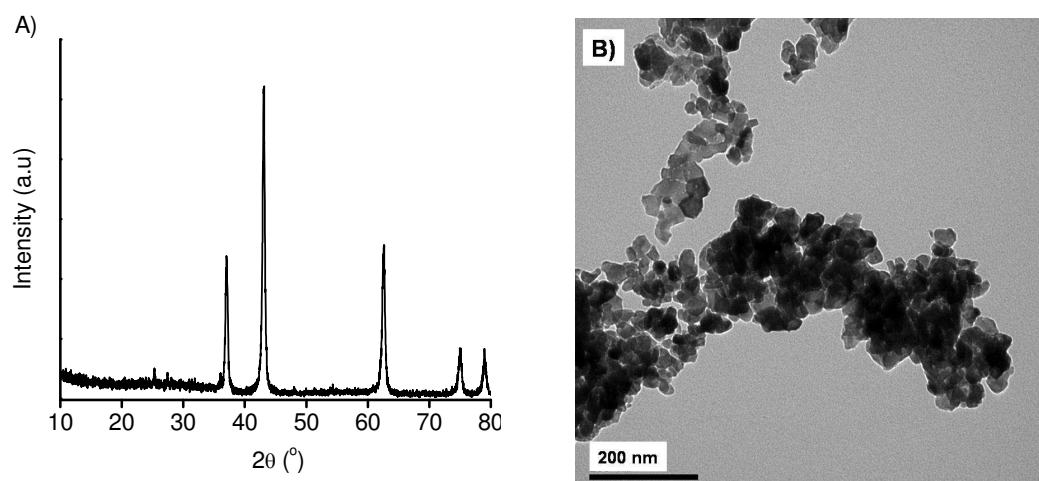
**Figure S1** TEM images of ordered mesoporous TiO<sub>2</sub>-C (A and B) and ordered mesoporous TiN-C nanocomposites (C and D).



**Figure S2** Cross sectional SEM image of OM TiN-C nanocomposite counter electrode. The electrodes were prepared by tape casting the slurry of OM TiN-C on FTO glass substrate followed by heat treatment at 200°C for 1 h in air.

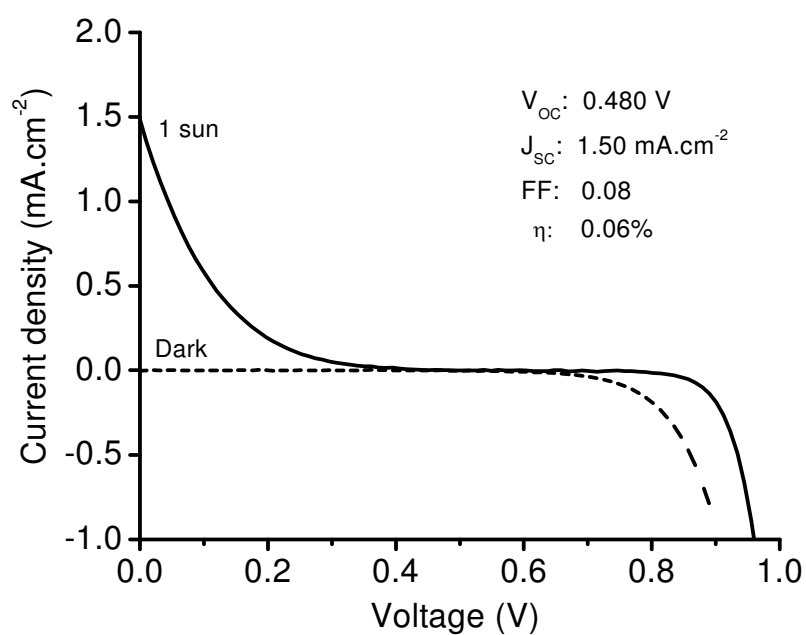


**Figure S3** A) Pore-size distribution curve and  $N_2$  sorption isotherm (inset) and B) TEM image of ordered mesoporous carbon (OMC).

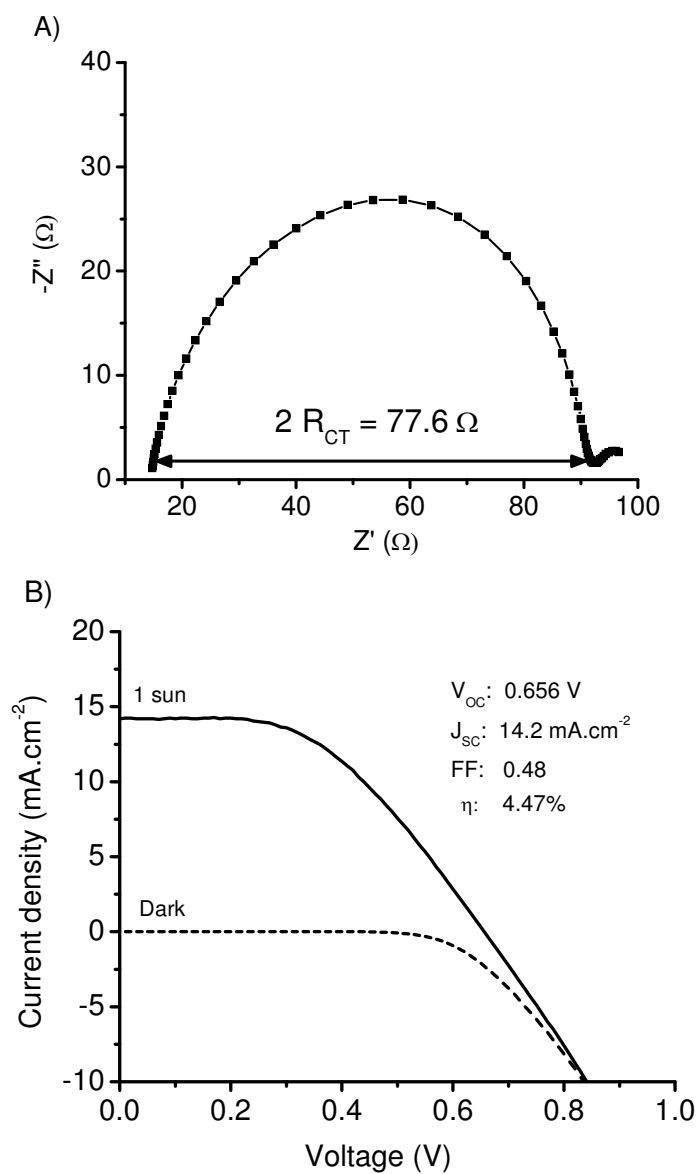


**Figure S4** A) X-ray diffraction pattern and B) TEM image of the TiN nanoparticles.

## 2.2 Photovoltaic characterizations



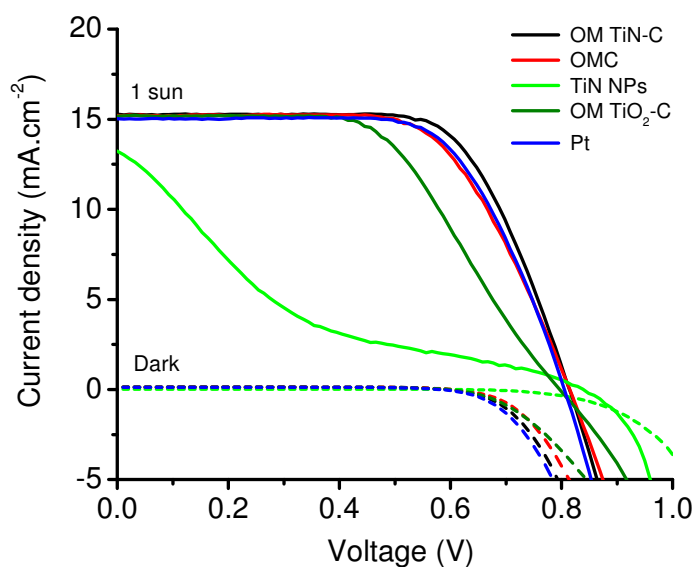
**Figure S5** Current-voltage characteristics of  $\text{T}_2/\text{T}^+$  redox couple electrolyte DSC with bare FTO glass substrate as counter electrode.



**Figure S6** A) Nyquist plot of electrochemical symmetric cell constitutes of two identical OM  $\text{TiO}_2\text{-C}$  nanocomposite electrodes. B) Current-voltage characteristics of  $\text{T}_2/\text{T}^+$  redox couple electrolyte DSC with OM  $\text{TiO}_2\text{-C}$  nanocomposite counter electrode.

### 2.3 Application of OM TiN-C in Iodide Electrolyte Dye-Sensitized Solar Cells

In order to show the versatility of OM TiN-C as an efficient counter electrode in DSC, its performance was also tested in tri-iodide/iodide ( $I_3^-/I^-$ ) electrolyte DSCs (see Table S1 and figure S7 in Supporting Information). Under 1 sun illumination, the OM TiN-C counter electrode device exhibited an energy conversion efficiency of 8.41% and  $FF$  of 0.67%, which are slightly higher than those of the Pt counter electrode. As expected, the conversion efficiency of the OM TiN-C counter electrode was enhanced compared with that of the OMC counter electrode, which is in agreement with Organic Electrolyte DSC results. This indicates that TiN nanocrystals embedded in the mesostructured walls were electrochemically more active than the amorphous carbon materials.



**Figure S7** Current-voltage characteristics of iodine/tri-iodide ( $I_3^-/I^-$ ) redox couple electrolyte DSCs with various counter electrodes.

**Table S1.** Photovoltaic parameters of tri-iodide/iodide ( $I_3^-/I^-$ ) redox couple electrolyte<sup>a</sup> DSCs with various counter electrodes.<sup>b</sup>

Counter electrode	$V_{OC}$ [V]	$J_{SC}$ [mA cm <sup>-2</sup> ]	FF	$\eta$ [%]
OM TiN-C	0.820	15.3	0.67	8.41
OMC	0.818	15.2	0.63	7.83
TiN NPs	0.839	13.2	0.13	1.44
OM TiO <sub>2</sub> -C	0.800	15.2	0.55	6.69
Pt	0.808	15.0	0.66	8.00

<sup>a</sup>Electrolyte composition: 0.5 M 1-butyl-3-methylimidazolium iodide, 0.05 M I<sub>2</sub> and 0.5 M 4-*tert*-butylpyridine in acetonitrile. <sup>b</sup>All other experimental parameters (i.e., photoanode, dye, counter electrode, device fabrication, and I-V characterization) were similar to those described in the main text.



## References

- (1) M. Wang, N. Chamberland, L. Breau, J. E. Moser, R. Humphry-Baker, B. Marsan, S. M. Zakeeruddin, M. Grätzel, *Nature Chem.* **2010**, 2, 385.
- (2) R. Liu, Y. Shi, Y. Wan, Y. Meng, F. Zhang, D. Gu, Z. Chen, B. Tu, D. Zhao, *J. Am. Chem. Soc.* **2006**, 128, 11652.
- (3) E. Ramasamy, J. Chun, J. Lee, *Carbon* **2010**, 48, 4563.
- (4) Y. Zhu, L. Zhang, C. Gao, L. Cao, *J. Mater. Sci.* **2000**, 35, 4049.