Supplementary Material (ESI) for Journal of Materials Chemistry

SUPPORTING INFORMATION

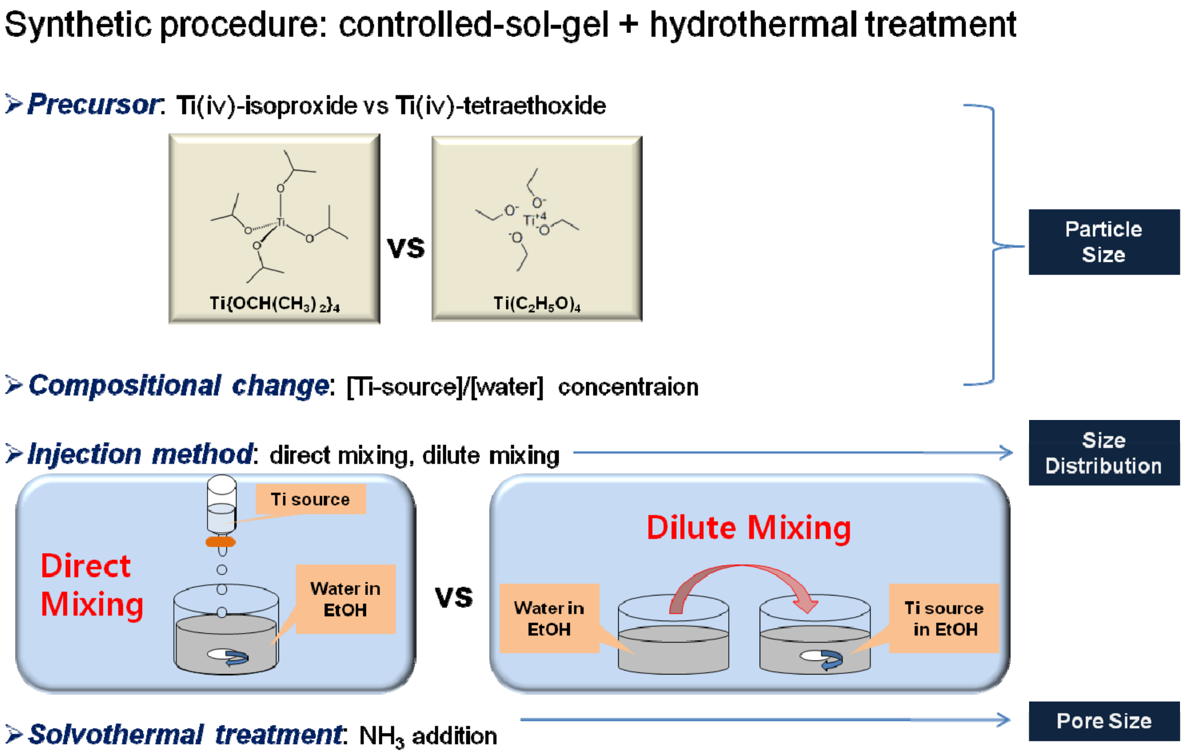
Size-Tunable Mesoporous Spherical TiO_2 as a Scattering Overlayer in High-Performance Dye-Sensitized Solar Cells

Yoon-Cheol Park,[a§] Yong-June Chang,[a,§] Byung-Gon Kum,[a] Eui-Hyun Kong,[a] Jong Yeog Son,[b] Young Soo Kwon,[c] Taiho Park,[c] and Hyun Myung Jang [a,*]

[a]Department of Materials Science and Engineering, and Division of Advanced Materials Science, Pohang University of Science and Technology (POSTECH), Pohang 790-784 (Korea).
[b]Department of Applied Physics, Collage of Applied Science, Kyung Hee University, Suwon 446-701 (Korea)
[c]Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784 (Korea).
[§]Co-first authors. *Corresponding author. Tel : +82-54-279-2138, Fax : +82-54-279-2399, Email : hmjang@postech.ac.kr

Preparation of pore size-controlled MS TiO_2.

Experiments Mesoporous spherical TiO_2 (MS TiO_2) with large surface area and high reflectance was obtained through “dilute mixing”-driven hydrolysis and subsequent solvothermal treatement as shown in **Schematic S1**. For a titanium source, widely used titanium alkoixdes were tested. Titanium tetraethoxide (TTE) was chosen to produce size-tunable amorphous TiO_2 spheres along with [TTE]/[water] concentration. Then, the amorphous TiO_2 spheres underwent sovothermal treatment at 160 °C for 16 hours, resulting in the MS TiO_2 with particle diameter variation (1554 nm for T1, 757 nm for T2, 587 nm for T3). As-prepared three different MS TiO_2 particles interestingly possess the same primary pore sizes of around 10 nm. With the presented synthetic route, not only the particle size but the primary pore size can be adjusted simply by adding NH_3 during the solvothermal process. To investigate the effect of NH_3 on the internal pore sizes, 0-2 mL of NH_3 was added at a fixed [TTE]/[water] ratio (synthetic condition for T3). Therefore, three NH_3-MS TiO_2 samples (T3-0 mL NH_3, T3-1 mL NH_3, T3-2 mL NH_3) were prepared.



Schematic S1. (Color online). Synthetic procedure of size-tunable MS TiO_2.

Nitrogen sorption analysis of NH_3-MS TiO_2 samples Nitrogen isotherms of three NH_3-MS TiO_2 samples are shown in the **Figure S1**. All the samples had type IV isotherms and H1 hysteresis at high relative pressure region (P/P_0=0.8-0.9), indicating the presence of meso-scale internal pores. **Figure S2** shows pore size distribution of each sample. It was observed that pore size was increased as the NH_3 concentration was increased. As summarized in **Table S1**, T3-0 mL NH_3 had the highest surface area of 110.6 m^2/g with the smallest pore size of 8.57 nm and crystallite size of 9.21 nm. After adding 1 and 2 mL of NH_3, their surface areas were reduced with increased pore and crystallite sizes.

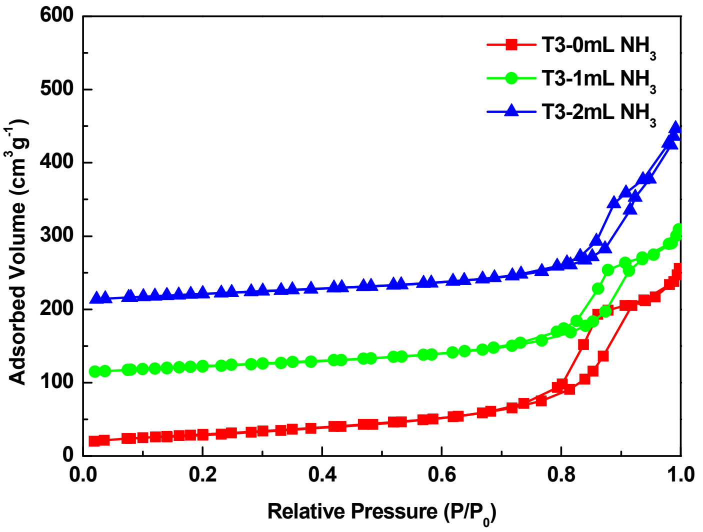


Figure S1. (Color online). Nitrogen sorption isotherms of the NH_3-MS TiO_2 samples (T3-0 mL NH_3, T3-1 mL NH_3, T3-2 mL NH_3). The isotherms of T3-1 mL and T3-2 mL are shifted by 100 and 200 cm^3 g^{-1}, respectively, for the sake of clear presentation.

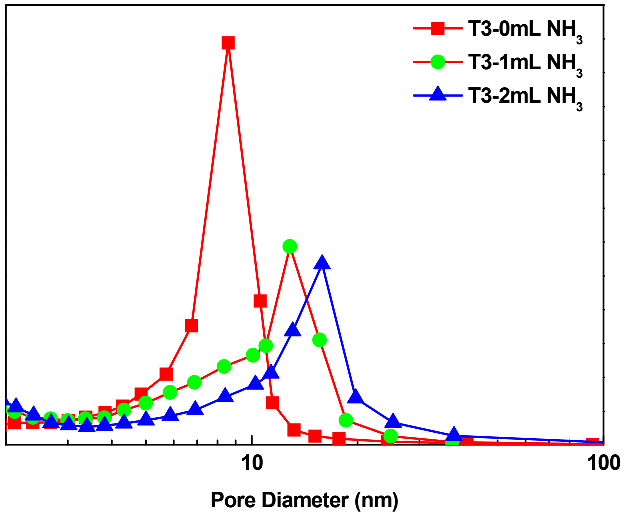


Figure S2. (Color online). Pore size distribution of three NH_3-MS TiO_2 samples (pore size: 8.57 nm, 12.85 nm, 15.87 nm)

Smaple	Surface area (m^2/g)	Pore size (nm)	d_{xrd} (nm)[a]
T3-0 mL NH_3	110.6	8.57	9.21
T3-1 mL NH_3	80.2	12.85	14.94
T3-2 mL NH_3	76.0	15.87	15.79

[a] The crystal size was calculated by applying the Scherrer equation to the anantase (101) peak from the XRD spectra.

Table S1. Physical properties of samples T3-0,1,2 mL NH_3.

Diffuse reflection spectra Light scattering effect can be quantified by measuring the diffuse reflection spectra. T3-0mL NH_3 exhibited the highest reflectance among three NH_3-MS TiO_2 samples over whole spectral range (**Figure S3**). T3-1 mL NH_3, T3-2 mL NH_3 ranked behind T3-0 mL NH_3.

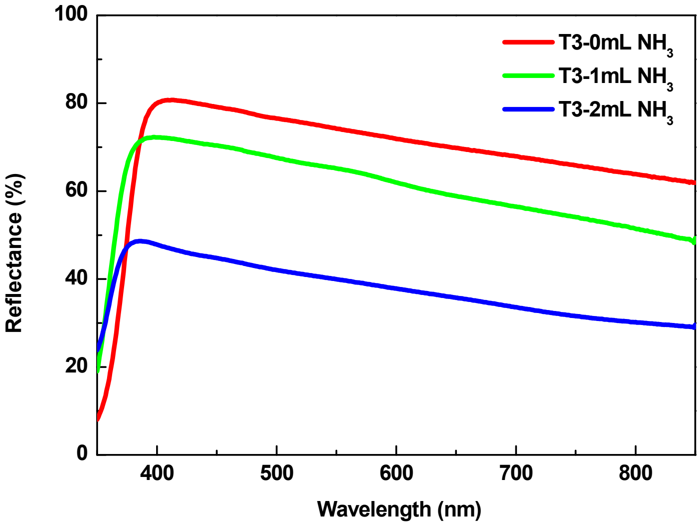


Figure S3. (Color online). Diffuse reflectance of three films made of the NH_3-MS TiO_2 samples.

It is reasonable to conclude that MS TiO_2 without adding NH_3 (T3-0 mL NH_3) is the best choice for a scattering overlayer in dye-sensitized solar cells to achieve high photovoltaic performance, due to the largest surface area for dye-loading and the highest reflectance value for light scattering. Therefore, three distinct size-tunable MS TiO_2 particles were prepared without addition of NH_3 in the solvothermal treatment in the present research. Since as-synthesized MS TiO_2 particles possess almost same pore and crystallite sizes, size-dependent scattering efficiency of hierarchical structures on the light harvest could be studied. NH_3-added MS TiO_2 particles are also being tested as a main layer that can facilitate the dual effects of efficient dye loading and optical confinement.