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Supporting Information

Synthesis and hydrogenation of anatase TiO_2 microspheres composed of porous single crystals for significantly improved photocatalytic activity

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Experimental details

1. Materials

All the chemicals are analytical grade reagents and used as received. Ammonia water (NH_4OH, 30%), ethanol, tetraethyl orthosilicate (TEOS), ammonium fluorotitanate ($(NH_4)_2TiF_6$) were purchased from Sinopharm.

2. Synthesis of PSCs

Porous anatase was synthesized by a very simple hydrothermal method. 396 mg $(NH_4)_2TiF_6$ and 650 mg of silica template were added to 60 ml water in a Teflon-lined stainless autoclave. The sealed vessel was held at 180℃ for 10h. After the reaction, the template product was formed on the bottom of the vessel and rinsed with H_2O by vacuum filtration.

Then the silica template was selectively etched in aqueous 2M NaOH at 80℃ for 10 h. The remaining TiO_2 was collected by vacuum filtration and washed with H_2O and dried at 80℃ (Ms-PSCs).

In the control experiments, solid TiO_2 single crystals were prepared in the same hydrothermal system without the addition of silica template (Ms-BSCs).

3. Hydrogenation of M-PSCs

Ms-PSCs were heated under a H_2 gas flow (50 sccm, atmospheric pressure) at 600°C for 15h [1], leading to the formation of gray hydrogenated microspheres composed of PSCs (HMs-PSCs).

4. Preparation of silica templates

60 nm silica template spheres were synthesized following our previous work [2]. Briefly, 17 ml deionized water, 5 ml ammonia water and 28 ml TEOS were added into 200 ml ethanol and stirred at 700 r.p.m for 24 h at 50 ℃. A translucent solid was prepared by centrifugation of the reaction solution (10000 r.p.m for 30 min). The solid was sintered at 500 ℃ for 30 min to obtain the final close-packed template.

5. Characterization

The crystal structures of the synthesized samples were characterized by XRD (Bruker

D8 Advanc with Cu Kα radiation at 40 kV and 30 mA). The morphology was examined by using field emission SEM (JOEL 6700F) and HRTEM (JEOL2010) equipped with a selected area electron diffraction. DRS was performed on a fiber optic spectrometer spectrophotometer (HR3000-Pro, Jingyi Electronic Science & Technology Co., Ltd.), equipped with an external integrating sphere, by using $BaSO_4$ as the reference. PL spectra were measured on a Fluorescence Spectrophotometer (Varian Cary-Eclipse 500). The exciting wave-length was 315 nm, and the widths of the excitation and emission slits were 10.0 nm. The BET specific surface area and pore size were determined by nitrogen adsorption–desorption isotherm measurements at 77 K on a BELSORP-max system. The chronoamperometry responses were measured on an electrochemical analyzer (RST5200, Zhengzhou Shiruisi Instrument Technology Co., Ltd) in a standard three-electrode system using the prepared samples as the working electrodes with an active area of 1 cm^2, a Pt plate as the counter electrode, and Ag/AgCl electrode as a reference electrode, under a simulated AM 1.5 solar irradiation. Na_2SO_4 (0.1 mol/L) aqueous solution was used as the electrolyte. Working electrodes were prepared as follows: 0.2g of photocatalyst were ground with 5 wt.% of polyvinyl alcohol (PVA) and 0.5 mL of water to make a slurry. The slurry was then coated onto a 1 cm * 1 cm FTO glass electrode by the doctor blade technique. Next, these electrodes were dried in an oven and calcined at 450 ℃ for 30 min.

6. Photoreactivity Measurement

The photocatalytic activity of the samples was evaluated in the decolorization of MO dye under UV light irradiation at 20 ℃. 5 mg of samples were suspended in 20 mL of 10mg/L MO aqueous solution. Before exposure to UV-vis light irradiation, the suspension was stirred in the dark for 1 h. Then, 1 mL of solution was taken out every 10 min (or 20 min), and the TiO_2 was separated from the solution by centrifugation. The remaining clear liquid was used for absorbance measurements at a wavelength of 464 nm on a UV–visible spectrophotometer (T6-1650F, Beijing Persee General Instrument Co., Ltd.). The light source employed in photoreactions is a 250 W high

pressure mercury (Shanghai Jiguang Special Lighting Factory) with predominantly light at 365 nm wave length.

7. Recyclability Measurement

The vacuum filtration experiments were designed to test recyclability of each sample. The separate time from aqueous suspension and the recovery ratio of TiO_2 were measured on a sand core filtration device including a vacuum pump (SHZ-D(III), Shanghai Lichen Science & Technology Co., Ltd.) with the exhaust volume of 10 L/min and the maximum vacuum level of 0.098 MPa. 100 mg TiO_2 was added into 100 ml water to form a suspension, then this suspension was poured into the vacuum filtration device with 0.15 μm membrane to separate solids. The full separation between solid and liquid was achieved when no water was drawn out; after this, the membrane loading TiO_2 was dried at 80 ℃, then TiO_2 was scraped from membrane and compared with its starting state in weight.

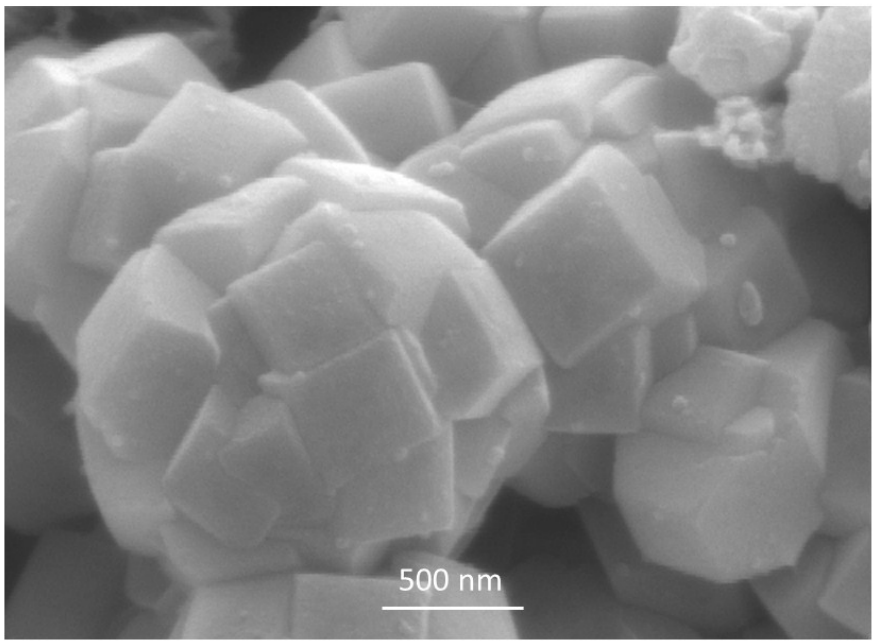

Fig.S1 SEM image of anatase TiO_2 Ms-PSCs before alkaline etching

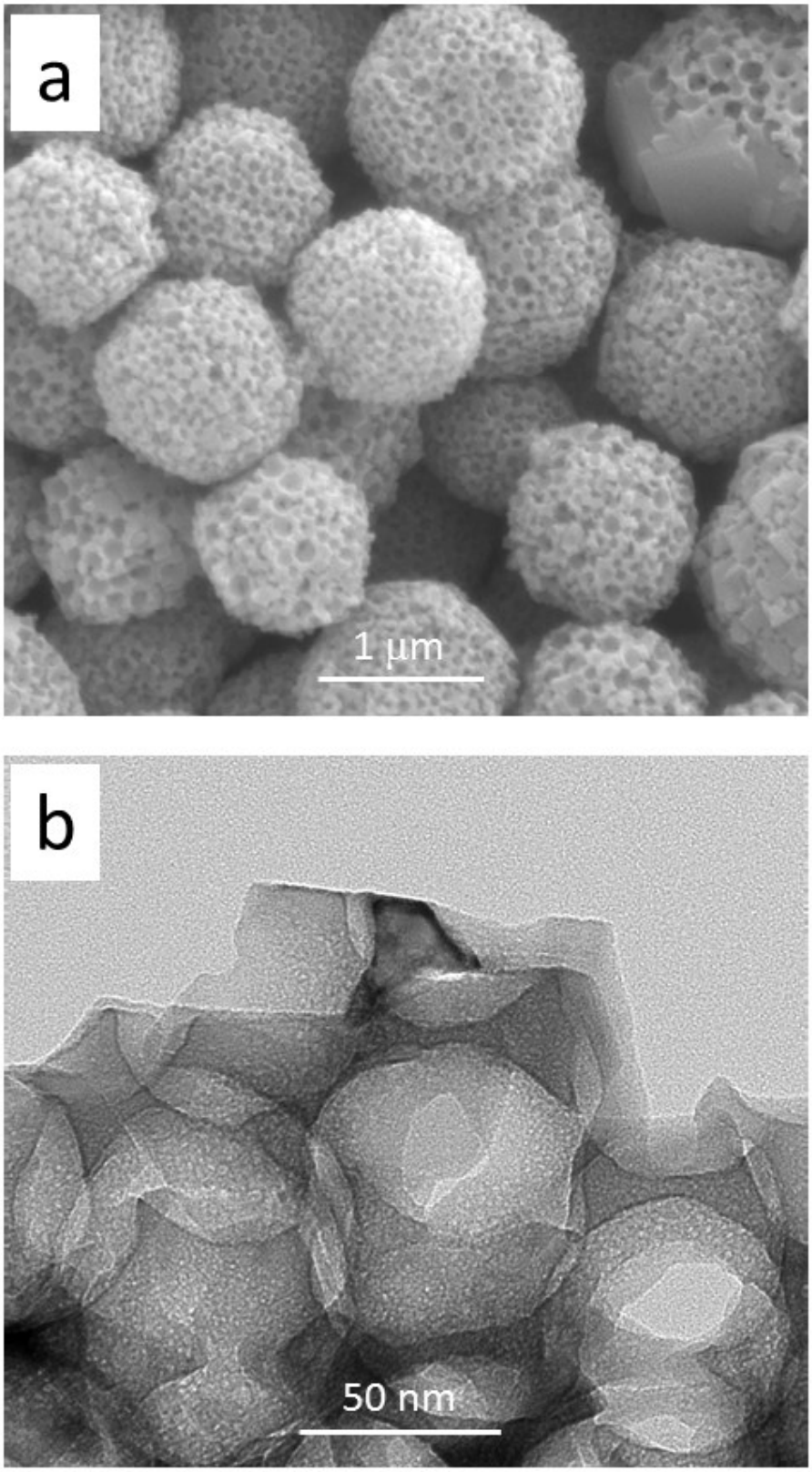

Fig. S2 (a) SEM image of anatase TiO_2 Ms-PSCs; (b) local TEM image of a M-PSC from which pores with the average size of about 60 nm can be clearly seen.

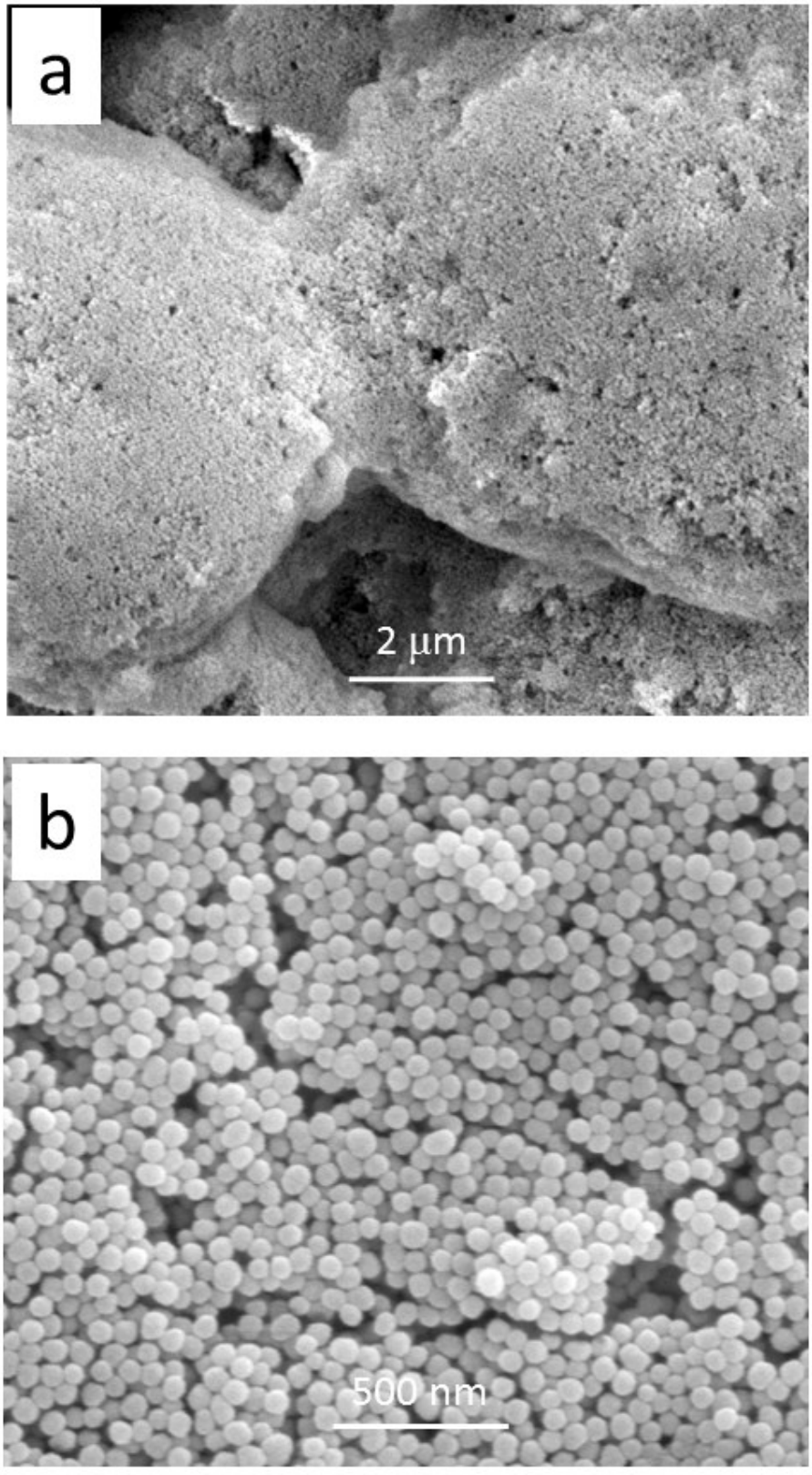

Fig. S3 SEM images of SiO_2 template with low magnification (a) and high magnification (b).

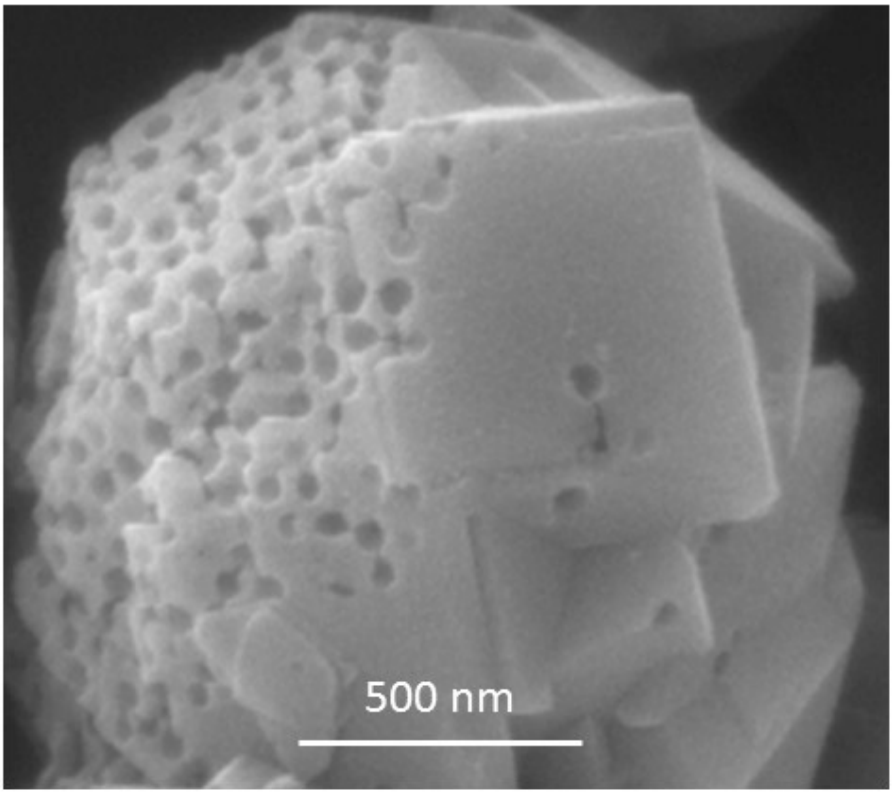

Fig. S4 SEM image of a partial M-PSCs.

Tab. S1 BET surface area values of samples

Samples	BET values
Ms-BSCs	2.58 m2/g
Ms-PSCs	11.70 m2/g
HMs-PSCs	12.45 m2/g
Nano-P25	50.33m2/g

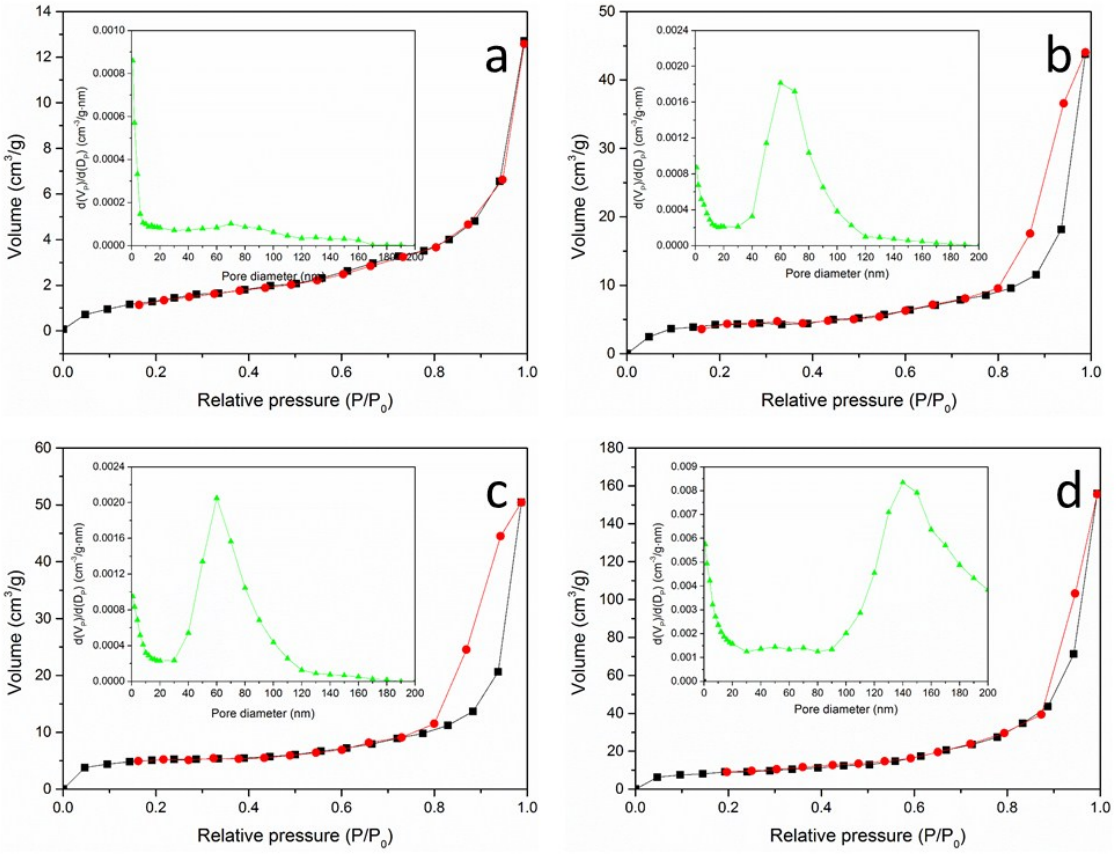

Fig. S5 N_2 adsorption-desorption isotherms of Ms-BSCs (a), Ms-PSCs (b), HMs-PSCs (c) and Nano-P25 (d).

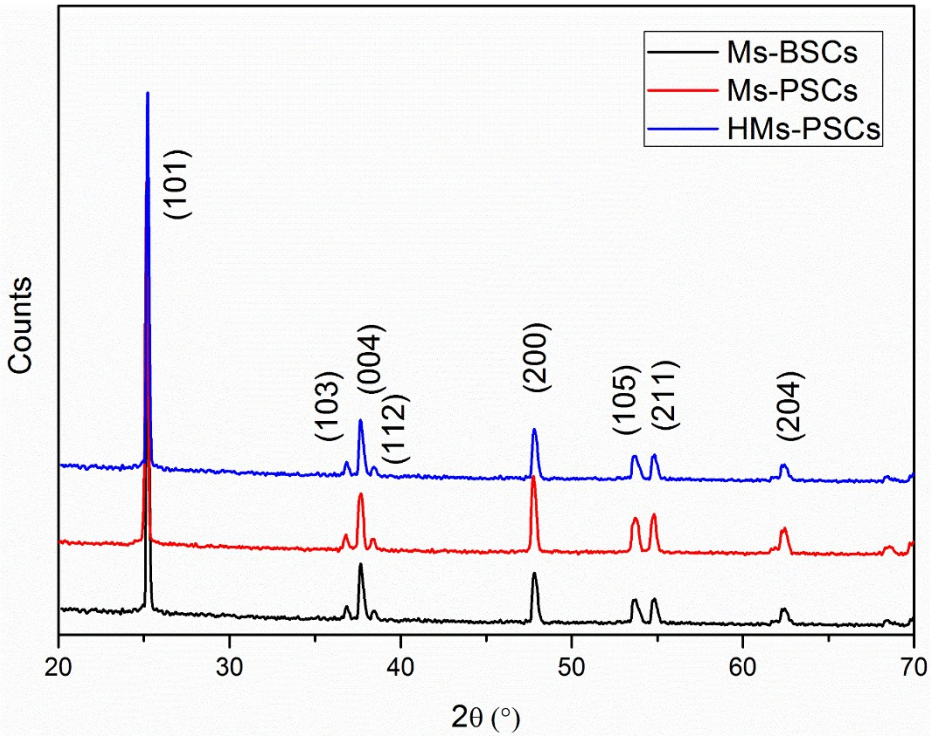

Fig. S6 XRD patterns of samples.

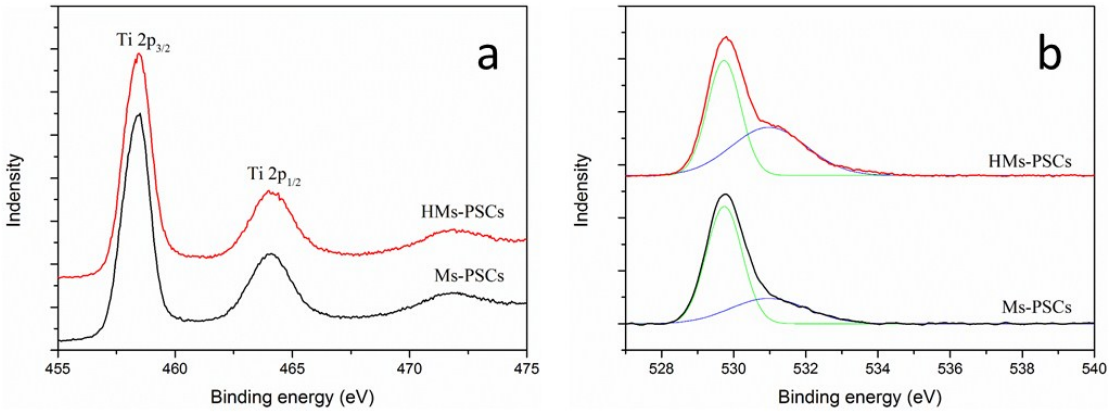

Fig. S7 XPS spectra of Ti 2p (a) and O 1s (b) for Ms-PSCs and HMs-PSCs

References

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[2] Niu, J.; Shen, S.; He, S.; Liu, Z.; Feng, P.; Zhang, S.; Ou, X.; Qiang, Y.; Zhu, Z., Synthesis and photoactivity of anatase porous single crystals with different pore sizes. *Ceram. Int.* 2015, 41, 11936-11944.