

Supporting Information

Anatase TiO₂ microspheres with exposed mirror-like plane {001} facets for high performance dye-sensitized solar cells (DSSCs)

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Experimental Section

Chemicals and Materials. Titanium (Ti) foils (0.25 mm thick, 99.7% purity) were supplied by Aldrich Corporation. Hydrofluoric acid (HF, 48%), acetone, 2-propanol, and methanol (analytical grade) were purchased from Sigma-Aldrich without further treatment prior to use. High-purity deionized water (Millipore Corp., 18 M Ω cm) was used for the reaction solution preparation and the rinse of Ti foils. *Caution in handling Hydrofluoric acid (HF) must be taken as it is an extremely corrosive reagent and can cause great harm when in direct contact!*

Fabrication. Ti foils (50 mm $\times$ 15 mm) were degreased prior to experiments by sonication in acetone, 2-propanol, and methanol, subsequently rinsed with Milli-Q water, and finally dried in a nitrogen stream.¹ The pre-treatment Ti foils as titanium source were put into an autoclave, and 60 mL of 0.5% (v/v) HF solution (pH 1.3) was added to the autoclave as reaction solution. The hydrothermal reaction was carried out at 180 °C for 3 h (or 24 h). After hydrothermal reaction, the product was collected, and then rinsed with Milli-Q water and dried in a N₂ stream. To obtain a clean fluorine-free surface, the as-synthesized product was calcined in air at 600 °C for 1.5 h with heating and cooling rates of 2 °/min.

TiO₂ films composing of anatase TiO₂ microspheres with exposed mirror-like plane {001} crystalline facets and TiO₂ nanoparticles (Degussa P25) were fabricated on pre-treatment FTO conducting glass substrates by a screen-printing technique.² For comparison, commercially available TiO₂ nanoparticles (Degussa P25) and TiO₂ microspheres without exposed mirror-like plane {001} crystalline facets were also used to prepare photoanodes for DSSCs. The fabricated photoanodes were calcined at 450 °C for 1 h, and then sensitized with the dye solution (3×10^{-4} M) and kept for 24 h to complete dye adsorption before DSSCs measurement. The dye solution was

prepared by dissolving N719 ($\text{RuL}_2(\text{NCS})_2(\text{TBA})_2(\text{H}_2\text{O})_4$, $\text{L} = 2,2'$ -bipyridyl-4,4'-dicarboxylic acid, $\text{TBA} =$ tetrabutylammonium, from Dyesol) in butanol and acetonitrile (1:1, v/v).

Characterization. The synthesized samples were comprehensively characterized by SEM (JSM-6300F), TEM (Philips F20), and XRD (Shimadzu XRD-6000 diffractometer, equipped with a graphite monochromator). Diffuse reflectance spectra of the TiO_2 films were recorded on a Varian Cary 5E UV-vis-NIR spectrophotometer. Dye loading measurements were conducted by desorbing the dye molecules from the dye-anchored TiO_2 films in NaOH ethanolic solution (10^{-4} M).³ The loading amount was calculated from the absorbance of the completely desorbed dye solutions by the spectrophotometer (Varian, Cary 4500).

Measurements. A series of DSSCs were fabricated with traditional sandwich type configuration by using a dye-anchored TiO_2 film and a platinum counter electrode deposited on FTO conducting glass. A mask with a window area of 0.15 cm^2 was applied on the TiO_2 film side to define the active area of the cells. A 500 W Xe lamp (Trusttech Co., Beijing) with an AM 1.5G filter (Sciencetech, Canada) was used as the light source. The Light intensity was measured by a radiant power meter (Newport, 70260) coupled with a broadband probe (Newport, 70268). The photovoltaic measurements of DSSCs were recorded by a scanning potentiostat (Model 362, Princeton Applied Research, US).

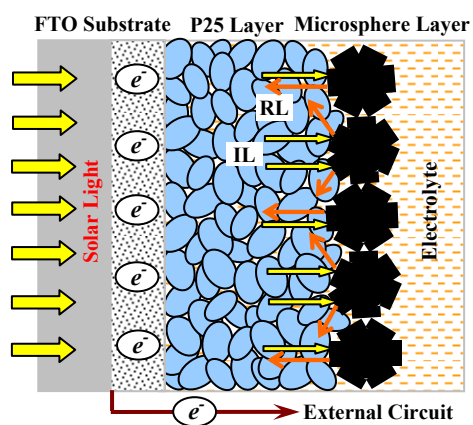


Fig. S1 Schematic illustration of the role of TiO_2 microspheres with exposed mirror-like plane $\{001\}$ crystalline facets as light scattering top layer. IL: Input light; RL: Reflected light.

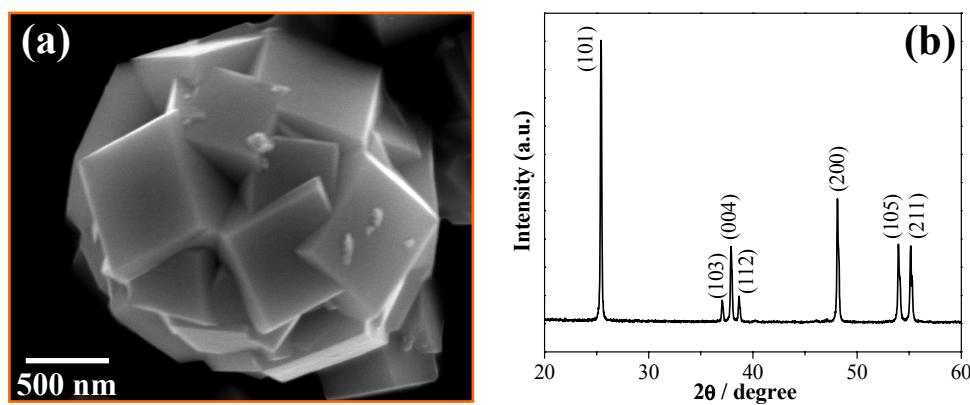


Fig. S2 SEM image and XRD pattern of the TiO₂ microspheres with exposed mirror-like plane {001} crystalline facets after calcination at 600 °C for 1.5 h.

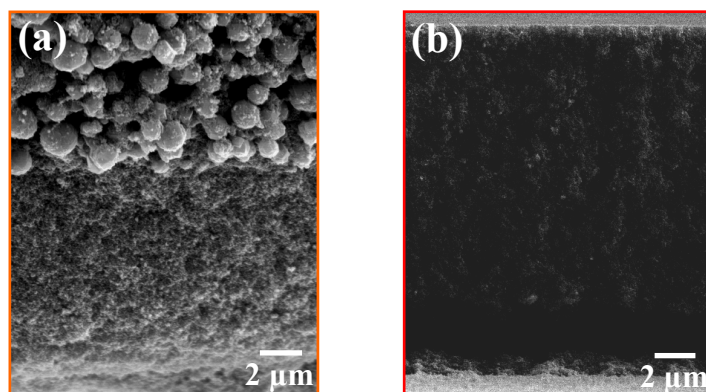


Fig. S3 Cross-sectional SEM images of the TiO₂ film composing of TiO₂ microspheres with exposed mirror-like plane {001} crystalline facets and TiO₂ nanoparticles (a) and P25 film (b).

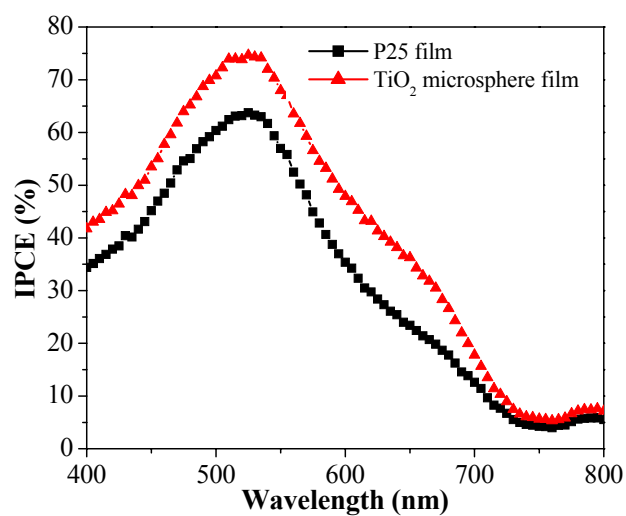


Fig. S4 Incident photon to current conversion efficiency (IPCE) curves of the TiO₂ photoanode composing of TiO₂ microspheres with exposed mirror-like plane {001} crystalline facets and TiO₂ nanoparticles and P25 photoanode.

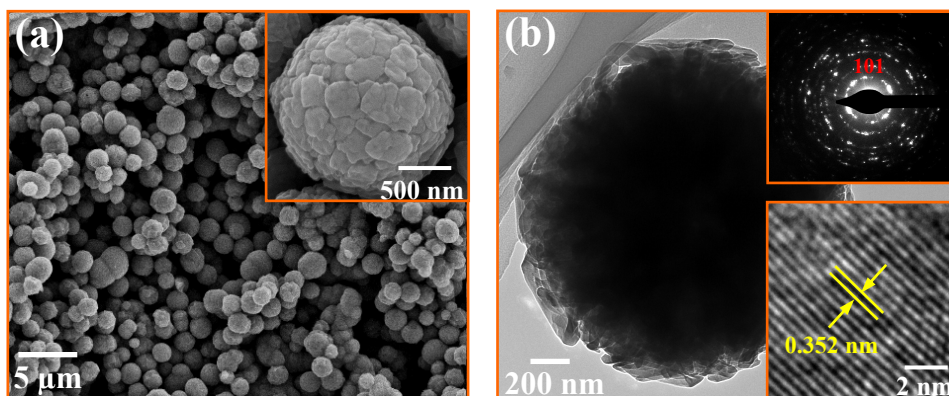


Fig. S5 (a) SEM image of as-synthesized TiO_2 microspheres without exposed mirror-like plane $\{001\}$ crystalline facets fabricated at $180\text{ }^\circ\text{C}$ for 24 h, the inset of high magnification SEM image. (b) TEM image of individual TiO_2 microsphere after hydrothermal reaction of 24 h, the insets of corresponding SAED pattern and HRTEM image. After hydrothermal reaction of 24 h, the exposed mirror-like plane $\{001\}$ facets on microsphere surface are disappeared owing to HF etching/dissolving.^{4,5} The (101) surface of microsphere becomes dominant, which is $d_{101} = 3.52\text{ }\text{\AA}$.⁵⁻⁷

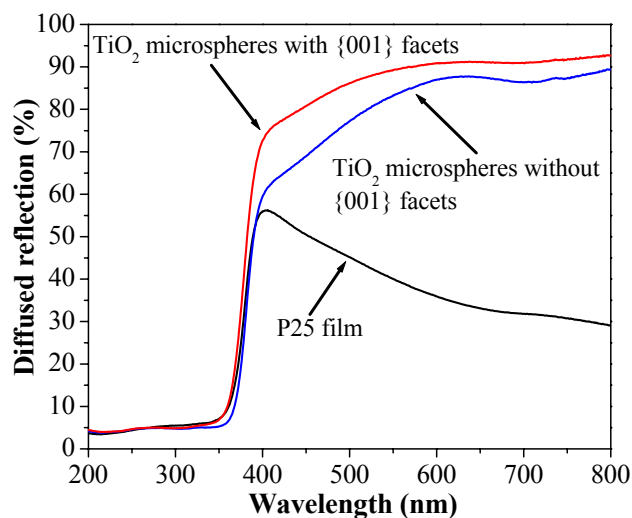


Fig. S6 Diffuse reflectance spectra of the TiO₂ microsphere with exposed mirror-like plane {001} crystalline facets, TiO₂ microsphere without exposed mirror-like plane {001} crystalline facets, and P25 films.

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