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Supplementary Materials for

Radially oriented mesoporous TiO₂ microspheres with single-crystal– like anatase walls for high-efficiency optoelectronic devices

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This PDF file includes:

Materials and Methods

Fig. S1. Photographs of the mixed solution for the preparation of the mesoporous TiO₂ microspheres during the evaporation of the solvent THF.

Fig. S2. TEM images with different magnifications of the sample taken from the preparation solution after the solvent evaporation at 40°C for 6 hours.

Fig. S3. STEM image and EDX elemental maps of the sample taken from the preparation solution after THF evaporation at 40°C for 6 hours.

Fig. S4. WAXRD patterns of the precipitates obtained at different solvent evaporation times without calcination.

Fig. S5. The proposed mechanism for oriented growth of the anatase single-crystal–like pore walls.

Fig. S6. HAADF-STEM images of a single ultramicrotomed 3D open radially oriented mesoporous TiO₂ microspheres.

Fig. S7. SEM images of the products obtained after the second-step evaporation at a high temperature of 120°C.

Fig. S8. TEM images of an ultramicrotomed radially oriented mesoporous TiO₂ microsphere with different integrity.

Fig. S9. SAED and HRTEM images taken from the cylindrical pore bundle regions with different orientation.

Fig. S10. HRTEM and SEAD images of the mesoporous TiO₂ spheres taken from the area of the cylindrical pore bundles.

Fig. S11. Detail photovoltaic parameters of 15 individual mesoporous TiO₂ microsphere-based cells.

Fig. S12. Independent certificate by the National Center of Supervision and Inspection on Solar Photovoltaic Products Quality.

Fig. S13. Cross-sectional and top-view SEM images of the photoanode film based on the uniform mesoporous TiO₂ microspheres.

Fig. S14. Photocatalytic decomposition of methylene blue dye over the mesoporous TiO₂ microspheres.

Fig. S15. Cryo-SEM images of the samples harvested at different intervals of solvent evaporation time.

Fig. S16. STEM image and EDX elemental maps of a single ultramicrotomed mesoporous TiO₂ microsphere.

Fig. S17. SEM images of the products obtained under similar conditions in the absence of Pluronic F127.

Fig. S18. Field-emission SEM (FESEM) and TEM images of the ordered mesoporous TiO₂ bulks with randomly oriented cylindrical pores.

Fig. S19. HRTEM images, nitrogen adsorption-desorption isotherms, pore size distributions, and SAXS integral curves of the randomly oriented mesoporous TiO_2 bulk samples.

Materials and Methods

- 1. Synthesis of 3D-open radially oriented mesoporous TiO₂ microspheres with single-crystal-like anatase walls. The mesoporous TiO₂ microspheres were synthesized by an evaporation-driven oriented assembly (EDOA) approach in an acidic THF/Pluronic F127/H₂O/HCl/Acetic acid (HOAc)/Titanium tetrabutoxide (TBOT) mixed solution. For a typical synthesis, 1.6 g of Pluronic F127 (PEO₁₀₆PPO₇₀PEO₁₀₆, Mw = 12600 g/mol), 0.2 g of H₂O, 2.4 g of HOAc and 2.4 g of concentrated HCl (36 wt%) were dissolved in 30 ml of THF. The mixture was stirred vigorously for 30 min to form a clear and transparent solution. Sequentially, 3.4 g of TBOT was added dropwise under vigorous stirring for 30 min to form a clear golden yellow solution. After that, the obtained clear golden yellow solution was transferred into a volumetric flask, and left it in a drying oven to evaporate solvent THF at 40 °C for 8 h, then second-step evaporate at 80 °C for another 20 h to completely remove the solvents. To retain the mesostructure, the obtained milky white precipitate was first pyrolyzed in a tubular furnace under N₂ at 350 °C for 2 h to obtain a dark grey carbon-supported mesoporous TiO₂ microspheres powder. Finally, the white mesoporous TiO_2 microsphere powder was obtained by further calcination of the carbon-supported TiO_2 microspheres in air at 400 °C for 3 h to burn out the carbon supports.
- 2. Materials characterization. Synchrotron radiation small-angle X-ray scattering (SAXS) measurements were performed at Beamline BL16B of Shanghai Synchrotron Radiation Facility (SSRF). The *d*-spacing values were calculated from the formula $d = 2\pi/q$. Transmission electron microscopy (TEM) experiments were conducted on a JEOL JEM-2100F (UHR) microscope (Japan) operated at 200 kV. To investigate the interior structures of the resultant mesoporous TiO₂ microspheres, the samples were embedded in a

white resin and cut in ultramicrotome to thin sections with a thickness below 100 nm. Field-emission scanning electron microscopy (FESEM) images were collected on the Hitachi Model S-4800 field-emission scanning electron microscope. To obtain information during the EDOA process, cryo-scanning electron microscopy (cryo-SEM) images were taken on the samples from the preparation solution functioned with the evaporation time. Small amount of reactant solution (about 0.1 mL) was withdrawn at different stages during the solvent evaporation. The solution was dropped on a concave copper sample holder and quickly emerged into a soil nitrogen (a kind of semisolid nitrogen made by treating liquid nitrogen under vacuum) to form a solid specimen. X-ray diffraction (XRD) patterns were recorded with a Bruker D8 powder X-ray diffractometer (Germany) using Cu K α radiation (40 kV, 40 mA). Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyzer (USA). Before measurements, the samples were degassed in a vacuum at 180 °C for at least 6 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions were derived from the adsorption branches of isotherms. X-ray photoelectron spectroscopy (XPS) was recorded on an AXIS ULTRA DLD XPS System with MONO Al source (Shimadzu Corp). Photoelectron spectrometer is recorded by using monochromatic Al K_R radiation under vacuum at $5\times 10^{\text{-9}}$ Pa. All of the binding energies were referenced to the C1s peak at 284.6 eV of the surface adventitious carbon. The intensity-modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS) measurements were conducted on a electrochemical workstation (Zahner, Zennium) with a frequency response analyzer under modulated blue light emitting diodes (457 nm) driven by a source supply (Zahner, PP211), which could provide both DC and AC components of the

illumination. The frequency range was set from 100 kHz to 0.1 Hz. The incident light intensity was controlled from 30 to 150 mW cm⁻². Diffuse reflectance spectra of the resultant mesoporous TiO₂ films were collected on a Cary 5000 UV-Vis-NIR spectrophotometer with an integrating sphere (Internal DRA-2500) accessory. The TiO₂ films prepared on the fluorine-doped SnO₂ glass (FTO) substrates were placed in the analysis chamber and scanned from 900 to 400 nm wavelengths.

3. Photovoltaic Measurements. To prepare dye-sensitized solar cell (DSSC) working electrodes, 0.24 g of TiO₂ samples were first ground for 60 min in the mixture of ethanol (1.0 ml), acetic acid (0.2 ml), terpilenol (0.5 ml) and ethyl cellulose (0.05 g) to form slurry, and then the slurry was sonicated for 30 min to form a viscous white TiO₂ paste. Then, the resultant paste was coated on the FTO substrate by screen printing technology. The working electrode was heated to 450 °C for 30 min and annealed in air. It was then immersed in an aqueous solution of TiCl₄ (40 mM) at 70 °C for 30 min and washed with deionized water and ethanol, followed by sintering at 450 °C for 30 min. After the temperature decreased to 120 °C, it was immersed into an N719 solution (0.3 mM) in dry acetonitrile and tertbutanol (1: 1) for 16 h. The N719-incorporated electrodes were carefully rinsed with dry acetonitrile. The working and counter electrodes with a Surlyn frame as the spacer were sealed by pressing them together at a pressure of about 0.2 MPa and a temperature of 125 °C. The redox electrolyte (composed of 0.1 M lithium iodide, 0.05 M iodine, 0.6 M 1, 2-dimethyl-3-propyl-imidazolium iodide and 0.5 M 4-tert butyl-pyridine in dehydrated acetonitrile) was introduced into the cell through the back hole of the counter electrode. Finally, the hole was sealed with the Surlyn and a cover glass. A platinum counter electrode was prepared by coating H₂PtCl₆ onto FTO glass, followed by thermal decomposition at 500 °C in air for 30 min. The J–V characteristics were measured by a Keithley 2400 Source Meter under the illumination (100 mW/cm²) of AM1.5 simulated solar light coming from a solar simulator (Oriel-Sol3A94023A equipped with a 450 W Xe lamp and an AM1.5 filter). The light intensity was calibrated by using a reference Si solar cell (Oriel-91150). A black metal mask with aperture area of 0.16 cm² was attached to the device surface to avoid stray light during the measurements. For the DSSC based on the oriented mesoporous TiO₂ microspheres, a white paper was placed below the device during the measurement. Incident photon-to-current conversion (IPCE) measurements were measured using a 300 W xenon light source (ILC Technology, USA). The produced white light passed through a double monochromator (Jobin Yvon Ltd., UK) and focused on the DSSC at a certain wavelength.

4. Photocatalytic Activity: The photocatalytic degradation of methylene blue was carried out in an aqueous solution at room temperature under UV light irradiation. A 300-W Mercury lamp (main wavelength 365 nm) was used as a light source. The reactor was open to air in order to reach the air-equilibrated condition. In a typical experiment, 50 mg of the photocatalyst powders were dispersed in 50 mL of methylene blue solution $(1 \times 10^{-4} \text{ M})$ with stirring. The suspension was stirred for 12 h in the dark to reach adsorption equilibrium. At given time intervals, 4.0 mL of aliquots was collected, centrifuged, and then filtered to remove the catalyst particles for analysis. The filtrates were finally analyzed by a UV-Vis spectrophotometer (UV-2450).



Evaporation of THF in the THF/ F127/ H₂O/TBT/HCl/ HOAc mixed solution

Fig. S1. Photographs of the mixed solution for the preparation of the mesoporous TiO₂ microspheres during the evaporation of the solvent THF.

The photographs of the mixed preparation solution after the evaporation of the solvent THF at 40 °C for (**A**), 0 h; (**B**), 6 h; (**C**), 20 h; and (**D**), then the second-step evaporation at 80 °C for 8 h; As THF solvent evaporates slowly under static conditions, the preparation solution experienced dramatic changes from a clear yellow solution (**A**), to a suspension with milk colloidal solution (**B**-**C**), and finally to a white precipitates (**E**).



Fig. S2. TEM images with different magnifications of the sample taken from the preparation solution after the solvent evaporation at 40°C for 6 hours.

The white nanospheres in TEM images represent the PEO-PPO-PEO spherical micelles and the tiny black dots represent titania oligomers. The TEM images above show that the spherical composite micelles are initially packed three-dimensionally to form the membrane at the interface between the THF-rich and water-rich phases. The spherical micelles have a typical core-shell structure with amphiphilic Pluronic triblock copolymer PEO-PPO-PEO as a core and titania oligomers as a shell.



Fig. S3. STEM image and EDX elemental maps of the sample taken from the preparation solution after THF evaporation at 40°C for 6 hours.

(A), The STEM image of the sample taken from the preparation solution after THF solvent evaporation at 40 °C for 6 h. (**B-D**), EDX elemental maps of Ti, O and Cl, respectively.



Fig. S4. WAXRD patterns of the precipitates obtained at different solvent evaporation times without calcination.

The inset is the photograph of the precipitates obtained at different solvent-evaporation times during evaporation-driven oriented assembly process. The XRD patterns show that the oriented growth of the anatase TiO_2 single-crystal-like pore walls occurs at a temperature as low as 80 °C.



Fig. S5. The proposed mechanism for oriented growth of the anatase single-crystal-like pore walls.

The proposed mechanism for the oriented growth of anatase TiO_2 single-crystal-like pore walls within the mesoporous TiO_2 microspheres at a low temperature of 80 °C during the evaporation-driven oriented assembly process.



Fig. S6. HAADF-STEM images of a single ultramicrotomed 3D open radially oriented mesoporous TiO₂ microspheres.

(A-B), HAADF-STEM images with different magnification taken from the area of the cylindrical pore bundles of a single mesoporous TiO_2 microsphere. A large number of inter-channel pores with diameters of ~5-15 nm were observed on the wall surface of cylindrical mesochannels (marked by red circles in Fig. S6B). Insets are the corresponding schematic representation of the structure models for the radially oriented mesopore channels.





(A-C), SEM images of the products obtained after the second-step evaporation at a high temperature of 120 °C with different magnification (first-step evaporation at 40 °C for 20 h, then at 120 °C for another 12 h). The pore size of the mesoporous TiO₂ microspheres could be increased to 8-10 nm when the second-step evaporation temperature increased to a high temperature of 120 °C. It is proposed that the PPO chain of the PEO-PPO-PEO micelles may experience a slight volume expansion at the high temperature, resulting in a large cylindrical pore size of the radially oriented mesoporous TiO₂ microspheres.



Fig. S8. TEM images of an ultramicrotomed radially oriented mesoporous TiO₂ microsphere with different integrity.



Fig. S9. SAED and HRTEM images taken from the cylindrical pore bundle regions with

different orientation.

(A-D), SAED patterns taken from the cylindrical pore bundle regions with different orientation. (E-F) HRTEM images taken from the area of the cylindrical mesopore bundles of an ultramicrotomed mesoporous TiO_2 microspheres with [010] incidence, perpendicular to the mesochannels.

The spot size for the SAED patterns shown in Fig. S9A-D is about 400 nm recorded on the different cylindrical pore bundle domains, which almost cover the half of the sphere. The diffraction spots in SAED patterns and continuous crystal lattice in the HRTEM images confirm that the whole assembly of the anatase nanocrystals is highly oriented, leading to the formation the "single-crystal-like" pore walls.



Fig. S10. HRTEM and SEAD images of the mesoporous TiO₂ spheres taken from the area of the cylindrical pore bundles.

(A), HRTEM images taken from the area of the cylindrical pore bundles with [010] incidence, perpendicular to the mesopore channels; (B), SEAD pattern taken from the circular region marked in red (about 400 nm in diameter) (inset of B) with the [010] incidence; (C-D), HRTEM images and the corresponding Fast-Fourier-Transform-Filtered TEM images recorded from the dotted square area.



Fig. S11. Detail photovoltaic parameters of 15 individual mesoporous TiO₂ microspheres-based cells.

Detailed four key photovoltaic parameters: (**A**), the open-circuit voltage (*Voc*), (**B**), shortcircuit photocurrent (*Jsc*), (**C**), fill factor (*FF*) and (**D**), power conversion efficiency (*PCE*) of 15 individual mesoporous TiO₂ microspheres-based cells under AM 1.5 sunlight illumination (100 mW cm⁻²). The active area of the devices with a metal mask was 0.16 cm². The DSSC performance tests have been repeated for several times based on 15 individual mesoporous TiO₂ microspheres-based cells to verify the reliability. The four key photovoltaic parameters (*Voc*, *Jsc*, *FF*, and *PCE*) ontained show a stable value and exhibit excellent stability during exposure to full AM 1.5 simulated sunlight.



Fig. 12. Independent certificate by National Center of Supervision and Inspection on Solar Photovoltaic Products Quality.

Independent certificate by the National Center of Supervision & Inspection on Solar Photovoltaic Products Quality (CPVT) on the dye-sensitized photovoltaic cells based on the radially oriented mesoporous TiO₂ microspheres. The accredited CPVT laboratory confirms a power conversion efficiency of 12.26 % and a short circuit photocurrent density of about 24 mA/cm² (masked area: 0.16 cm²) for the mesoporous TiO₂ microspheres based DSSCs under AM1.5G full sun. Notably, the radially oriented mesoporous TiO₂ microspheres-based photoanode in our work exhibits a high dye loading capacity (2.13×10⁻⁷ mol cm⁻² for N719), efficient charge collection and extended electron lifetime (Fig. 4E), and remarkably strong light-scattering ability (Fig. 4A), which may be responsible to their high *J*sc of the solar cell.



Fig. S13. Cross-sectional and top-view SEM images of the photoanode film based on the uniform mesoporous TiO₂ microspheres.

The cross-section (A) and top-view (B) SEM images of the photoanode film based on the uniform mesoporous TiO_2 microspheres. The top-view of SEM images shows that some domains of the photoanode films are closely packed, which is contributed from the uniform diameter size. However, the visible gaps in between the TiO_2 microspheres are caused to the mechanical slicing of the films for cross-sectional SEM characterization, which does not influence the electron transport as well as dye adsorption.



Fig. S14. Photocatalytic decomposition of methylene blue dye over the mesoporous TiO₂ microspheres.

(A) UV-vis absorption spectra and corresponding color changes of the methylene blue solution (inset). (B) $C_t/C_0 vs$ time curves of methylene blue photodegration over oriented mesoporous TiO₂ microspheres, the conventional bulk mesoporous TiO₂ and Degussa P25.

The photocatalytic decomposition of methylene blue dye over the mesoporous TiO_2 microspheres could be completed in 12 min under UV irradiation (365 nm), which was much shorter than that of the conventional bulk mesoporous TiO_2 and Degussa P25. The excellent photocatalytic performance of the mesoporous TiO_2 microspheres is related to their unique 3D open pore configuration with a large accessible surface area, the "single-crystal-like" pore walls with dominant (101) exposed facets and the pronounced light-harvesting efficiency.



Fig. S15. Cryo-SEM images of the samples harvested at different intervals of solvent evaporation time.

Cryo-SEM images of the samples harvested at different intervals of evaporation time (A), 0 h,

(**B**), 2 h, (**C**), 6 h and (**D**), 20 h from the preparation solution.

To shed more light on the formation mechanism of the radially oriented mesoporous TiO_2 microspheres, their growth process was followed by examining the products harvested at different intervals of evaporation time from the preparation. Before the electron microscopy analysis, the samples were frozen by soil nitrogen. The corresponding cryo-SEM image (Fig. S15b) showed that uniform spherical particles were well dispersed in the solution, suggesting that the spherical F127/titania-oligmer composite micelles were firstly formed at the interface between the THF-rich and water-rich phases. As further THF solvent evaporates for 6 h, the big spherical particles (about 1.0 μ m in diameter) were derived from the liquid-liquid interface (Fig. S15c), suggesting that the spherical composite micelles were spontaneously aggregated into the big spheres at the high concentration of micelles and separated from the liquid phase. After these colloidal spheres were further dried at 80 °C for 12 h (second-step solvent evaporation, during this step THF and residue solvents were completely evaporated), the aggregated PEO-PPO-PEO/titania spherical micelles tended to fuse into cylindrical micelles and form a close-packed layer aligned perpendicular to the outer surface of the particle, which could be seen from the striped surface (Fig. S15d).



Fig. S16. STEM image and EDX elemental maps of a single ultramicrotomed mesoporous TiO₂ microsphere.

(A), The STEM image of a single ultramicrotomed radially oriented mesoporous TiO_2 microspheres after calcination in N₂ at 350 °C for 2 h; (B-D), EDX elemental maps of Cl, Ti and O, respectively, for the single mesoporous TiO_2 microspheres, showing that the selective adsorption of Cl⁻ ions on the crystallographic plane (101) may play an important role in the anisotropic growth of the radially oriented TiO_2 microspheres.



Fig. S17. SEM images of the products obtained under the similar conditions in the absence of Pluronic F127.



Fig. S18. Field-emission SEM (FESEM) and TEM images of the ordered mesoporous TiO₂ bulks with randomly oriented cylindrical pores.

FESEM images (**A**, **B**) and TEM images (**C**, **E**) of the highly ordered mesoporous TiO_2 bulks with randomly-oriented cylindrical pores. The samples were synthesized under a low vacuum condition (about 200 Pa) at 40 °C. The inset (**C**) is a sequence of diffraction rings consistent with anatase TiO_2 (PDF No. 21-1272), indicating the polycrystalline wall structures. (**D**), Schematic representation of the pore arrangement model for the randomly oriented bulk mesoporous TiO_2 .



Fig. S19. HRTEM images, nitrogen adsorption-desorption isotherms, pore size distributions, and SAXS integral curves of the randomly oriented mesoporous TiO₂ bulk samples.

(**A**, **B**), HRTEM images, (**C**), nitrogen adsorption–desorption isotherms and pore size distributions (inset), and (**D**), SAXS integral curves of the randomly-oriented mesoporous TiO₂ bulk samples prepared under a low vacuum condition (about 200 Pa) at 40 °C. The TEM images were taken along (**A**), the uniform [110]-oriented channels; (**B**), the [001] with crystalline frameworks. Inset (**D**) is the corresponding 2-D SAXS pattern.

Similarly, the mesoporous TiO₂ bulk samples exhibit type-VI nitrogen sorption isotherms with a specific surface area of ~ 134 m²/g. The pore size is estimated based on the BJH method to be 5.3 nm (inset C). The SAXS pattern shows three resolved scattering peaks, which are indexed as the (100), (110) and (200) planes of a 2D hexagonal mesostructure with a space group *p6mm*.