Electronic Supplementary Information (ESI†)

Rapid (~10 min.) synthesis of single-crystalline, nanorice TiO₂ mesoparticles with a high photovoltaic efficiency >8%

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One-pot one-step minute-synthesis of single-crystalline nanorice TiO₂ mesoparticles: To synthesize the single-crystalline anisotropic nanorice-like anatase TiO₂ mesoparticles, first a precursor mixture was made in a Teflon vessel (volume~100 ml) by mixing Ti-isopropoxide (TIP; 97%; Aldrich) with acetylacetone (acac; 99.5%; Cica-reagent; acac is a monoanionic charge bidenate ligands which acts as the stabilizing¹-⁴ and structural directing agent) in 1:2 molar ratio under constant magnetic stirring. After 5 min. of stirring, ca. ~70 ml of aqueous alkaline solvent (deionized water; Millipore, 18 MΩ.cm; pH~11.7 adjusted using an aqueous NH₃ solution; 28~30%; Samchun Chem., Korea) was directly poured to this mixture. A flaky precipitate was kept stirring for another 5 min. and then microwave-assisted hydrothermal process (MDS-2000, CEM Corporation, 300W, 2.45GHz, 100% power) was carried out at 180 °C for 10 min. only. The resulted precipitate was collected by centrifugation and thoroughly washing with distilled water. The final TiO₂ powder was then obtained by drying the precipitate at 100 °C for 2 hr. followed by manual hand grinding.

Physical characterizations of minute-made nanorice TiO₂: The structural and electronic properties of nanorice TiO₂ were investigated using XRD (PRO-MPD, Philips diffractometer; Cu-Kα, 1.5404 Å), X-ray photoelectron spectroscopy (XPS; VG Scientific ESCALAB 220-IXL; Mg-Kα radiation source, 1253.6 eV), TEM, HRTEM and ED pattern (Cs-corrected JEM-2200FS) and SEM (JEOL JSM-6330F). The thickness of photoanodes is determined by the cross-section profile of SEM image. Specific BET surface area, BJH pore size and pore volume were measured and calculated from N₂-adsorption-desorption isotherms at 77 K (Micromeritics ASAP-2010). The pore size and pore volume was determined using adsorption branch. Diffuse reflectance spectra of nanorice TiO₂ were measured by a Shimadzu UV/Vis spectrophotometer (model UV-2401PC) equipped with integrated sphere method. The BaSO₄ is used as a calibrating reference.

Photoanode and DSC fabrication: According to the simple method⁵ the photoanodes and DSC were fabricated as follow:-
1) 1.5 g of powder was homogenously mixed with 3.14 g of α-terpineol plus 0.07 g of ethyl cellulose. This mixture is grinded by hands with the help of a mortar and a spatula for about 30 min.

2) Prior to that coating, a hole of 1 mm diameter is drilled to the FTO substrates and then these FTO substrates were cleaned with acetone, rinsed with triple distilled water and dried at 80 °C in an oven.

3) Using a screen printing method, the photoanodes were made by coating the resulted viscous paste into an area of 5 mm × 5 mm of a commercially available FTO glass substrate (TEC15; sheet resistance ~ 15 Ω/square).

4) After drying in air (~130 °C for 10 min.), the coating was done again to increase the thickness of photoanode. The drying and coating processes were carried out several times to obtain the thicker photoanodes.

5) The coated substrates were heated in a furnace (500 °C for 30 min.). The naturally cooled coated substrates were then immersed in 0.5mM of TiCl₄ ethanol solution for about 30 min.

6) The TiCl₄ treated coated substrates then heat treated again in a furnace (500 °C for 30 min.). Each single layer screen printing produces ~4μm thick photoanode.

7) When the temperature of naturally cooled furnace was around 80 °C, the substrates were removed from the oven and then soaked in a 0.5 mM solution of N719 dye solution (mixture of acetonitrile and tert-butanol in 1:1 volume ratio) for 24 hours. As received N719 dye from Solaronix was used (no purification was done).

8) Pt-counter electrode was made by coating a drop of H₂PtCl₆ solution (5 mM in isopropanol) onto clean FTO glass substrate and heating this at 400 °C for 15 min.

9) Dye-sensitized photoanodes were rinsed with anhydrous ethanol, dried in nitrogen flow, and then sandwich types DSC were assembled by stacking and sealing the dye-sensitized photoanode with Pt-counter electrode with a 60 μm thick spacer (Surlyn sheet, Solaronix).

10) The redox couple electrolyte (consisting 0.5M 1-butyl-3-methylimidazolium iodide, 0.05M I₂, 0.5M 4-tert-butylpyridine in acetonitrile) was introduced into the DSC through the vacuum back filling method.

11) The electrical (ohmic) connections onto the photoanode and counter electrodes sides were made by silver soldering the copper wires.

12) The schematic illustration to assemble the final DSC is shown below.

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**Photovoltaic, EIS and IPCE measurements:** Photovoltaic characteristics of assembled DSC were measured under simulated 1 sun (100 mW.cm⁻², AM 1.5G) solar illumination condition with Peccell solar simulator (Model: PEL-L11). The intensity of solar light was adjusted to 1 sun condition using NREL certified silicon reference cell equipped with a KG-5 filter. Electrochemical impedance spectra (EIS) of Bode phase-diagrams and Nyquist-plots were measured under 1 sun bias light at open circuit condition using Reference 600 Potentiostat (Gamry instruments). The IPCE spectra were collected over the wavelength range of 300 to 800 nm with a chopping frequency of 10 Hz (PV Measurements, Inc.).
Figure ESI 1†. Indexed XRD patterns of TiO$_2$ mesopowders made by microwave-hydrothermal process with varied molar ratio (δ=TiP:acac).

(i) Reaction is carried out at 150 °C for 60 min.: δ=0.5 (a); δ=1 (b); δ=2 (c); δ=3 (d). The legend B (2θ=30.81°) represents the brookite-phase. When δ is less than 2, the small amount (<2 w/w%) of brookite was formed as an impurity phase.

(ii) With δ=2, e is as-prepared at 180 °C for 10 min., and e' is obtained after calcining the c at 500 °C for 30 min.

Figure ESI 2†. Comparison between the crystallinity (101 peaks) of single-crystalline nanorice TiO$_2$ powder (see Fig.1; 180 °C, 10 min.) and reference Degussa P25 TiO$_2$ powder. The average anatase particles sizes are ca. ~23 nm (P25) and ~12 nm (TiO$_2$) respectively. The legend R (20=27.46°) represents the rutile-phase.
Figure ESI 3†. High resolution sharp lattice fringes of single-crystalline anatase nanorice TiO$_2$ particles made in aqueous media (one-step, one-pot) only in 10 min. (see Fig. 1; Figs. ESI† 1-ii and 2). Some of the acetylacetone still remains as a residue onto the particles’ surface even after excessive washing.

Figure ESI 4†. N$_2$ adsorption-desorption curves and pore-size distribution curves of nanorice TiO$_2$ powders: (a) before calcination; (b) after calcination (500 °C, 30 min.). Prior to N$_2$ measurement, the nanorice TiO$_2$ powders were degassed at 120 °C for 3 hr.
Figure ESI 5†. Measured diffuse reflectance spectra of Degussa P25 powders and nanorice TiO$_2$ powders. (a) before calcination; (b) after calcination (500 °C, 30 min.). The diffuse light scattering properties depends on the size, shape, optical density (refractive index) and the spatial distribution/position of nanoparticle. BaSO$_4$ is used as a reference.
**Figure ESI 6†.** (Left) High magnification top and the cross-section SEM views of nanorice TiO$_2$ photoanode on FTO (see Fig. 2). (Right) SEM images of nanorice TiO$_2$ mesopowders: (a) before calcination; (b) after calcination (500 °C, 30 min.). (see Fig. ESI† 1-ii). The secondary clustering type structures of agglomerated nanoparticles are easily seen. Such structures enhance the optical path of light, so more diffuse light scattering is expected into the longer wavelength region (red to near IR) (see Fig. 2D; Fig. ESI† 5 and ESI† 9).
Figure ESI 7†. High resolution X-ray photoelectron spectroscopy (XPS) spectra of Ti2p peak and O1s peak of nanorice TiO₂ photoanode. C1s peak was used as a calibrating reference. The XPS also confirmed the pure anatase tetragonal structure (space group I41/amd). Only Ti (Ti2p₁/₂, 464.5 eV; Ti2p₃/₂, 458.6 eV) and O (O1s, 530 eV) were found with the expected O/Ti ratio of ca. ~2.

Figure ESI 8†. Measured photovoltaic characteristics of DSC systems with different photoanode thickness fabricated using minute made nanorice TiO₂ mesoparticles. The size of iodide redox (I⁻/3I⁻) couple electrolytes ca. ~4 nm and the size of N719 molecules ca. ~1.5 nm. So to obtain a deep electrolytes wetting (penetration/diffusion) more than 5 nm pore size is required between the fused nanoparticles in the fabricated photoanodes.
Figure ESI 9†. The measured IPCE curves of DSC systems. The IPCE of nanorice TiO₂ is much higher in the whole wavelength region (400 nm to 800 nm). The better light scattering properties of nanorice TiO₂ is clearly seen in the longer wavelength region (see Fig. ESI† 6). The optical absorption cross-section of photosensitizing N719 dye molecule is ca. ~530 nm.

Figure ESI 10†. Thickness dependent measured photovoltaic parameters of DSC photoanodes (electrodes): (A) P25 and (B) nanorice TiO₂.

Reference:

4. A. Leaustic, F. Banonneau, J. Livage.; Structural investigation of the hydrolysis-condensation process of titanium alkoxides Ti(OR)₄ (OR = OPr, OEt) modified by acetylacetone. 2. From the modified precursor to the colloids; Chem. Mater., 1989, 1, 248.