Synthesis of anatase TiO$_2$ rods with dominant reactive \{010\} facets for the photoreduction of CO$_2$ to CH$_4$ and use in dye-sensitized solar cells

Experimental Details

Preparation of Cs$_{0.68}$Ti$_{1.83}$O$_4$/H$_{0.68}$Ti$_{1.83}$O$_4$. Layered titanate precursor of Cs$_{0.68}$Ti$_{1.83}$O$_4$ was prepared according to a procedure previously reported [1]. Its protonated form of H$_{0.68}$Ti$_{1.83}$O$_4$ was prepared by ion-exchange of Cs$_{0.68}$Ti$_{1.83}$O$_4$ with H$^+$ in a 1 mol·L$^{-1}$ HCl solution for three days.

Micro-sized anatase TiO$_2$ rods: 200 mg of the Cs$_{0.68}$Ti$_{1.83}$O$_4$ powder dispersed in 40 mL deionized water was hydrothermally treated at 180°C for 24 h in a Teflon-lined stainless autoclave with a volume of 80 mL. The resultant product was washed several times with deionized water and then dried in air.

Nano-sized anatase TiO$_2$ rods: 100 mg of the H$_{0.68}$Ti$_{1.83}$O$_4$ powder dispersed in 20 mL of a 0.3 mM Cs$_2$CO$_3$ solution was hydrothermally treated at 180°C for 24 h in a Teflon-lined stainless autoclave with a volume of 80 mL. The resultant product was washed several times with deionized water and then dried in air.

Removal of cesium from as-prepared anatase TiO$_2$ rods: The as-prepared anatase TiO$_2$ rods were dispersed in a 1 mol·L$^{-1}$ HCl solution while stirring for 24 h and then fully washed with deionized water. The recovered powder was heated in a static air atmosphere in a furnace at 600 °C for 2 h and then cooled naturally to room temperature.

Characterization. X-ray diffraction patterns of the samples were recorded on a Rigaku diffractometer using Cu k$\alpha$ irradiation. Their structure was determined using transmission electron microscopy (TEM, Tecnai F30) and scanning electron microscopy (SEM, SUPRA 35). The Brunauer-Emmett-Teller (BET) surface area was determined by nitrogen adsorption-desorption isotherm measurements at 77 K (ASAP 2010).
Chemical compositions and valence band spectra of TiO$_2$ were analyzed using X-ray photoelectron spectroscopy (Thermo Escalab 250, a monochromatic Al K$_\alpha$ X-ray source). All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon. The optical absorbance spectra of the samples were recorded in a UV-visible spectrophotometer (JACSCO-550). Raman spectra were collected with LabRam HR 800.

**Photoreduction of CO$_2$ Tests.** The photoreduction experiments of CO$_2$ were conducted in a home-made Teflon-lined stainless reaction chamber with a quartz window at the top for light irradiation. The volume of the chamber was 50 cm$^3$. 50 mg of the Pt-loaded sample was laid at the bottom of the reaction chamber. Prior to filling the gaseous CO$_2$, the chamber was evacuated by a mechanical pump. Then, CO$_2$ bubbled from water was added to the chamber to reach a pressure of 0.06 MPa. The total amount of products generated in the chamber after light irradiation was determined by analyzing a 1.0 mL gas from the chamber with a gas chromatograph (Agilent Technologies: 6890N). The light source was a 300 W Xe lamp (Beijing Trusttech Co. Ltd, PLS-SXE-300UV).

**Fabrications of Dye sensitized solar cells.** TiO$_2$ Pastes were prepared following a reported procedure [2]. A TiO$_2$-coated test cell glass plate (transparent) as a reference was received from Dyesol. TiO$_2$ films were deposited on fluorine-doped tin oxide (FTO) glass plates (2.3 mm thickness, 8Ω/sq, Dyesol Glass, cleaned with a 2-propanol using an ultrasonic bath for 30 min, and then thoroughly rinsed with water) by the doctor-blade method, and were then gradually heated at 100°C for 6 min and 550°C for 30 min. The resulting TiO$_2$ films were immersed into a 0.5 mM N719 (Dyesol) dye solution in a 1:1 (v/v) mixture of acetonitrile (HPLC, Lab-scan) and tert-butanol (LR, Ajax Chemicals) and kept for 24 h. Subsequently, the dye-covered TiO$_2$ electrode and Pt-counter electrode (Dyesol) were assembled into a sandwich type cell and sealed with a spacer of 30 μm thickness (Surlyn, DuPont) with a drop of the I$^-$/I$_3^-$ organic solvent based electrolyte solution (EL-HPE, Dyesol) introduced by vacuum back-filling.

**Performance measurements of dye sensitized solar cells.** Current-voltage curve measurements were performed using a Keithley 2420 Source Meter under illumination of simulated sunlight (100 mW cm$^{-2}$) provided by a solar simulator (Oriel) equipped with
150 W xenon lamp and an AM 1.5G type filter (Newport, 81094). The light intensity was adjusted using an optical power meter (Newport, 1918-c). The IPCE was recorded using a 300 W xenon lamp (Oriel), a monochromator (Oriel, Cornerstone 260), and a power meter (Newport, 1918-c). The quantity of incident photons on the device at each wavelength was calculated using a calibrated Si detector as a reference.

References


Fig. S1 SEM images of (a) $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$ and (b) $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_4$ precursors.

Fig. S2 XRD patterns: (a) $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_4$; (b) $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$; (c, d) the synthesized anatase TiO$_2$ rods with (a) and (b) as precursor.
Fig. S3 XPS spectra and high resolution XPS spectra of Cs 3d, Ti 2p and O 1s of the nano-sized anatase TiO$_2$ rods before (a) and after (b) removing Cs.

Fig. S4 Raman spectra of the anatase rods before (a) and after (b) removing Cs.
**Fig. S5** XRD patterns of the solid products by hydrothermally treating Cs$_{0.68}$Ti$_{1.83}$O$_4$ for different reaction time.

**Fig. S6** SEM images of the products by hydrothermally treating Cs$_{0.68}$Ti$_{1.83}$O$_4$ for different reaction time: a, 0 h; b, 6 h; c, 12 h; d, 18 h. Scale bars: 250 nm. e, Schematic of growth mechanism of {010} dominant anatase rods from lepidocrocite-type cesium titanate.
Fig. S7 (a, b) SEM images and (c) XRD patterns of {010} dominant anatase rods prepared with H$_{0.68}$Ti$_{1.83}$O$_4$ and sodium carbonate/potassium carbonate as precursor and pH mediator.