

## Electronic Supplementary Information

Synthesis of anatase TiO<sub>2</sub> rods with dominant reactive {010} facets for the photoreduction of CO<sub>2</sub> to CH<sub>4</sub> and use in dye-sensitized solar cells

### Experimental Details

**Preparation of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/H<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>.** Layered titanate precursor of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> was prepared according to a procedure previously reported [1]. Its protonated form of H<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> was prepared by ion-exchange of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> with H<sup>+</sup> in a 1 mol·L<sup>-1</sup> HCl solution for three days.

**Micro-sized anatase TiO<sub>2</sub> rods:** 200 mg of the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> power 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<sub>2</sub> rods:** 100 mg of the H<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> powder dispersed in 20 mL of a 0.3 mM Cs<sub>2</sub>CO<sub>3</sub> 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<sub>2</sub> rods:** The as-prepared anatase TiO<sub>2</sub> rods were dispersed in a 1 mol L<sup>-1</sup> 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<sub>2</sub> were analyzed using X-ray photoelectron spectroscopy (Thermo Escalab 250, a monochromatic Al K<sub>α</sub> 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<sub>2</sub> Tests.** The photoreduction experiments of CO<sub>2</sub> 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<sup>3</sup>. 50 mg of the Pt-loaded sample was laid at the bottom of the reaction chamber. Prior to filling the gaseous CO<sub>2</sub>, the chamber was evacuated by a mechanical pump. Then, CO<sub>2</sub> 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<sub>2</sub> Pastes were prepared following a reported procedure [2]. A TiO<sub>2</sub>-coated test cell glass plate (transparent) as a reference was received from Dyesol. TiO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sup>-</sup>/I<sup>3-</sup> 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<sup>-2</sup>) 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

- [1] (a) T. Sasaki, M. Watanabe, H. Hashizume, H. Yamada and H. Nakazawa, *J. Am. Chem. Soc.*, 1996, 118, 8329. (b) G. Liu, L. Z. Wang, C. H. Sun, X. X. Yan, X. W. Wang, Z. G. Chen, S. C. Smith, H. M. Cheng and G. Q. Lu, *Chem. Mater.*, 2009, 21, 1266.
- [2] S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin and M. Grätzel, *Thin Solid Films*, 2008, 516, 4613.

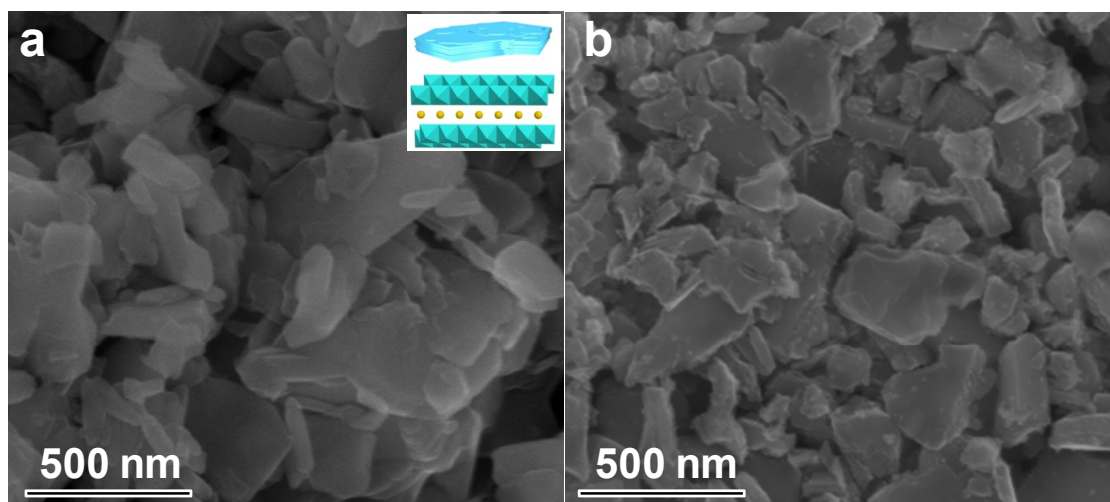


Fig. S1 SEM images of (a)  $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$  and (b)  $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_4$  precursors.

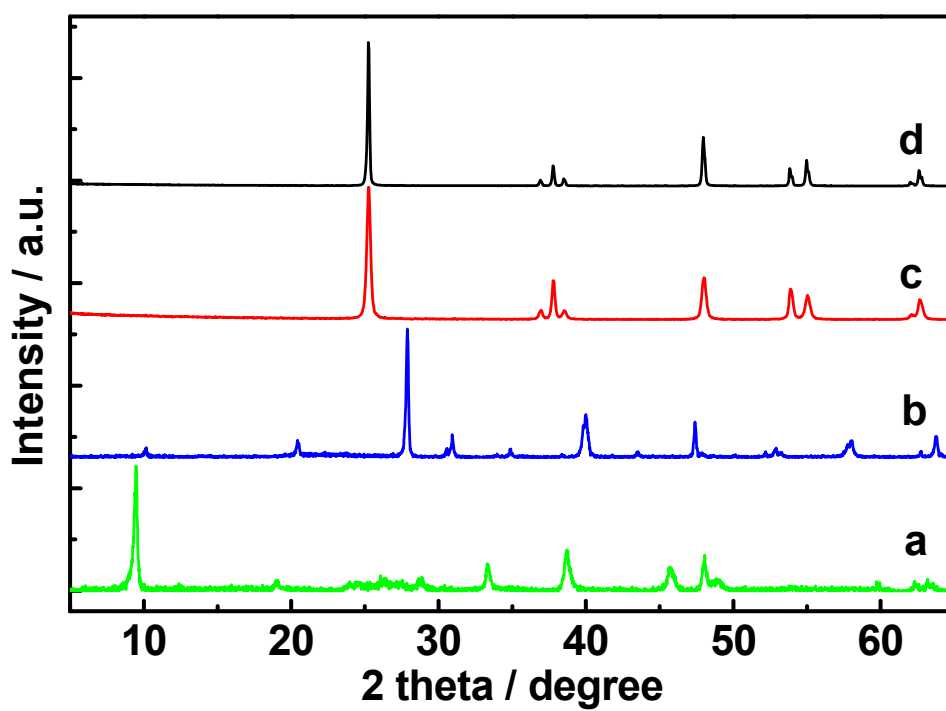
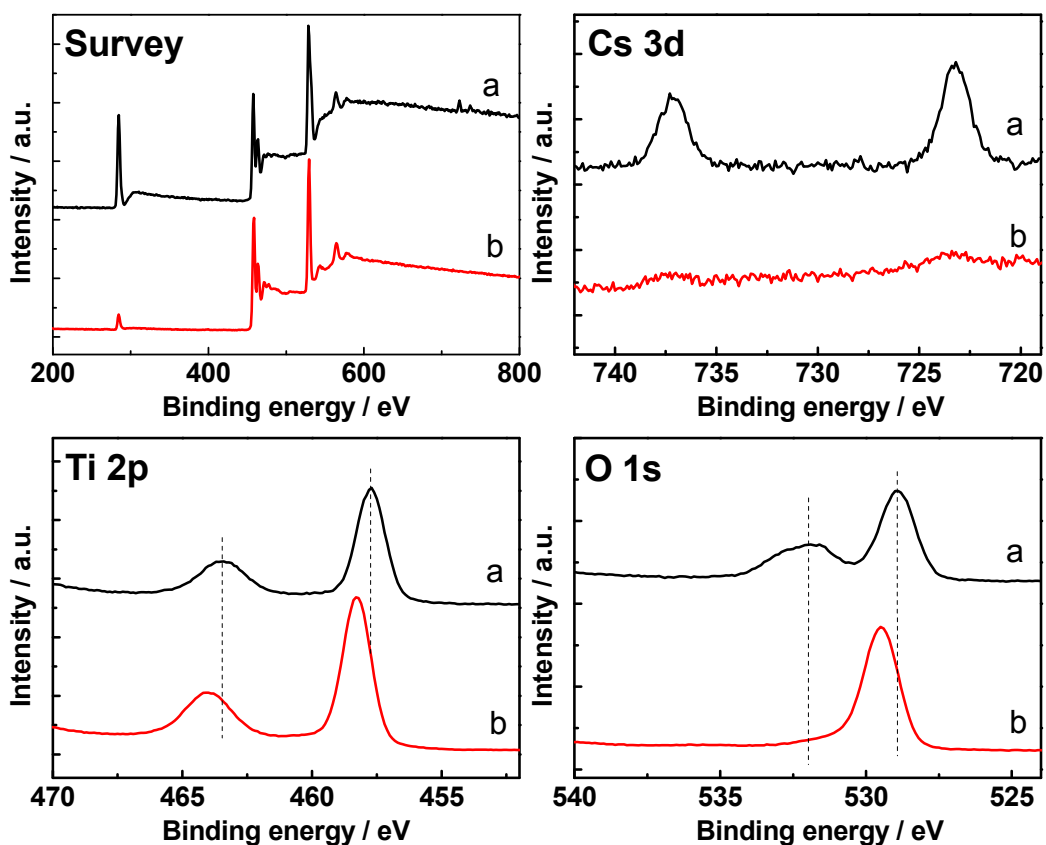
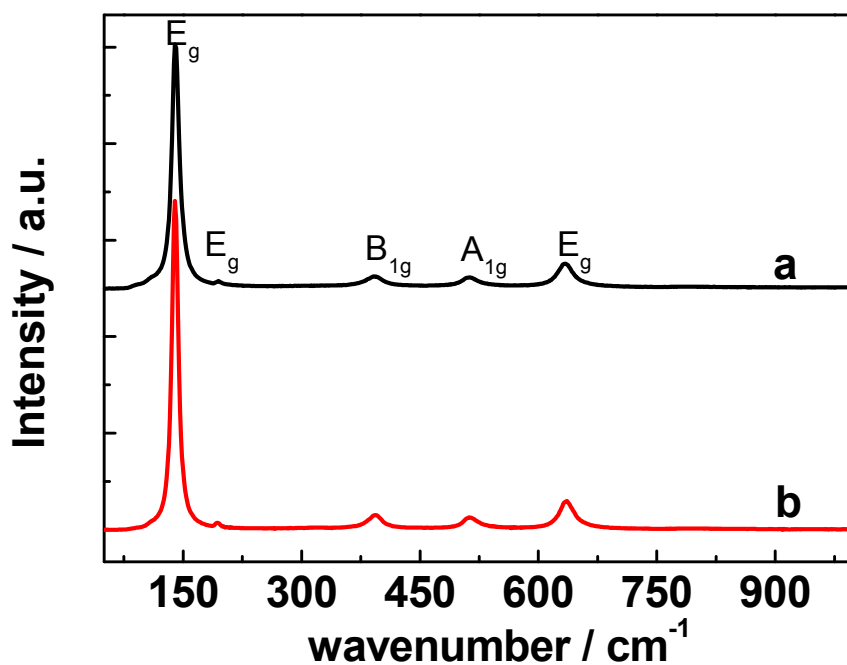


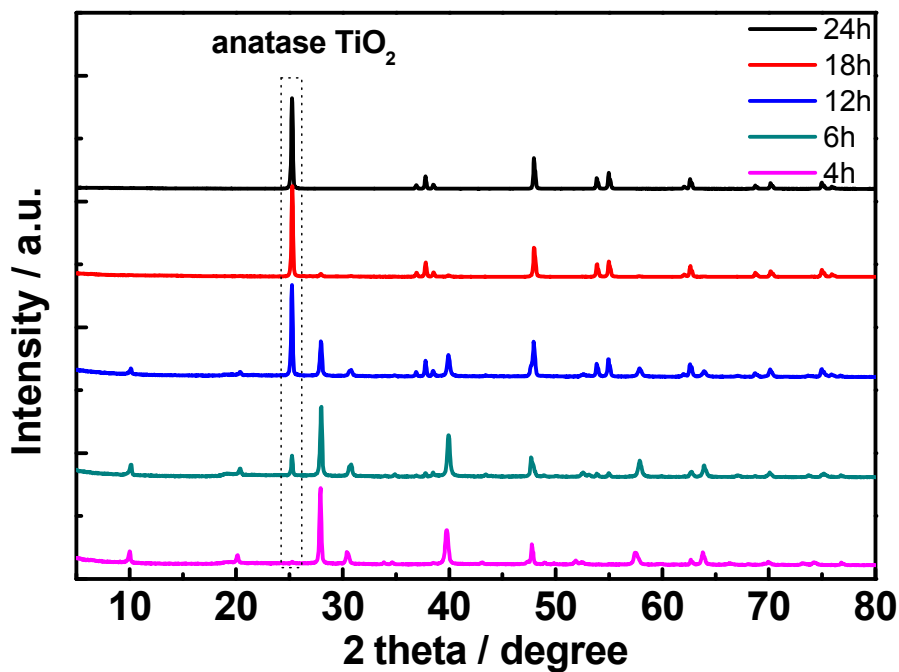
Fig. S2 XRD patterns: (a)  $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_4$ ; (b)  $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$ ; (c, d) the synthesized anatase  $\text{TiO}_2$  rods with (a) and (b) as precursor.



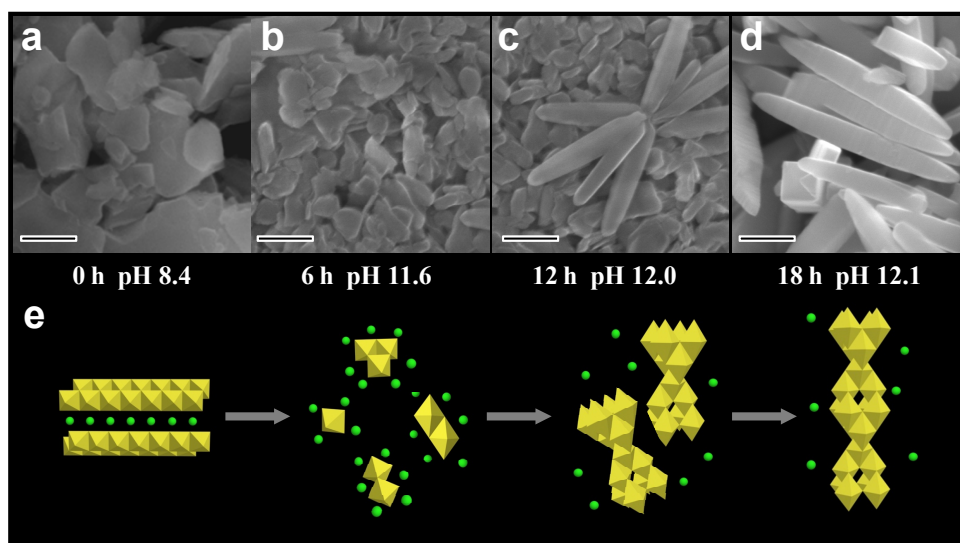
**Fig. S3** XPS spectra and high resolution XPS spectra of Cs 3d, Ti 2p and O 1s of the nano-sized anatase TiO<sub>2</sub> rods before (a) and after (b) removing Cs.



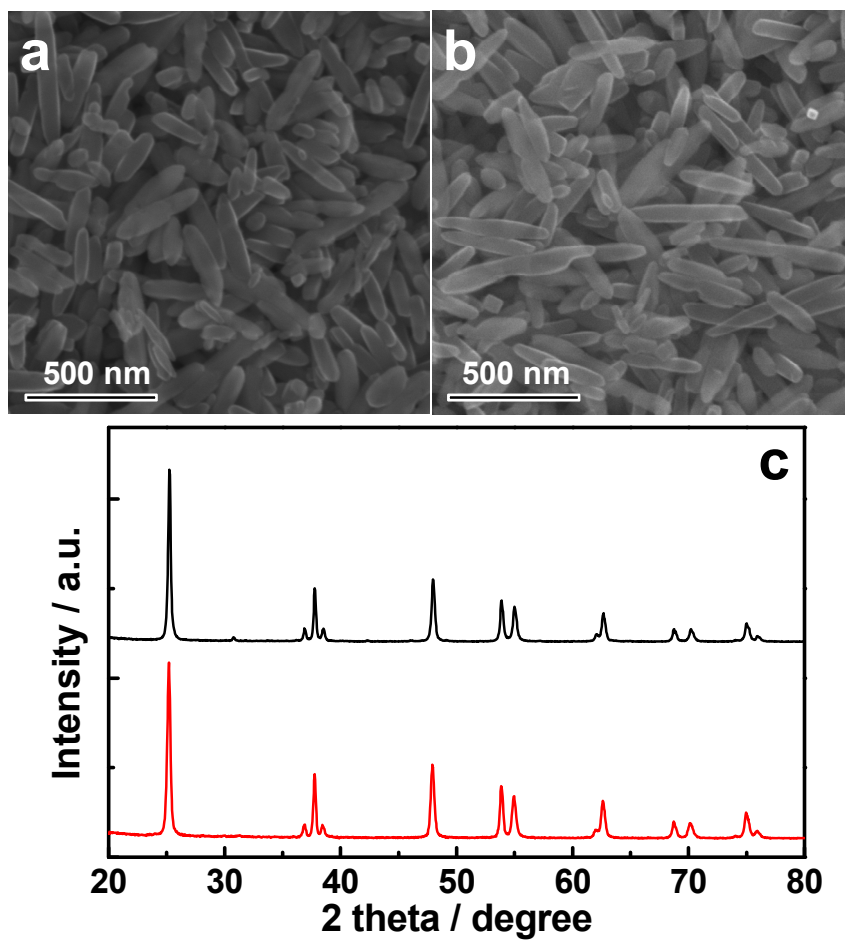
**Fig. S4** Raman spectra of the anatase rods before (a) and after (b) removing Cs.



**Fig. S5** XRD patterns of the solid products by hydrothermally treating  $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$  for different reaction time.



**Fig. S6** SEM images of the products by hydrothermally treating  $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$  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  $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_4$  and sodium carbonate/potassium carbonate as precursor and pH mediator.