Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2017

Supplementary Information

Reduced {001}-TiO_{2-x} photocatalyst: noble-metal-free CO_2 photoreduction for selective CH_4 evolution

Wenzhang Fang[a,b], Lhoussain Khrouz[c], Yi Zhou[a], Bin Shen[a], Chunyang Dong[a], Mingyang Xing[a*], Shashank Mishra[b], Stephane Daniele[b]* and Jinlong Zhang[a]*

a. Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry and Chemical Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China

b. Université Claude Bernard Lyon 1, Institut de Recherches sur la Catalyse et L'environnement de Lyon (IRCELYON), CNRS, UMR 5256, 2 avenue Albert Einstein, 69626 Villuerbanne, France

c. Univ Lyon, Ens de Lyon, CNRS, Université Lyon 1, Laboratoire de Chimie, F69342, Lyon, France

Corresponding authors: mingyangxing@ecust.edu.cn, stephane.daniele@ircelyon.univ-lyon1.fr, jlzhang@eucst.edu.cn

1. Preparation method

Deep blue TiO_{2-x} catalysts were prepared through hydrothermal method. In a 50 mL Teflon-lined stainless-steel autoclave, 10 mL $TiCl_3$ (12% in hydrochloric acid, Sigma-Aldrich) was added into a mixture of 20 mL 1M HCl aqueous solution and certain amount (*m* mL) of HF aqueous solution (40%, Merck KGaA) under magnetic stirring. The autoclave was kept in an oven at 180 ^{o}C for 24 h. Finally, the sample was centrifuged and washed by water 3 times (4000 rpm, 10 min), and dried. The collected samples are named as TiO_{2-x}-*m* (*m* refers the adding volume of HF solution), which show deep blue color. A colorless reference sample, named as TiO_{2-x}-0, was also synthesized in the same condition but without using HF.

2. Characterization techniques

Powder X-ray diffraction (XRD) was tested on Bruker D8 and the results were analyzed by EVA software platform. The scanning electron microscopy (SEM) was performed on Hitachi S800. The morphologies were also recorded by high-resolution transmission electron microscopy (HRTEM) on JEOL JEM-2100. Elemental mapping of the sample was collected by energy dispersive spectroscopy (EDS) for TEM on JEOL JEM-2100 equipped with EDAX. Thermo Scientific ESCALAB 250 equipped with Al Kα radiation was employed for X-ray photoelectron spectroscopy (XPS) test. UV-Vis-NIR diffuse reflectance spectroscopy analysis was recorded on a PerkinElmer UV-Vis-NIR spectrometer Lambda 950, the data was recorded from 200 – 2500 nm. Raman was collected on Renishaw inVia Raman microscope. Photoluminescence (PL) measurement was conducted on Shimadzu RF-5301PC. The excitation wavelength is 325 nm. Electron paramagnetic resonance (EPR) was recorded on Elexsys E500 (9.4 GHz, 0.6 mW)

equipped with cavity 4102ST at 110 K, the obtained data was simulated by MATLAB. 4 mg $CuSO_4 \cdot 5H_2O$ was used as EPR signal reference (2.41×10^{21} spins/g).

3. Photocatalytic CO_2 reduction tests

0.030 g catalyst was put into a petri dish and dispersed in water under supersonic treatment. The water was then evaporated in an oven at 120 ^oC for 5 h, leaving behind the catalyst on the surface of the dish. The dish was shifted in a homemade reactor (300 mL) equipped with water-cooling system for CO_2 reduction. The reactor was kept under vacuum for 0.5 h to remove the remaining gases and then CO_2 (99.995%) and 1 mL pure water were injected into the reactor. A 300 W Xenon lamp was used as the light source and an AM1.5 filter was used to simulate the sunlight. A certain amount of the gases was taken from the mixture at the given time intervals by the GC (gas chromatograph, Shimadzu 2014). H_2, O_2, N_2 and CO_2 gases were detected by thermal conductivity detector (TCD), while CH_4, CO and CH_3OH were detected by flame ionization detector (FID).

4. Photoelectrochemical performance

Photoelectrochemical properties were performed on Zahner electrochemical workstation Zennium. For photocurrent testing, a standard three-electrode system was employed using Pt wire as counter electrode, saturated calomel electrode as the reference electrode, a working electrode and 0.5 M $NaSO_4$ aqueous solution as the electrolyte. A 300 W Xenon lamp was used as the light source, and an AM1.5 filter was equipped to simulate the sunlight. 25 mM $K_3[Fe(CN)_6]$ aqueous solution was used instead of Na_2SO_4 as the electrolyte while testing the EIS Nyquist plots.

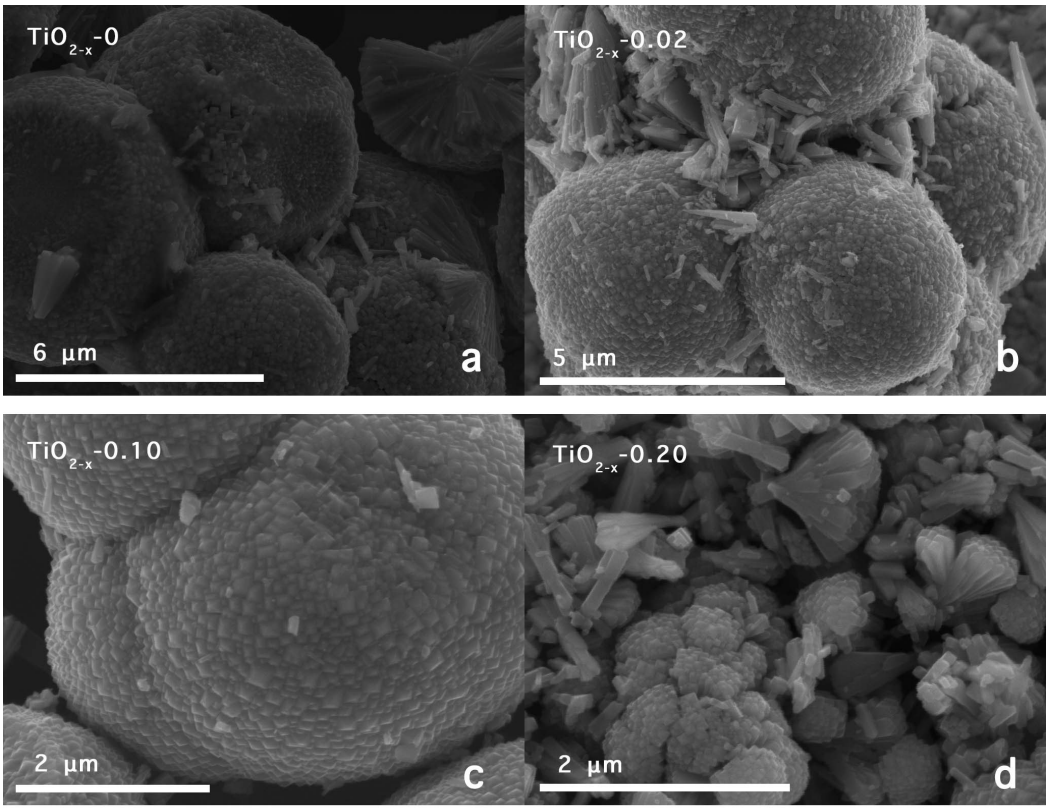

Fig. S1. SEM of the synthesized reduced TiO_2 samples: (a) TiO_{2-x}-0, (b) TiO_{2-x}-0.02, (c) TiO_{2-x}-0.10 and (d) TiO_{2-x}-0.20.

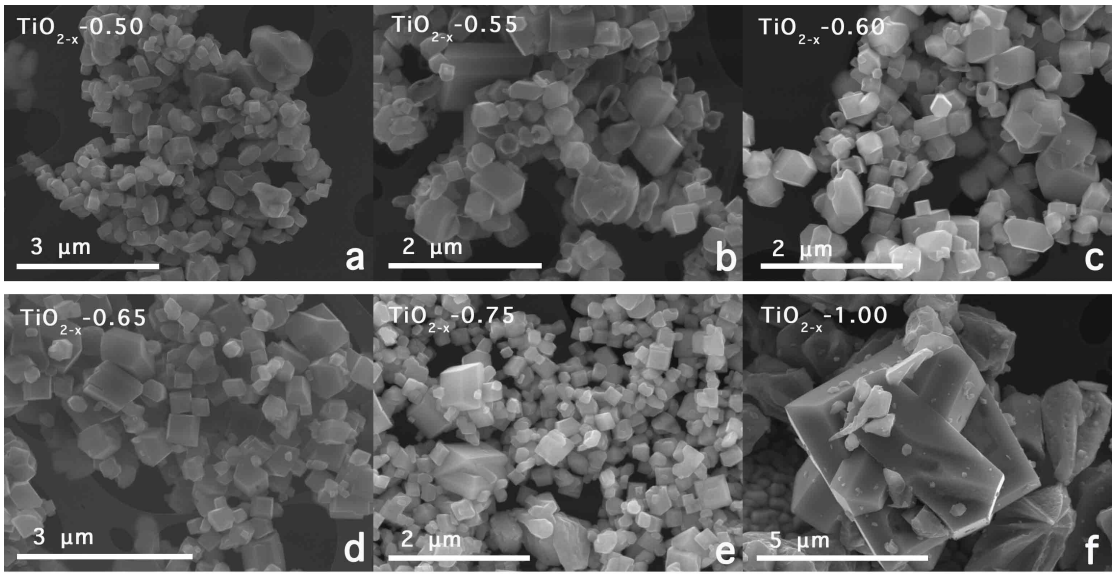

Fig. S2. SEM images of reduced TiO_2 samples: (a) TiO_{2-x}-0.50, (b) TiO_{2-x}-0.55, (c) TiO_{2-x}-0.60, (d) TiO_{2-x}-0.65, (e) TiO_{2-x}-0.75 and (f) TiO_{2-x}-1.00. All these samples show {001} facets.

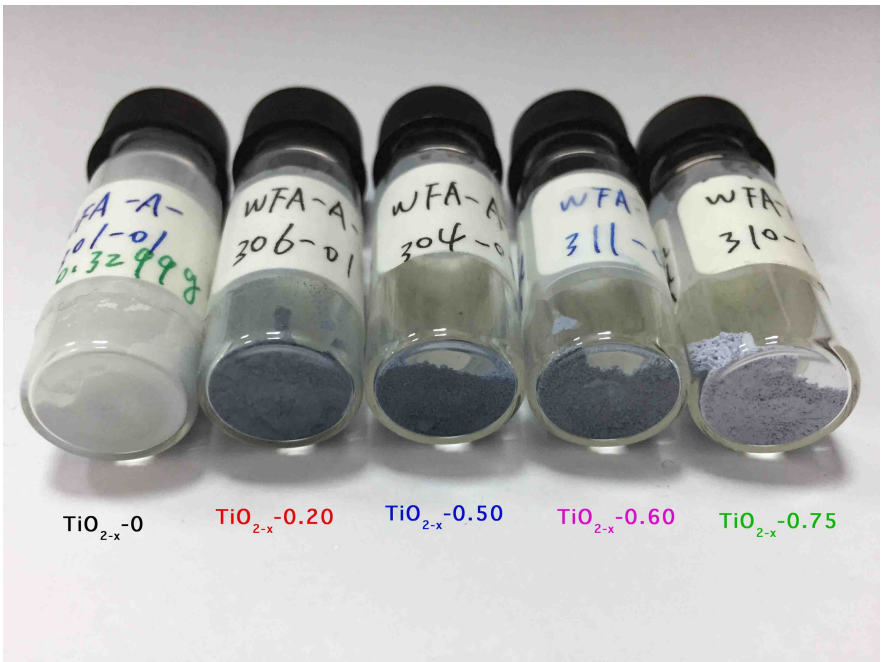

Fig. S3. Photo of some selected reduced TiO_2 samples: TiO_{2-x}-0, TiO_{2-x}-0.20, TiO_{2-x}-0.50, TiO_{2-x}-0.60, TiO_{2-x}-0.75. Compared to the reference TiO_{2-x}-0 sample, all the catalysts treated by HF are blue-colored, and stable in air.

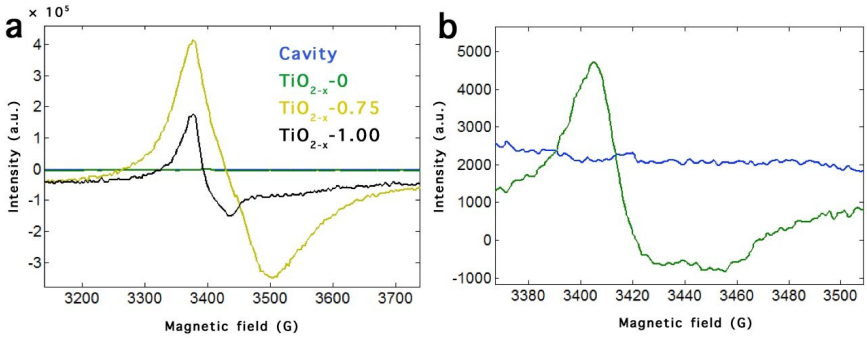

Fig. S4. EPR spectra of the selected samples: (a) TiO_{2-x}-0, TiO_{2-x}-0.75 and TiO_{2-x}-1.00; (b) TiO_{2-x}-0 and Cavity. The curves are marked with different colors related to the sample names.

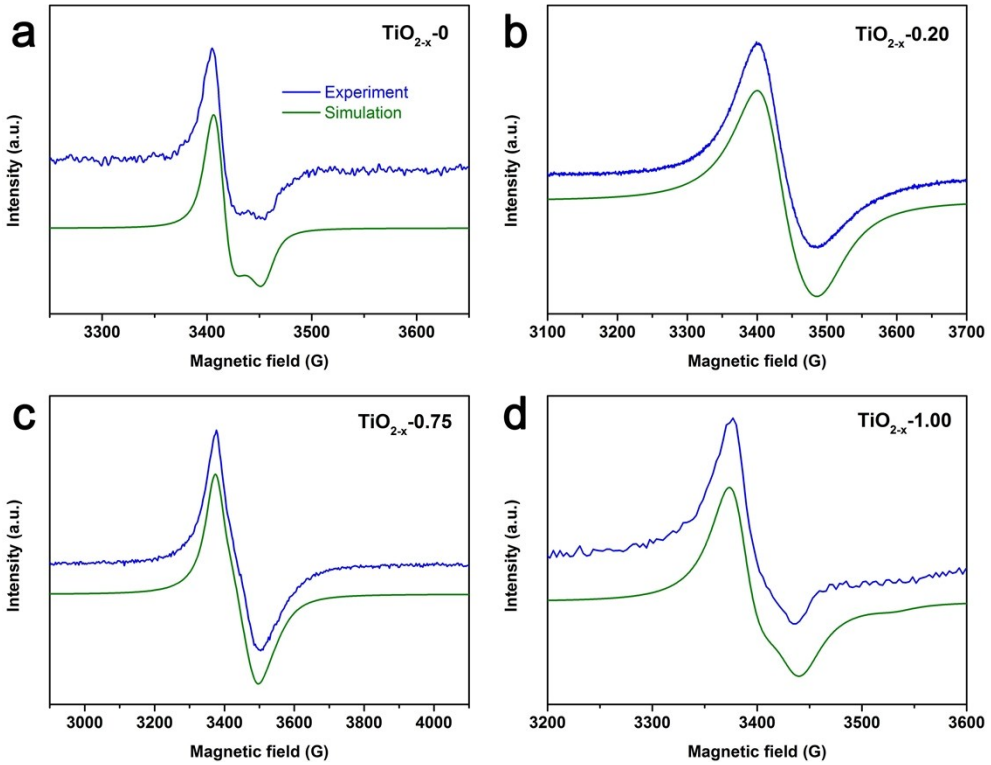

Fig. S5. Experimental (blue curve) and simulated (green curve) EPR spectra of reduced TiO_2 catalysts: (a) TiO_{2-x}-0, (b) TiO_{2-x}-0.20, (c) TiO_{2-x}-0.75 and (d) TiO_{2-x}-1.00. The simulated curves perfectly fit to the experimental curves.

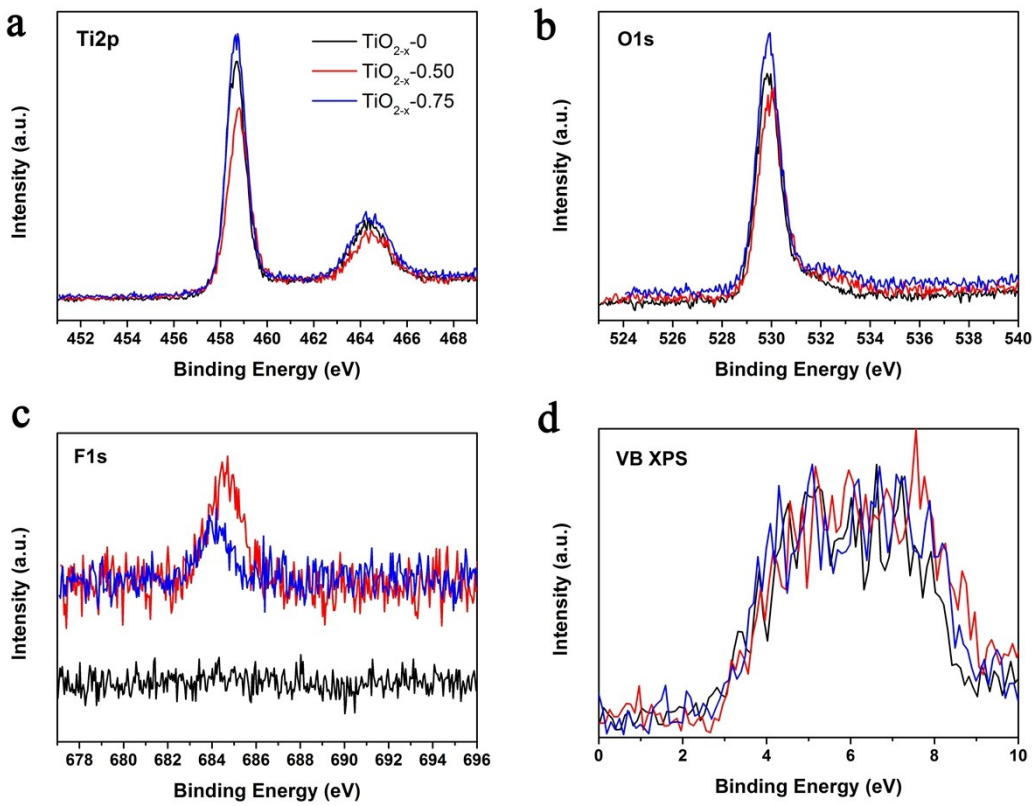

Fig. S6. XPS spectra of sample TiO_{2-x}-0, TiO_{2-x}-0.50 and TiO_{2-x}-0.75. (a) Ti2p XPS, (b) O1s XPS, (c) F1s XPS and (d) valence band XPS spectra of these reduced TiO_2 samples.

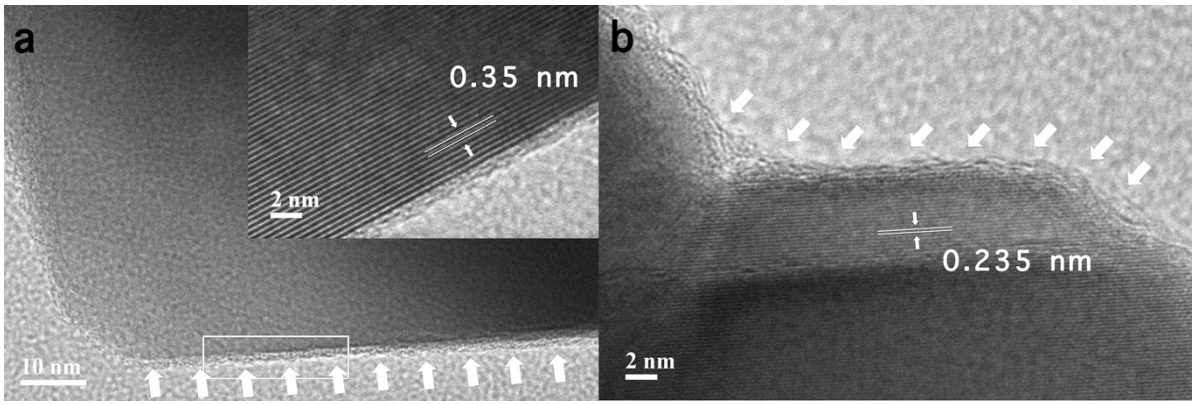

Fig. S7. HRTEM images of sample TiO_{2-x}-0.50. Disordered structural layers are generated on the surface of TiO_2 single crystals, which are marked with arrows in the figure. Insert image in (a) is the enlarged view of the selected area marked with white rectangle.

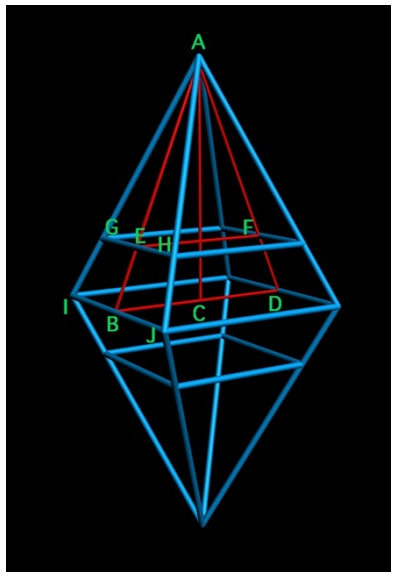

Fig. S8. Schematic diagram of reduced TiO_2 catalyst with {001} and {101} facets exposure and the formulae for calculating the percentage of {001} facets in TiO_{2-x} catalysts.

$$S_{001} = 2GH^2 \quad (S1)$$

$$S_{101} = 8\left(\frac{1}{2}IJ * AB - \frac{1}{2}GH * AE\right) = 8\left(\frac{1}{2}IJ * \frac{IJ}{2\cos\theta} - \frac{1}{2}GH * \frac{GH}{2\cos\theta}\right) \quad (S2)$$

$$S_{001}\% = \frac{S_{001}}{S_{001} + S_{101}} = \frac{\cos\theta}{\cos\theta + (\frac{IJ}{GH})^2 - 1} \quad (S3)$$

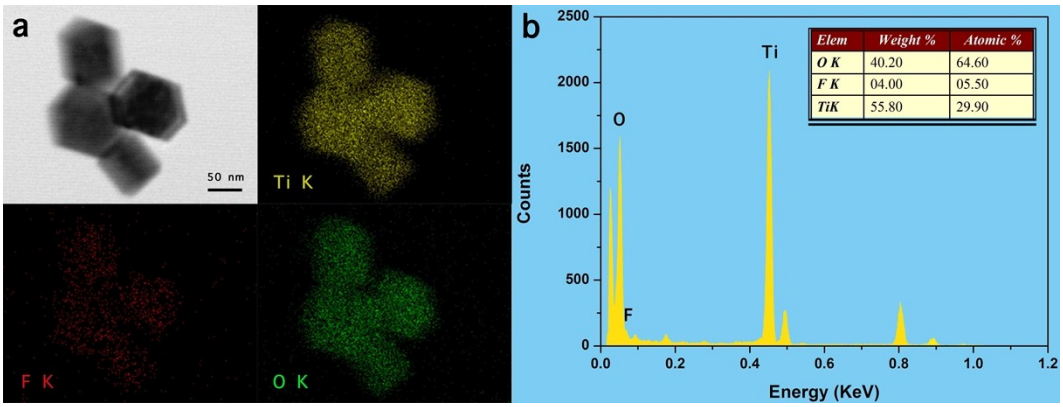

Fig. S9. (a) HRTEM-EDS image of TiO_{2-x}-0.50 and elemental mapping of Ti, O, F elements in this reduced TiO_2 sample. (b) EDS point spectrum of TiO_{2-x}-0.50. Insert table is the calculated atomic percentage of Ti, O, F elements.

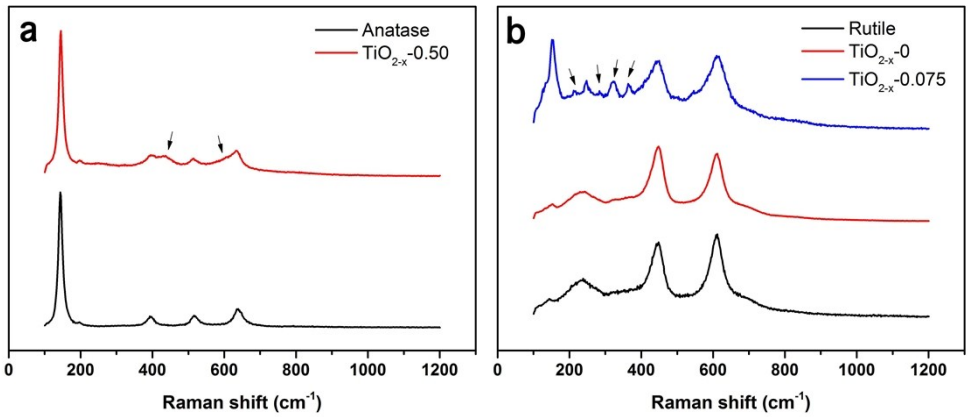

Fig. S10. Raman spectra of commercial anatase and TiO_{2-x}-0.50 (a), commercial rutile, TiO_{2-x}-0 and TiO_{2-x}-0.075 (b). Commercial anatase and rutile (Aladdin Reagent) nanoparticles are used as references.