Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information for

High quality sulfur-doped titanium dioxide nanocatalysts with visible light photocatalytic activity from non-hydrolytic thermolysis synthesis

Experimental Section:

1. ***Chemicals:*** Titanium(IV) fluoride (TiF_4; 99%, Sigma-Aldrich), Oleic acid (OA; >99%, Sigma-Aldrich), oleylamine (OM; 70%, Sigma-Aldrich), 1-octadecene (ODE; 90%, Sigma-Aldrich), Titania P25 (a commercial TiO_2), rhodamine B, methylene blue, absolute ethanol, acetone, hexane, toluene, were used as received.

2. ***Synthesis of TiO_2 Nanocrystals:*** In a typical synthesis, a slurry containing 1 mmol of TiF_4 powder, 10 mmol of oleic acid, 10 mmol of oleylamine, and 20 mmol of octadecene in a three-necked flask was heated to 130 °C to remove water and oxygen for 20 min. Along with vigorous magnetic stirring under vacuum in a temperature-controlled electromantle, an optically transparent solution was formed. The solution was then heated to 310 °C at a heating rate of 20 °C/min and kept for 1 h under an high purity nitrogen to give a slightly turbid solution. Then, an excess amount of mixture solvents of hexane and acetone was added into the solution. The resultant mixture was centrifugally separated and the products were collected. The precipitated nanocrystals were washed several times with absolute ethanol, and then dried in air at 80 °C overnight. The prepared nanocrystals could be dispersed in some nonpolar organic solvents, such as toluene, cyclohexane. **Caution:** The TiF_4 may releases HF in situ during the thermolysis of it in OA/OM/ODE solvents,[1] which is extremely dangerous. Thus the whole reaction is strictly conducted in the chemical fume hood and careful handled the as-resulted solution after the reaction.

3. ***Synthesis of S-TiO_2 Nanocrystals:*** The synthetic procedure was similar to that of TiO_2 nanocrystals, except that 1 mmol of S powder dispersed in 5 mmol of OM was swiftly injected into the solution at 310 °C under an high purity nitrogen atmosphere.

4. ***Characterization:*** Powder X-ray diffraction (PXRD) patterns were obtained from Bruker D8 diffractometer (German) with a slit of 1/2° at a scanning rate of 2° min^{-1}, using Cu Kα radiation (λ = 1.5406 Å). The lattice parameters were estimated with the least-squares method. Samples for transmission electron microscopy (TEM) and High-resolution TEM (HRTEM) characterizations were performed with a Philips Tecnai F20 FEG-TEM (USA) operated at 200 kV. The TEM samples were prepared by slowly vaporizing nanocrystal dispersion in toluene/hexane on amorphous carbon-coated copper grids. Room-temperature Raman spectra were measured with a WITec CRM200 confocal Raman microscopy system with the excitation line of 514.5 nm and an air cooling charge coupled device (CCD) as the detector (WITec Instruments Corp, Germany). With the use of Al K_α radiation (BE = 1486.6 eV) as the X-ray excitation source, X-ray photoelectron spectroscopic (XPS) measurements were carried out in an ion-pumped chamber (evacuated to 2×10^{-9} Torr) of an Escalad5 (U.K.) spectrometer. The UV-vis absorption spectrum of the nanocrystals was obtained on a Shimadzu/UV-1800 UV-vis spectrometer (Japan). The Fourier Transform Infrared (FTIR) absorption spectra of the nanocrystals were carried on Perkin Elmer/Spectrum GX FTIR Spectrometer (USA).

5. ***Photocatalytic Activity Test:*** The as-prepared TiO_2 and S-doped TiO_2 nanocrystals were firstly annealed in $Ar:H_2$ (80%:20%, volume) for several minutes at 700 °C before photoreaction. Photocatalytic reactions were carried on an open reactor with a cooling system to keep the reaction temperature constant. A 300W tungsten Xenon lamp with a 400 nm cutoff filter (λ = 420–770 nm) was used as visible light source. For a typical photocatalytic experiment, the 1 mg of catalysts were added to an aqueous solution of rhodamine B (10 mL, 15 mg/L) in a 100 mL quartz reactor. Before photoreaction, the suspension of TiO_2 and S-doped TiO_2 and rhodamine B was treated by sonication for 5 min and then vigorously stirred for 5 min in the dark to reach the adsorption/desorption equilibrium between the dye and the photocatalysts. Then 5 ml adequate aliquots of the sample were withdrawn after every 5 min irradiation, and centrifuged for subsequent measurements. The leftover rhodamine B was analyzed by a UV–visible spectrophotometer by monitoring the optical density of rhodamine B at 553 nm. The adsorbed amount of rhodamine B and photocatalytic degradation rate of nanocatalysts were calculated by Beer's law based on the absorption peak at 553 nm for rhodamine B by using UV-vis spectrophotometer (UV-2550, Shimadzu).

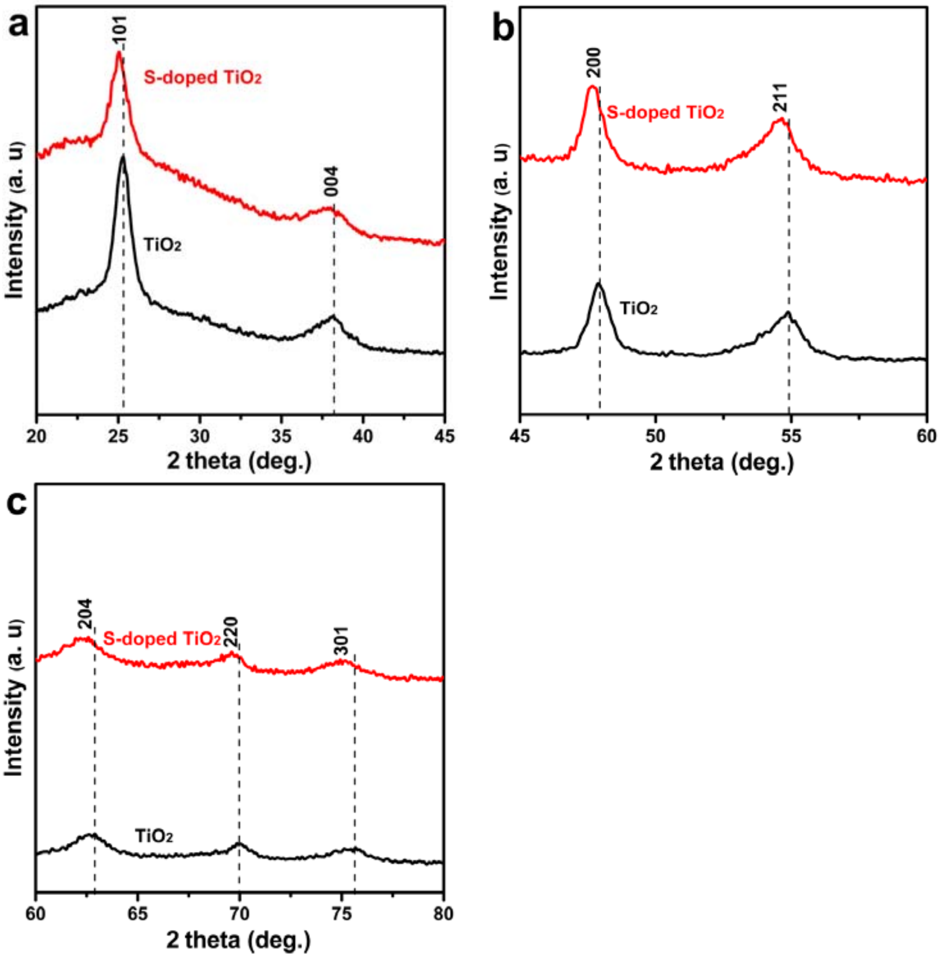

Figure S1. (a–c) The magnified diffraction peaks for TiO_2 and S-doped TiO_2 nanocrystals.

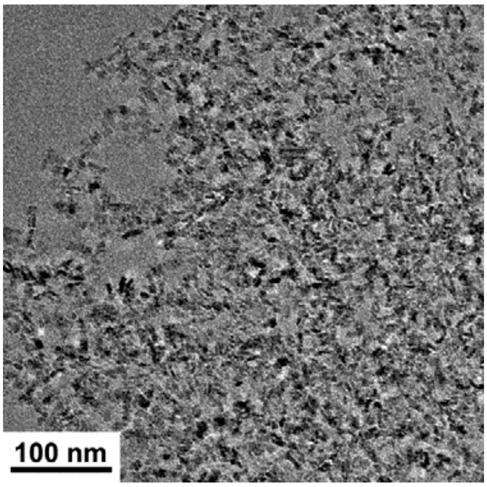

Figure S2. TEM image of undoped TiO_2 nanocrystals.

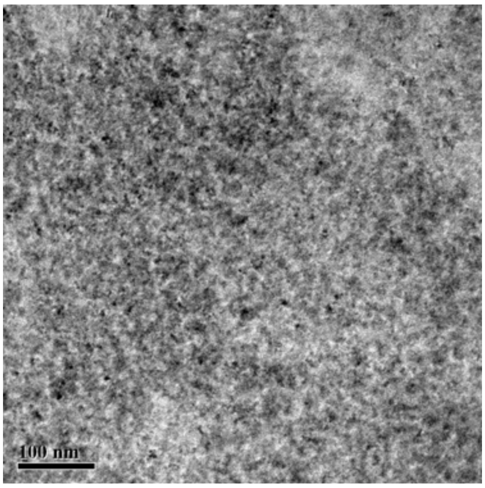

Figure S3. TEM image of as-obtained products without use of oleic acid and oleylamine surfactants.

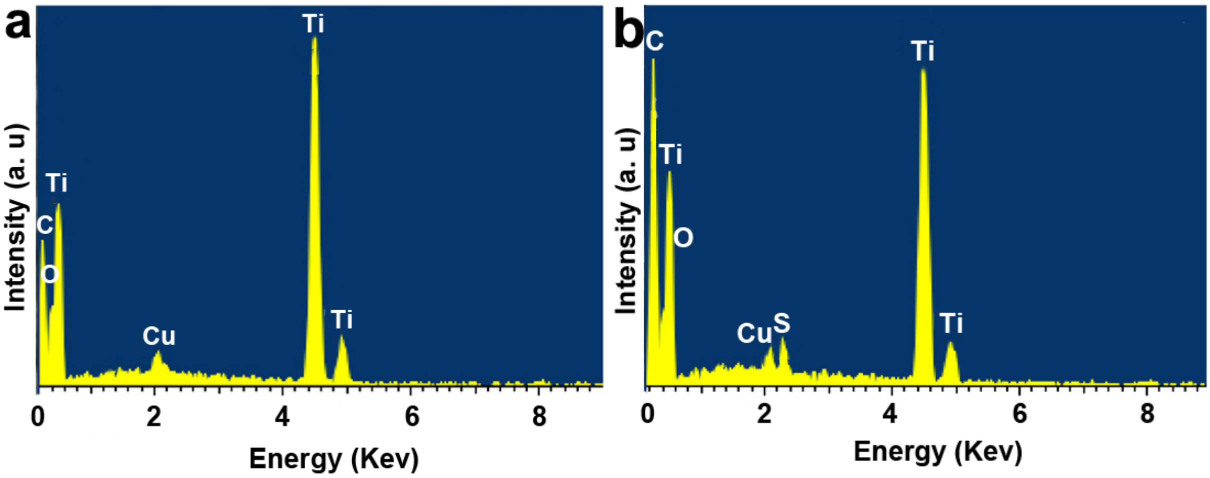

Figure S4. The energy dispersive X-ray analysis (EDAX) spectra of (a) undoped TiO_2 and (b) S-doped TiO_2 nanocrystals.

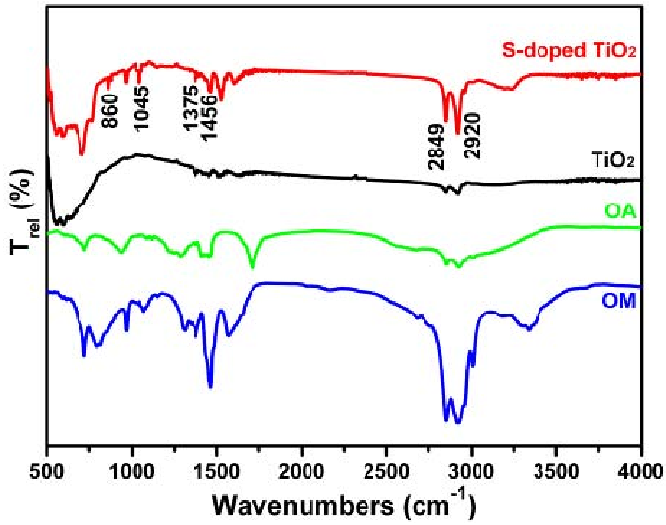

Figure S5. FTIR spectra of oleic acid, oleylamine, as-prepared TiO_2 and S-doped TiO_2 nanocrystals dispersed in toluene/hexane solutions.

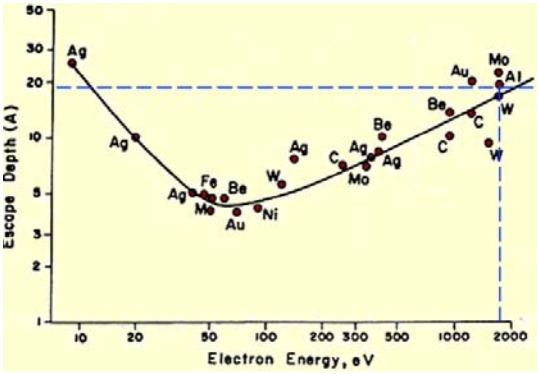

Figure S6. The relation between X ray light source energy and escape depth in XPS characterization.[2]

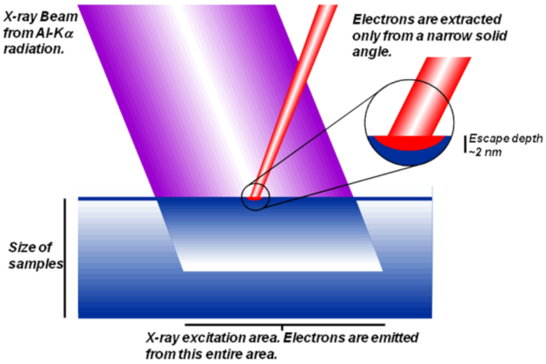

Figure S7. The schematic illustration of XPS characterization in our samples.

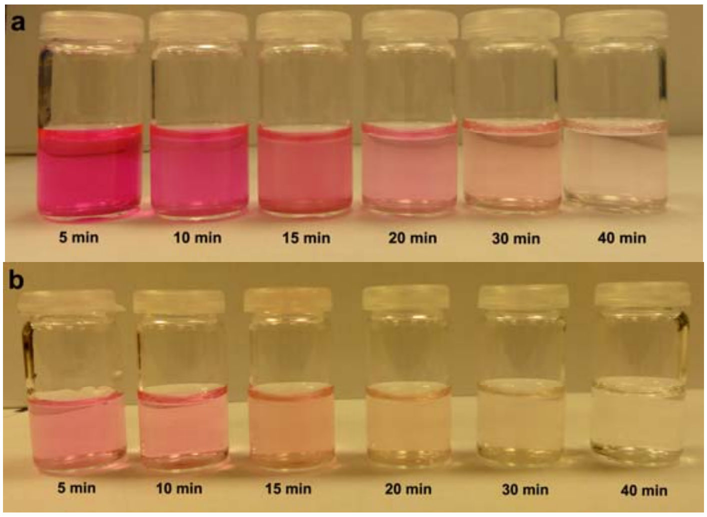

Figure S8. Photographs of leftover RhB dye solution centrifuged from the (a) undoped TiO_2 and (b) S-doped TiO_2 nanocatalysts suspensions after different reaction time.

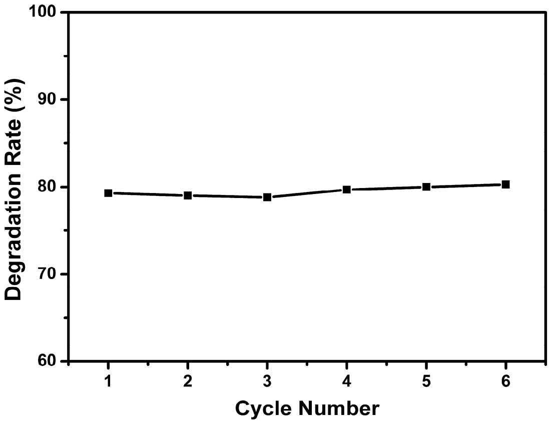

Figure S9. Photocatalytic stability under visible light irradiation of S-doped TiO_2 nanocrystals.

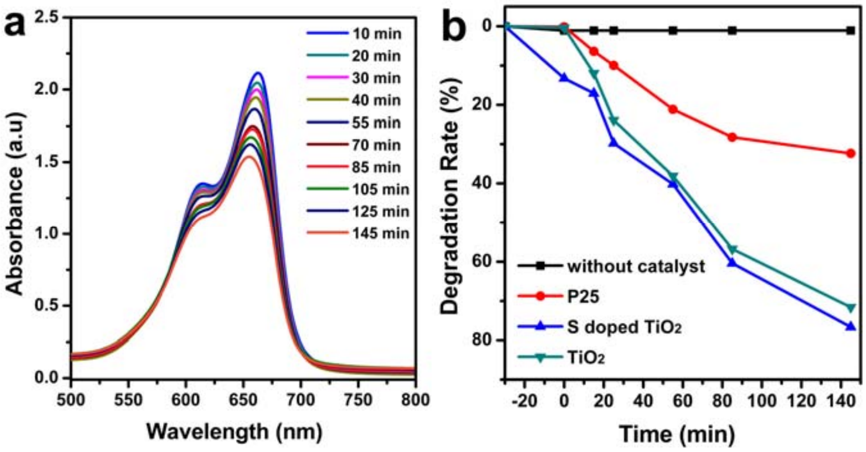

Figure S10. (a) UV-vis spectra of methylene blue (MB) dye vs. photoreaction time in the presence of S-doped TiO_2 nanocrystals. (b) Photocatalytic degradation of MB dye over without catalyst, commercial P25, TiO_2 and S-doped TiO_2 nanocatalysts under visible light irradiation (λ = 420–770 nm).

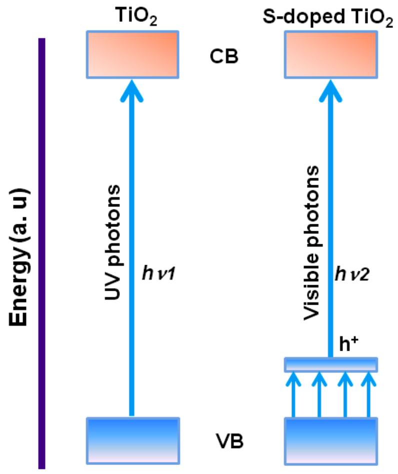

Figure S11. Plausible mechanism of S-doped TiO_2 nanocrystals for the visible-light activity photocatalysts. Herein, VB and CB are the abbreviations of valence band and conduction band.

References:

[1] T. R. Gordon, M. Cargnello, T. Paik, F. Mangolini, R. T. Weber, P. Fornasiero and C. B. Murray, *J. Am. Chem. Soc.*, **2012**, *134*, 6751.
[2] http://www.chem.qmul.ac.uk/surfaces/scc/scat5_1.htm