

Supporting Information

OPEN-CIRCUIT VOLTAGE IMPROVEMENT FROM TANTALUM DOPED TiO₂ NANOCRYSTALS

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EXPERIMENTAL METHODS

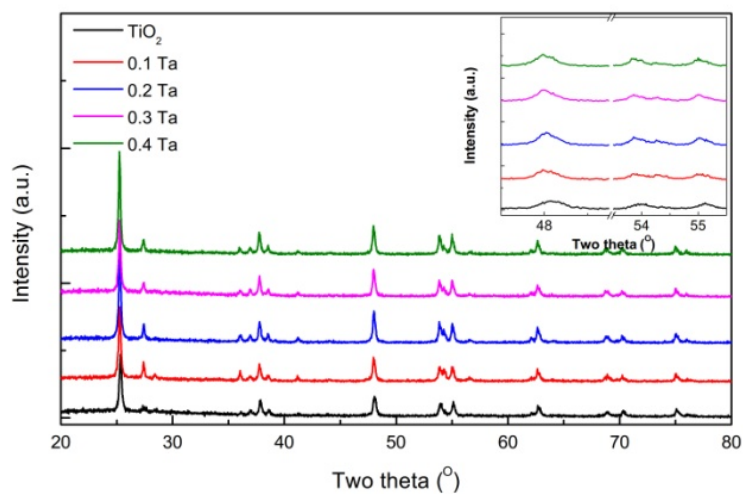
Particle preparation. Tantalum-doped TiO₂ nanoparticles were prepared via a liquid-feed flame spray synthesis. The reactor has three rings for titanium/tantalum precursor, H₂(fuel) and air(shield gas), respectively, from inside to out. There are 8 symmetrical pores (d=1mm) in the middle ring for H₂ flowing. The ethanol solution (0.4M) of titanium tetrabutoxide (98%, Lingfeng Chemical reagent Co.,Ltd., China) and tantalum chloride (99.7%, Sinopharm Chemical Reagent Co.Ltd, China) was sprayed out from the nozzle and ignited by a supported inverse H₂ /air diffusion flame (H₂: 0.38 m³ /h, air: 2.0 m³/h). The product stream was drawn from the combustion chamber by vacuum pump into powder collectors. The doping concentration was varied from 0-0.4% (with respect to Ti).

Device assembly. To prepare the DSSC working electrodes, 0.085 g of two kinds of ethyl cellulose (22 cps, 180~220 cps) were dispersed into 50 mL ethanol and stirred for 1 h. 0.22 g of Ta-doped TiO₂ nanoparticles and 1.5 mL terpinol were added in the mixture solution and stirred for 24 h. The mixture was dried at 70°C to obtain the viscous paste. Then the resulting paste was coated on FTO glass (15 Ω/square, Nippon Sheet Glass, Japan) using a doctor-blade method. The films were then sintered at 450°C for 30 min in air. The film were soaked in 0.5 mM N719 dye solution in a mixture of butylalcohol and acetonitrile (volume ratio, 1:1) and kept at room temperature for 24h to complete the sensitizer loading. The working electrodes (active area 0.25 cm²) were assembled and sealed with the counter electrodes made by thermal deposition of H₂PtCl₆ on FTO glass to produce a sandwich-type cell. The electrolyte, 0.60M BMII(1-butyl-3-methylimidazolium iodide), 0.03M I₂, 0.10M guanidinium thiocyanate, and 0.50M 4-tert-butylpyridine in acetonitrile, was introduced into the cell.

Characterization. Morphologies of the samples were observed by using a transmission electron microscope (TEM-100CXII) and scanning electron micrograph (Hitachi S-4800). X-Ray Diffraction (Rigaku D/max 2550 VB/PC diffract meter with Cu Kα radiation) was used to verify crystal phase. X-ray photoelectron spectra (XPS) measurements were carried out on an X-ray

photoelectron spectrometer (ESCALAB MK II) using Mg Ka (1253.6 eV) X-rays as the excitation source, with C 1s (284.6 eV) as the reference. The photocurrent and voltage of the DSSC devices were measured using a Newport solar simulator (91160A, Newport). The intensity of the lamp was adjusted using a Si reference cell for light intensity of 60 mW cm⁻². Electrochemical impedance spectra were measured using a potentiostat (Versastat, Ametek). The EIS measurements were carried out in darkness at the open-circuit voltage and 5 mV of amplitude over the frequency range of 0.1 Hz-100 kHz. We have added it in the supporting information. The dye-loading-amount experiment was performed by desorbing a dye-loaded photoanode in 0.05M NaOH solution in 1:1 H₂O/ethanol. A UV-vis spectrometer (Hewlett-Packard, Hayward, CA, USA) was used to measure the absorbance of the desorbing solution. By referring to the pre-established calibration curve, the dye-loading amount was determined. Mott-Schottky measurements were performed in 2M KCl at 10 kHz using a Solartron S1287 Electrochemical Interface and 255B Frequency Response Analyzer (Solartron Analytical, UK) at scan rate of 50 mVs⁻¹, and photocurrent density and the photovoltage of the dye sensitized solar cells were measured in 0.1M Na₂SO₄ solution using a CHI600C potentiostat at scan speed of 10 mVs⁻¹.

a



b

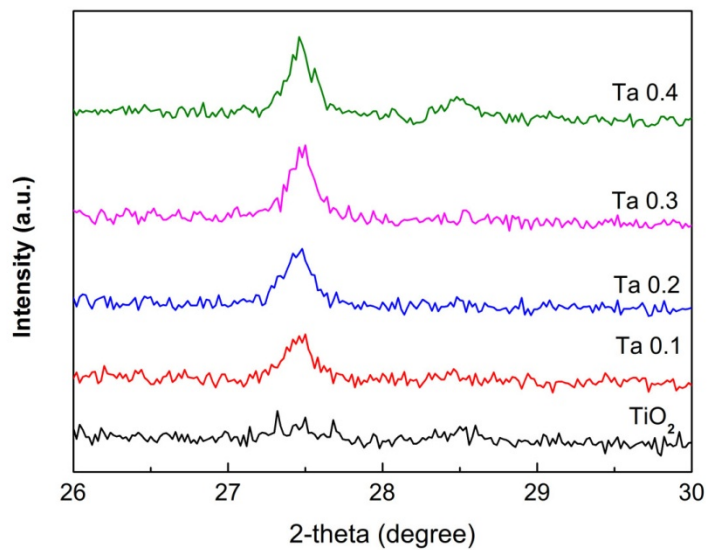


Figure S1. (a) XRD patterns of Ta-doped TiO₂ nanoparticles. (b) Details of XRD patterns in the range of 26-30°, showing the (110) diffraction peak of rutile TiO₂.

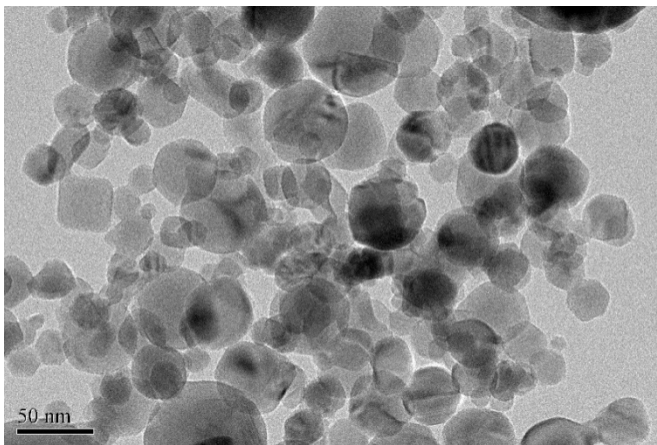
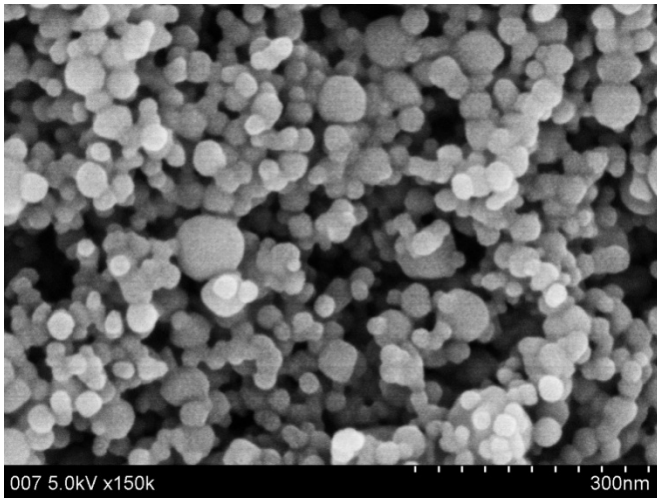


Figure S2. SEM and TEM images of TiO_2 nanoparticles prepared by FSP.

Table S1 Doping concentration estimated from XPS results.

Sample	0.2% Ta- TiO_2	0.3% Ta- TiO_2	0.4% Ta- TiO_2
Doping concentration (at. %)	0.1	0.16	0.23

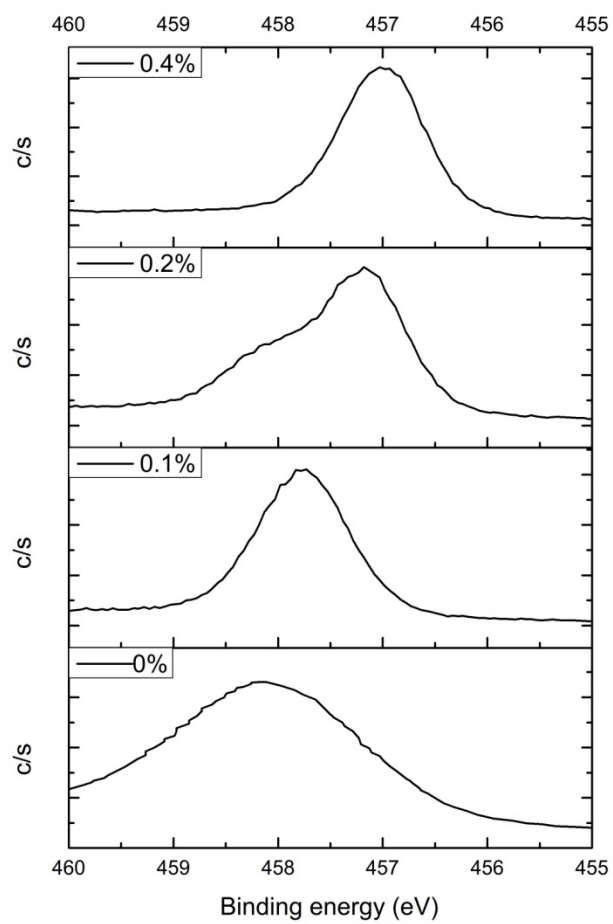


Figure S3. XPS survey spectra of Ti_{2p_{3/2}}.

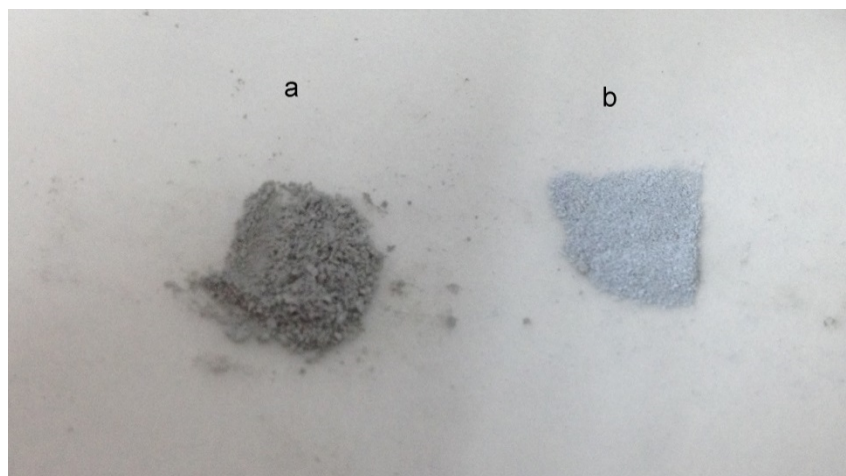


Figure S4. Photographs of doped powders under Ar (a) and air (b) heat treatment.