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A facile synthesis of anatase N,B codoped TiO_2 Anodes for Improved-Performance Dye-Sensitized Solar Cells

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Supplementary Figure & Table:

Experimental details

Preparation of the N,B codoped TiO_2: The undoped and N,B codoped TiO_2 were prepared by modified sol-gel method. For N,B codoped TiO_2 sample, Titanium isopropoxide (Fluka) was added drop by drop (2 mL/min) to 90 ml deionized water with the mixture of DD-water, H_3BO_3 and $CO(NH_2)_2$ at room temperature under vigorous stirring for 3-5 h. The formed precipitate solution，which were prepared by adding different amount of boric acid and urea(TiO_2: urea =20/7, 4/1, weight ratio), were washed and collected with deionized water thoroughly, then stirred for 10 h at 80 °C to formed transparent sol and heated at 200 °C in autoclave for 12 h to obtain gelatin which was added polyethylene glycol (PEG, molecular weight of 20 000, Aldrich) and terpineol (Fluka) to form the TiO_2 paste(N,B codoped-1(0.43 at.% N,

0.51 at.% B), N,B codoped-2). The whole process was under vigorous stirring. The preparation method for undoped sample was the same as above with the addition of precursors as required.

Assembly of DSCs:

N,B codoped and undoped photocathodes were fabricated by screen-printing technique using the our group's published procedures to achieve TiO_2 film thicknesses of **13.4** μm、 **13.0**μm and **12.8** μm, respectively.[S1] The N,B codoped and undoped photocathodes were immersed in an 0.5mM ethanol solution of dye N719 [cis-dithiocyanate-N,N'-bis-(4-carboxylate-4'-tetrabutylamonium-carboxylate-2,2'-ipyridine) ruthenium(II)] at room temperature for 12h. Liquid-junction solar cells were prepared by infiltrating the dye-coated TiO_2 electrode with redox electrolyte containing 0.1 mol·L^{-1}lithium iodide anhydrous, 0.1 mol·L^{-1} iodine, 0.6mol·L^{-1} 1, 2-dimethyl-3-propylimidazolium iodide, 0.5 mol·L^{-1} 4-tertbutylpyridine in acetonitrile. The effective cell area was 0.25 cm^2.

Characterization:

The particle morphology of undoped and N,B codoped electrodes microstructure were observed using a field emission scanning electron microscope (FE-SEM, sirion200, FEI Corp., Holland). Crystallite sizes, phases, and shapes were observed with transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) (TEM, JEOL-2010,Japan). The crystallinity of undoped and N,B codoped films were determined using X-ray diffraction analysis (XRD, TTR-III,

Rigaku Corp., Japan) measurement with Cu Kα (λ=0.1541 nm). The crystallite size D was calculated by the Sherrer equation. The photocurrent density-photovoltage (J-V) characteristics of DSCs with an active area of 0.25 cm^2 were measured under an illumination of AM 1.5 (100 mW cm^{-2}) which was realized on a solar simulator (Oriel Sol 3A, USA) with a Keithley 2420 source meter(Keithley, USA), calibrated with a NREL-certified silicon solar cell. The UV-vis spectrum was performed on a UV-vis spectrophotometer (TU-1901, PGeneral Instrument Inc., China). The flatband potential (V_{fb}) of the nanostructure TiO_2 electrode was performed by measuring absorbance at 780 nm as a function of the applied potential.[S2] For spectroscopic electrochemistry measurement, 4 μm-thick TiO_2 film formed the working electrode (2cm^2 surface area) of a three-electrode photoelectrochemical cell employing a platinum wire counter electrode and an Ag/AgCl reference electrode. Potential control was carried out on a CHI 660A potentiostat, and the applied potential being scanned at 5 mV/s. A 780 nm monochromatic light source was obtained from UV-Vis spectrophotometer (TU-1901, PGeneral Instrument Inc., China). The incident-phototo-current efficiency (IPCE) of the DSC was measured using a 300W Xe lamp light source with monochromatic light (Oriel Instrument, USA). For each determination of V_{fb}, a new working electrode and freshly prepared electrolyte solution were used. Impedance measurements were carried out with an IM6ex electrochemical workstation (Zahner-Elektrick, Germany) in the frequency range of 10 mHz-1000kHz at room temperature. The working electrode was a dyed TiO_2 electrode of DSC, and the auxiliary electrode and the reference electrode were a

platinized counter electrode of DSC. The amplitude of the alternative signal was 5mV.

References:

[S1]. H.J.Tian, L.H.Hu, C.N.Zhang, W.Q.Liu, Y.Huang, L.Guo, J.Sheng, S.Y.Dai, *J. Phys. Chem. C,* 2010, **114**, 1627-1632.

[S2]. G. Redmond, D. Fitzmaurice, *J. Phys. Chem.* **1993**, 97, 1426–1430.

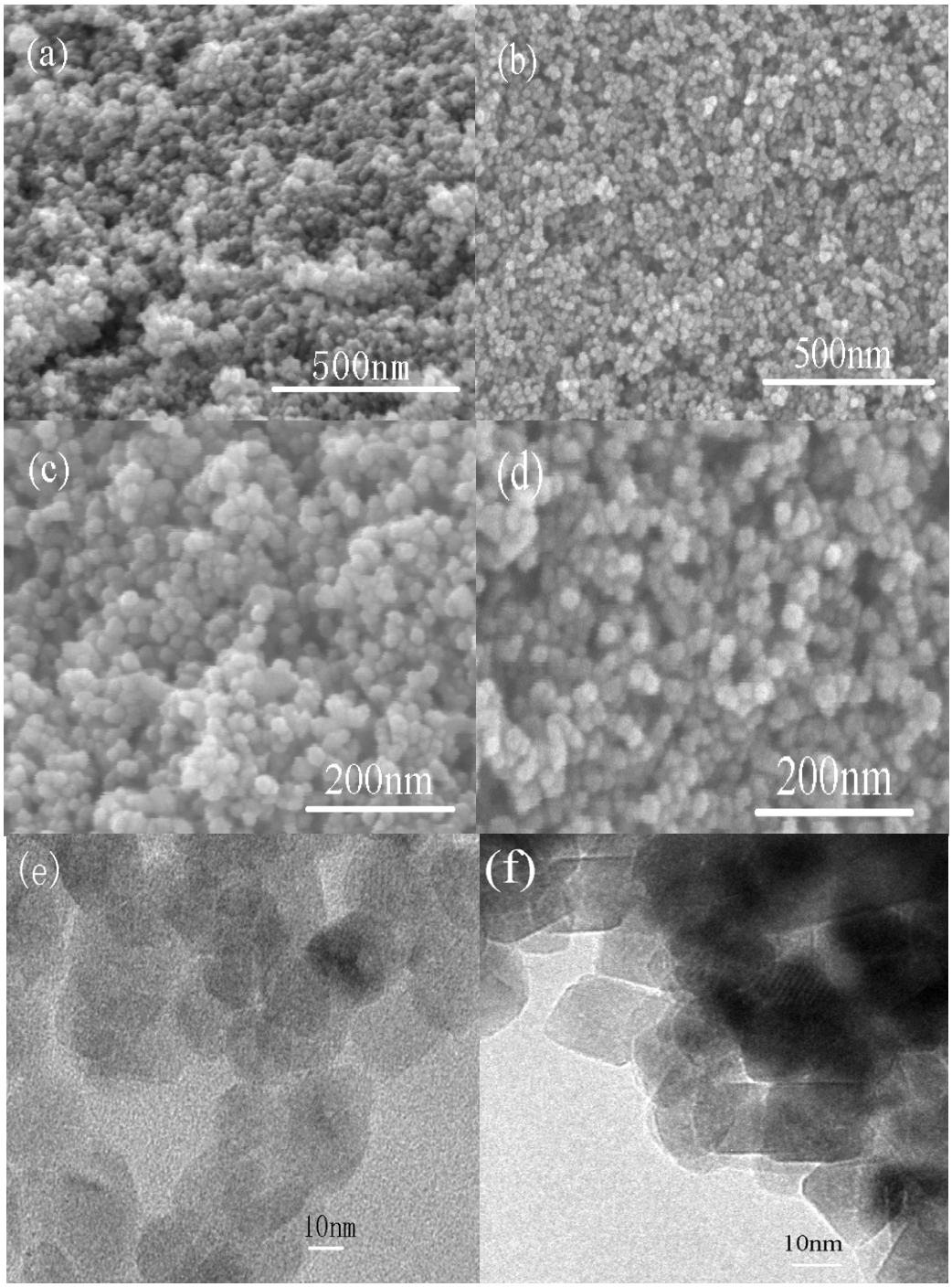

Fig.S.1. FE-SEM and HRTEM micrographs of the undoped and N,B codoped titania films. (a), (c), (e) undoped titania films; (b), (d) , (f) N,B codoped titania films.

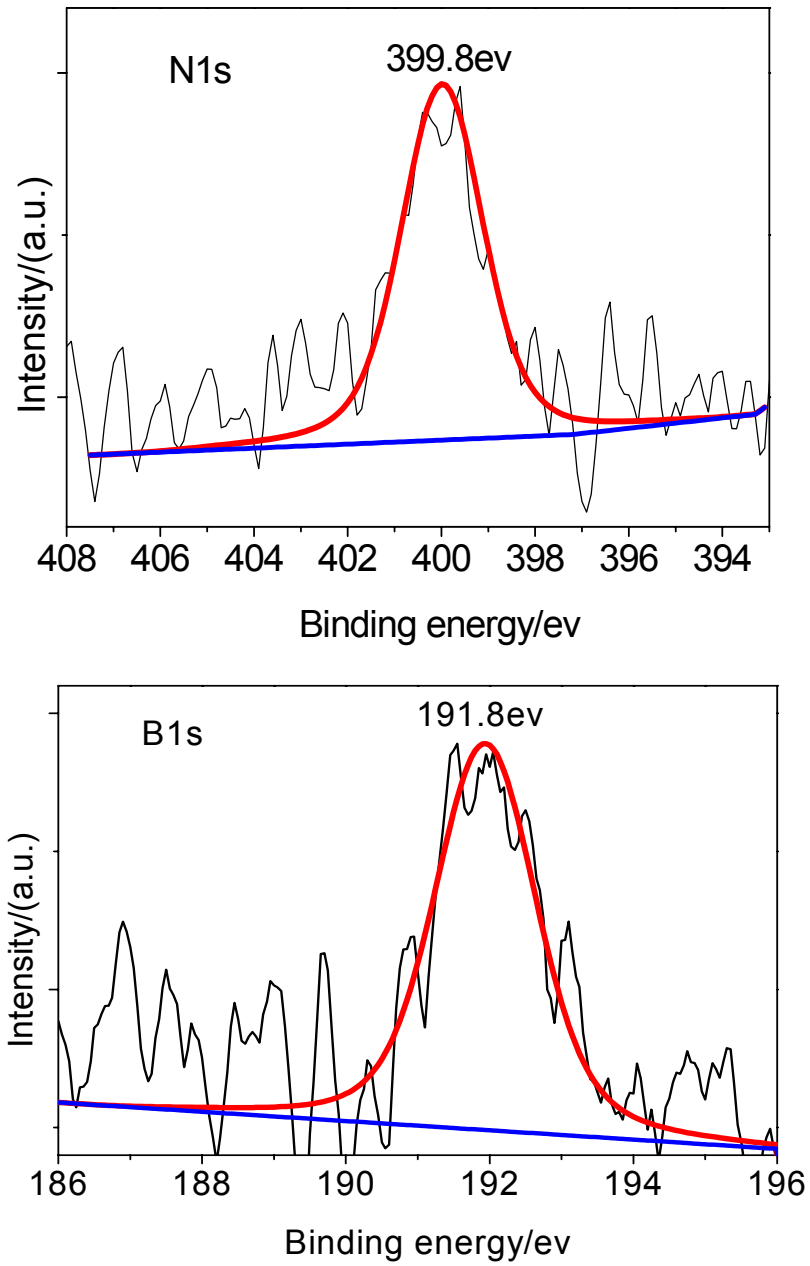

Fig.S.2. N 1s, B1s XPS spectrum of N,B codoped titania powder, showing that the binding energy of the N 1s, B1s peak centered at 399.8eV, 191.8ev eV, respectively. (0.43 at.% N, 0.51 at.% B)

Table S.1 Performances of the solar cells based on undoped and N,B codoped TiO_2 electrodes.

L/μm	DSC	V_{oc} [mV]	J_{sc} [mA/cm^2]	FF [%]	η [%]
13.4 (undoped)	undoped	771	14.04	74	8.0
13.0 (N,B codoped-1)	N,B codoped-1	823	13.76	74	8.4
12.8 (N,B codoped-2)	N,B codoped-2	792	14.67	70	8.1

Table S.2. Properties of the undoped and N,B codoped TiO_2 in the DSCs

Type of pastes	Crystallite size (nm)	BET Surface area(m^2/g)
undoped	15.3	82.4
N,B codoped-1	17.5	74.6
N,B codoped-2	17.1	76.6

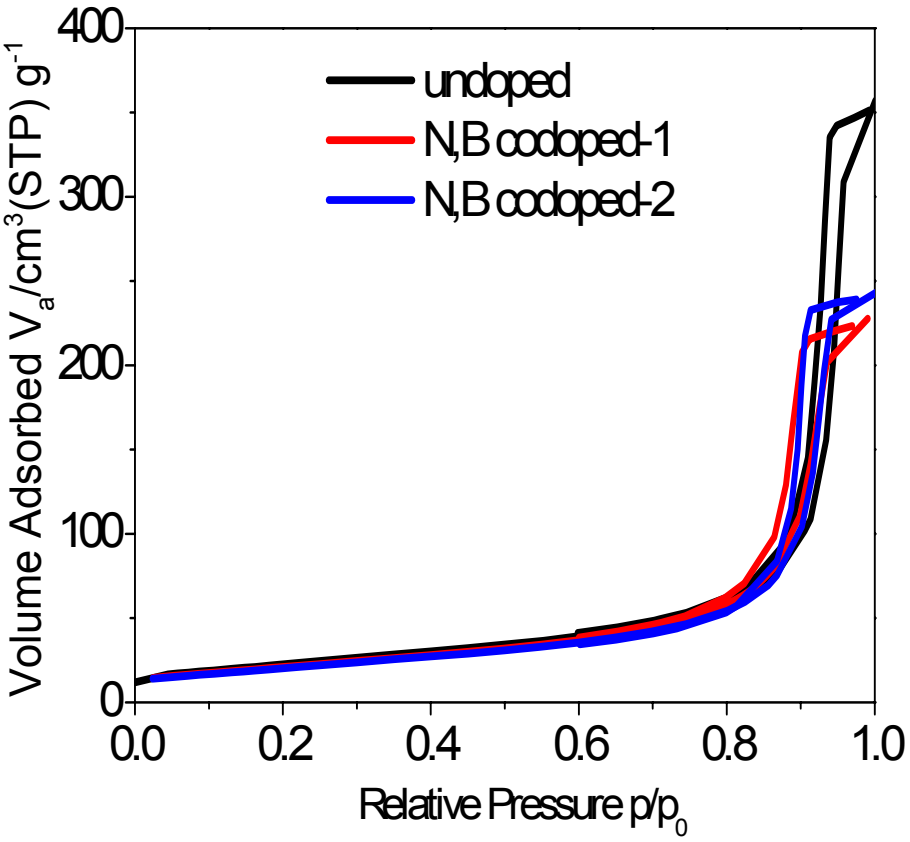

Fig. S.3. N_2 sorption curve of undoped and N,B codoped mesoporous TiO_2 powder

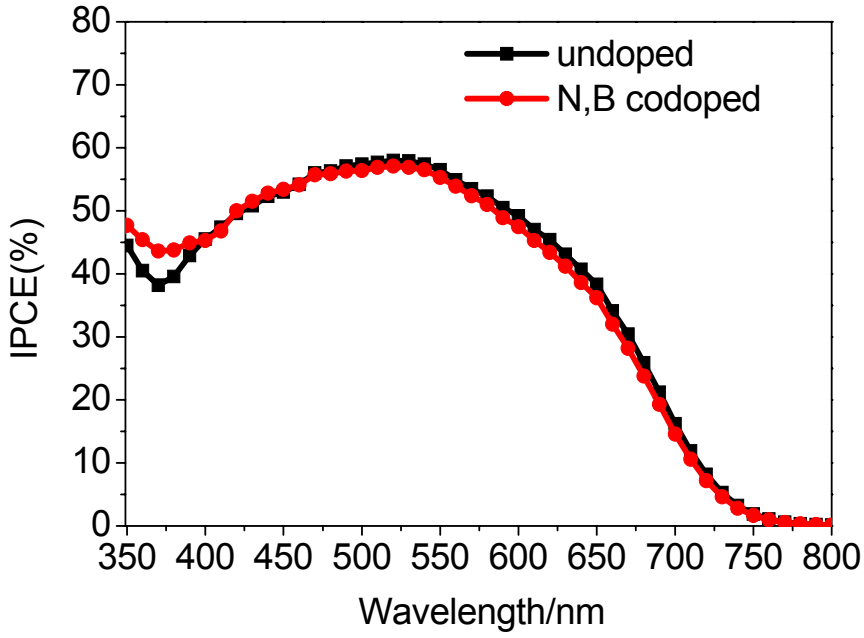

Fig.S.4. Action spectra of the dye-sensitized solar cells based on undoped and N,B codoped TiO_2 electrodes(0.43 at.% N, 0.51 at.% B).

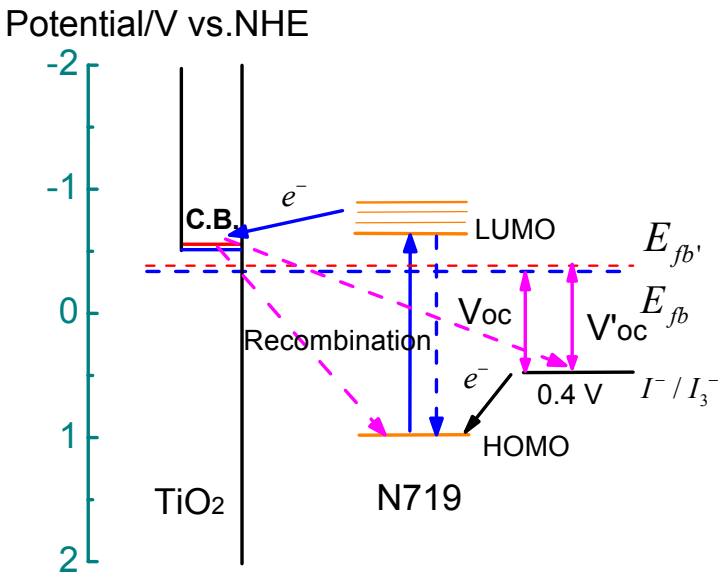

Fig.S.5. Schematic energy diagram for DSCs based on N719 as the photosensitizer, undoped TiO_2 electrode/N,B codoped TiO_2 electrode, and the I^-/I_3^- redox electrolyte.