

## Electronic Supplementary Information

### Morphology-Controlled Synthesis SrTiO<sub>3</sub>/TiO<sub>2</sub> Heterostructures and Their Photocatalytic Performance for Water Splitting

#### S1

#### Experimental details

##### Materials

Titanium Tetraisopropoxide (TTIP, Ti-(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>, 97%, Aldrich), TiO<sub>2</sub> (≥ 99.8%, 100 nm), Sr(OH)<sub>2</sub>·8H<sub>2</sub>O (≥ 98%), KCl (≥ 99.5%), HNO<sub>3</sub> (65-68%), C<sub>2</sub>H<sub>5</sub>OH (≥ 99.7%), CH<sub>3</sub>COOH (≥ 99.5%), Triethanolamine (C<sub>6</sub>H<sub>15</sub>NO<sub>3</sub>) were purchased from Sinopharm Chemical Reagent Company. Ltd., Shanghai Titanchem Co., Ltd. Deionized water was used in all experiments. All reagents were of analytical grade and were used without further purification.

##### Preparation of SrTiO<sub>3</sub>/TiO<sub>2</sub> heterostructures at different Sr/Ti mole ratios

The SrTiO<sub>3</sub>/TiO<sub>2</sub> NP heterostructures with different Sr(OH)<sub>2</sub>/TiO<sub>2</sub> (Sr/Ti) mole ratios were prepared by hydrothermal method.<sup>1</sup> Typically, different mole ratios Sr/Ti (TiO<sub>2</sub> NP, self-made followed in literature<sup>2</sup>) with 0, 20, 40, 60, 80 and 100% in 60 mL of distilled water. The suspension was transferred into an 80 mL Teflon-lined stainless steel autoclave and then placed in an oven at 160 °C for 12 h. The resulting white powders were collected by filtration, then washed with a 1.0 M aqueous acetic acid solution and ethanol thoroughly, and finally dried in an oven at 50 °C.

##### Preparation of different morphology-controlled SrTiO<sub>3</sub>/TiO<sub>2</sub> heterostructures

All the morphology-controlled TiO<sub>2</sub> precursors were self-made according to relevant literatures, TiO<sub>2</sub> NC,<sup>3</sup> NP,<sup>2</sup> NS,<sup>1</sup> and NF.<sup>4</sup> The final morphology-controlled SrTiO<sub>3</sub>/TiO<sub>2</sub> heterostructures were all fabricated via hydrothermal method in Sr(OH)<sub>2</sub> solution. Typically, 0.4g morphology-controlled TiO<sub>2</sub> precursor (NC, NP, NS and NF) and 1.06 g Sr(OH)<sub>2</sub>·8H<sub>2</sub>O were added into a 80 mL Teflon-lined stainless steel autoclave with a mole ratio of Sr/Ti = 40%, then 60mL deionized water was added under vigorous stirring for 30 min until Sr(OH)<sub>2</sub>·8H<sub>2</sub>O was completely dissolved. Then the autoclave was placed in an oven at 160 °C for 12 h and cooled to room temperature. The white powder (denoted as SrTiO<sub>3</sub>/TiO<sub>2</sub>) was washed by deionized water, then washed with a 1.0 M aqueous acetic acid solution and ethanol through centrifugation for several times and dried in an oven at 50 °C. Finally, the morphology-controlled SrTiO<sub>3</sub>/TiO<sub>2</sub> heterostructures samples were obtained.

##### Characterization

All the samples were characterized by an X-ray Diffractometer (Holland PANalytical X'pert Pro MRD) with Ni-filtered CuKα radiation (λ = 0.154056 nm; 40 kV, 40 mA) in the range of 20-80° (2θ) at a scanning rate of 10° min<sup>-1</sup>. Rietveld structure refinement was performed with the program X'Pert High Score Plus (PANalytical 2012) using a pseudo-Voigt profile function and polynomial background model. The morphology of each sample was characterized by a scanning electron microscopy (Phenom-World's Phenom Pro Desktop SEM, Netherlands). An energy dispersive X-ray spectrometer (EDS) detector attached to the SEM (S-3400N, Hitachi) was used to measure the element composition and distribution with the X-Flash Detector 4010 (Burker, ALX). Transmission electron microscopy (TEM) images were obtained by a FEI Tecnai G2 F20 with a beam energy of 300 keV. The specific surface area of each sample was measured by the BET technology using nitrogen adsorption and desorption isotherms at 77K on a Micrometrics ASAP 2020 HD88 system. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method in the P/P0 range 0.05-1. The pore-size distribution was calculated on the desorption branch

of the isotherm using the Barrett-Joyner-Halenda (BJH) model. UV-vis diffuse reflectance spectra of all the samples were measured in the range of 200-800 nm using a UV-vis spectrophotometer (Hitachi U-3900, Japan) with BaSO<sub>4</sub> as the reflectance standard. The band gap energy ( $E_g$ ) of the material was calculated from the absorption data by using the Tauc relation.<sup>5</sup>

$$(\epsilon h\nu) = C(h\nu - E_g)^n \quad (1)$$

Where C is a constant,  $\epsilon$  is molar extinction coefficient,  $E_g$  is the average band gap of the material and n depends on the type of transition. For n = 2,  $E_g$  in equation (1) is indirect allowed band gap.

## Photocatalytic activity measurements

The well prepared SrTiO<sub>3</sub>/TiO<sub>2</sub> heterostructures were investigated for photocatalytic H<sub>2</sub> generation in a methanol/water sacrificial reagent system under the irradiation of UV light using photocatalytic activity evaluation system CEL-SPH2N (Beijing CEALight, China). In a typical experiment, 0.1 g catalyst of each sample was dispersed in 100 mL 6 M methanol solution (methanol was used as the sacrifice agent). A 300 W high-pressure Xe lamp (CEL-HXUV300, spectral output 200-2500 nm, overall radiant output 50 W, UV output 6.6 W) was used as the light source and the distance from a point source of light to the water surface is 10 cm. The reaction temperature was set at 5 °C. Finally, the H<sub>2</sub> gas generated from the photocatalytic reaction was analyzed using a TCD-type gas chromatography<sup>6</sup> (GC-7900 with a 5A molecular sieve column). The whole system described above is shown in Figure S1.

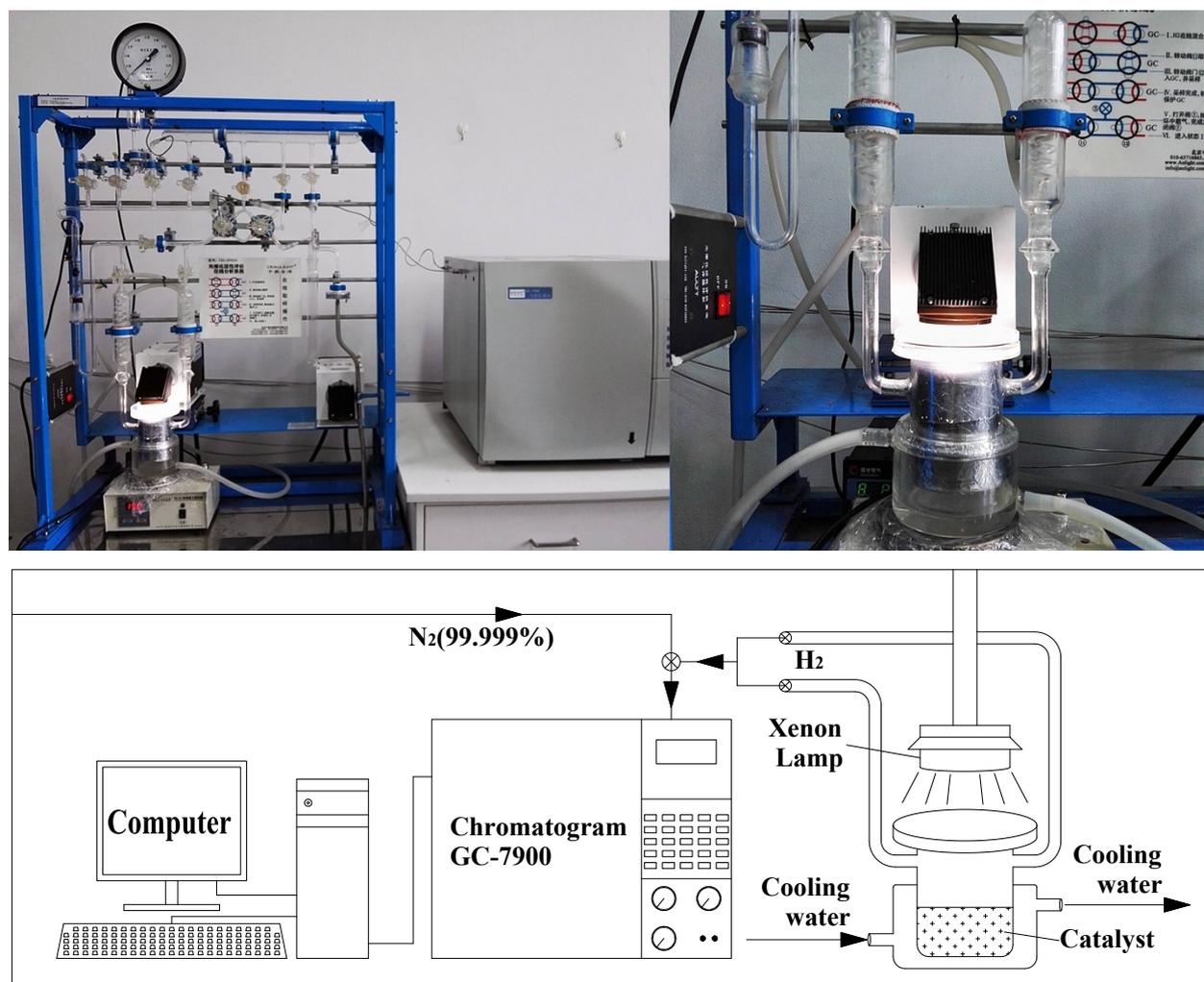


Figure S1. Photocatalytic water splitting system setup with Xe Lamp

**Table 2.** BET surface area and crystallite size of SrTiO<sub>3</sub>/TiO<sub>2</sub>

SrTiO <sub>3</sub> /TiO <sub>2</sub> heterostructures	2-Theta (degree)	d <sub>110</sub> (nm)	Unit cell (a, b, c, nm)	Crystallit e size (nm)	2-Theta (degree)	d <sub>101</sub> (nm)	Unit cell (a, b, nm)	Unit cell (c, nm)	Crystallit e size (nm)	BET surf e area (m <sup>2</sup> g <sup>-1</sup> )	Pore size (nm)	Pore volum e (cm <sup>3</sup> g <sup>-1</sup> )
	Rietveld structure refinement for SrTiO <sub>3</sub> Ref. code: 01-074-1296 Crystal system: Cubic, Bravais Type: Primitive (P), Space group: Pm-3m				Rietveld structure refinement for TiO <sub>2</sub> Ref. code: 01-084-1286 Crystal system: Tetragonal, Bravais Type: Body centered (I), Space group: I41/amd							
NC	32.397	0.27	0.39	71.652	25.195	0.35	0.38	0.96	80.187	11.78	13.66	0.040
		6	0			3	1	5		3	3	
NP	32.335	0.27	0.39	45.041	25.164	0.35	0.37	0.97	136.729	23.19	13.63	0.079
		7	1			4	7	4		5	6	
NS	32.334	0.27	0.39	93.489	25.132	0.35	0.37	0.95	148.813	15.94	20.48	0.082
		7	0			4	8	1		7	1	
NF	32.342	0.27	0.39	50.811	25.145	0.35	0.37	0.95	110.232	17.56	13.64	0.060
		7	1			4	9	1		0	9	

**Table 3.** H<sub>2</sub> production results with different SrTiO<sub>3</sub>/TiO<sub>2</sub> mole ratios and morphologies

Sr/Ti mole ratios and SrTiO <sub>3</sub> /TiO <sub>2</sub> heterostructures	8h amount of H <sub>2</sub> generation (mmol)	Velocity (mmol <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> )
0%	0.304	0.106
20%	0.457	0.178
40%	0.722	0.358
60%	0.625	0.313
80%	0.574	0.230
100%	0.372	0.130
NC	0.508	0.218
NP	0.731	0.367
NS	0.394	0.152
NF	0.612	0.281

## References

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