## **Supplementary Information**

### Zr-Al Co-doped SrTiO<sub>3</sub> with Suppressed Charge Recombination for Efficient

### Photocatalytic Overall Water Splitting

Jiwei Cui,<sup>a</sup> Xinmin Yang,<sup>a</sup> Zhongshan Yang,<sup>a</sup> Yanhui Sun,<sup>a</sup> Xin Chen,<sup>a</sup> Xiaolu Liu,<sup>a</sup>

Defa Wang,<sup>a</sup> Shaokun Jiang,<sup>b</sup> Lequan Liu<sup>\*a</sup> and Jinhua Ye<sup>ac</sup>

<sup>a</sup> TJU-NIMS International Collaboration Laboratory, Key Lab of Advanced Ceramics and Machining Technology (Ministry of Education) and Tianjin Key Laboratory of Composite and Functional Materials, School of Material Science and Engineering, Tianjin University, 92 Weijin Road, Tianjin 300072, P. R. China.

<sup>b</sup> Purification Equipment Research Institute of Handan, Handan 056000, Hebei, China

<sup>c</sup> International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 3050044, Japan.

#### **Experimental sections**

**Materials:** SrTiO<sub>3</sub> (Sigma-Aldrich Co, LLC. nanopowder), SrCl<sub>2</sub> (Kanto Chemicals Co., Inc., 98.0%, anhydrous), Al<sub>2</sub>O<sub>3</sub> (Sigma-Aldrich Co, LLC., nanopowder), ZrO<sub>2</sub> (Aladdin Biochemical Technology Co., Ltd., nanopowder). The experimental water was all deionized water. All chemicals were used without further purification.

**Synthesis of Al:SrTiO<sub>3</sub>:** SrTiO<sub>3</sub>, SrCl<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> were used as raw materials to prepare Al:STO. First, STO was fully mixed with Al<sub>2</sub>O<sub>3</sub> nanopowder to get a uniform mixture (Al:STO). Then, the Al:STO was thoroughly mixed with SrCl<sub>2</sub>. The mixture was placed in an alumina crucible at a heating rate of 10 °C/min to 1100 °C and calcined for 10 h. After the Al:STO was cooled to room temperature, it was washed with deionized water until the AgNO<sub>3</sub> solution was added to the centrifugal supernatant and there was no white precipitate. The mixture is placed in an oven at 150 °C and dried for 6 h.

**Synthesis of Zr,Al:SrTiO<sub>3</sub>:** SrTiO<sub>3</sub>, SrCl<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> were used as raw materials to prepare Zr,Al:STO. First of all, in order to ensure the same doping amount of Al, STO was fully mixed with Al<sub>2</sub>O<sub>3</sub> nanopowder to get a uniform mixture (Al:STO). Then take different proportions of ZrO<sub>2</sub> powder and mix it with Al:STO powder to get Zr,Al:STO. Finally, the Zr,Al:STO was thoroughly mixed with SrCl<sub>2</sub>.The mixture was placed in an alumina crucible at a heating rate of 10 °C/min to 1100 °C and calcined for 10 h. After the Zr,Al:STO was cooled to room temperature, it was washed with deionized water until the AgNO<sub>3</sub> solution was added to the centrifugal supernatant and there was no white precipitate. The mixture is placed in an oven at 150 °C and dried for 6 h.

**Deposition of cocatalyst:** Pt was loaded as a cocatalyst by the photodeposition method. The samples were loaded with 1 g/100ml  $H_2PtCl_6.nH_2O$  as Pt source, respectively, and use a 300 W Xenon lamp to illuminate for 10 min under vacuum conditions. The theoretical content of Pt was 0.5 wt%. The actual content was 0.45 wt% determined by ICP-OES.

#### Measurement of photocatalytic activity

The measurement of photocatalytic  $H_2$  and  $O_2$  evolution was carried out in a side-irradiationtype reactor connected with a closed gas circulation system. The photocatalyst of Zr,Al:STO (50 mg) was dispersed in 270 mL deionized water with a magnetic stirrer. 0.5 wt% Pt was loaded as cocatalyst via photodeposition method (300 W Xenon lamp). The reactor was irradiated by a 300 W Xenon lamp for overall water splitting. The production of overall water splitting was detected by a gas chromatograph (GC-8A with TCD, Shimadzu), using Ar as a carrier gas. All the overall water splitting experiments presented in the article were carried out under the full spectrum of 300 W Xe lamp.

#### Sample characterization

The crystal structure of the catalyst was characterized by X-ray diffraction (XRD; MiniFlex600) equipped with Cu Kα radiation at 40 kV and 200 mA at a scanning rate of 10°/min. The morphology of the catalyst was observed by scanning electron microscope (SEM; S-4800, Hitachi, Japan). Inductively coupled plasma optical emission spectroscopy (ICP-OES; Optima 5300DV) was used for elemental analysis. Transmission electron microscope (TEM; Tecnai G2 F30 FEI, U.S.A.) was used for the lattice analysis. X-ray photoelectron spectrum (XPS; ESCALAB-250Xi) is used to measure the chemical state of the catalyst surface elements, and the binding energy was referenced to C 1s peaks (284.6 eV) of contaminated carbon. Electron paramagnetic resonance (EPR) measurement was performed by JFS-FA200. Photoluminance spectra (PL; Horiba JobinYvon Fluorolog) was used for electron lifetime with the excitation light at 325 nm. The ultraviolet–visible diffuse reflectance spectra (UV–vis DRS; Shimadzu UV-2700) was used to study the optical performance.

Photoelectrochemical (PEC) measurement was carried out by using CHI 760E electrochemical analyzer with a conventional three electrode cell. A  $1 \times 1$  cm<sup>2</sup> FTO photoanode deposited samples, a Pt wire as the counter electrode and an Ag/AgCl as the reference electrode. A 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte solution. The electrochemical impedance spectroscopy (EIS) measurements were carried out with a sinusoidal ac perturbation of 5 mV applied over the frequency range of 0.01 to  $10^5$  Hz. The photocurrents were measured at 1.8 V initial voltage.

#### Calculation method for lattice mismatch

The difference of the dopants and the substituted ions in the ions radius is used to investigate the degree of lattice mismatch.  $D_R$  (%) was quantitatively estimated as

$$D_{R} (B) = \frac{R(Ti^{4+}) - R(B)}{R(Ti^{4+})} \times 100$$

where the R (B) (B = A1<sup>3+</sup> and Zr<sup>4+</sup>) is the radius of dopant ions.



Fig S1. H<sub>2</sub> generation rate of Al:STO with different molar ratio of STO/SrCl<sub>2</sub>.



Fig S2. High resolution XPS spectra of Al 2p region in (a) Al:STO and (b) Zr,Al:STO. (c)

High resolution XPS spectra of Zr 3d region in Zr,Al:STO.



**Fig S3.** Roman spectra of samples where the "◆" indicate the first-order Raman peak positions and "●" indicate the second-order Raman peak positions.

Two broad Raman peaks were observed from 200 cm<sup>-1</sup> to 500 cm<sup>-1</sup> and 600 cm<sup>-1</sup> to 800 cm<sup>-1</sup> which are attributed to second-order Raman scattering. The peaks located at 260, 310, 360, 625, 680, and 740 cm<sup>-1</sup> were ascribed to Ti–O and O–Sr–O modes. It was found that all peaks of Zr,Al:STO appeared a blue shift of 3cm<sup>-1</sup> as compared with Al:STO, indicating that the Zr ions successfully entered the lattice and the doping of  $Zr^{4+}$  caused internal tension in the crystal. The peaks observed at 174, 540, 790 cm<sup>-1</sup> can be ascribed to first-order Raman scattering. Remarkably, the first-order Raman scattering disappeared in Al:STO and Zr,Al:STO. It is accepted that the selection rules for cubic SrTiO<sub>3</sub> at room temperature led to the first-order Raman modes disappear.



Fig S4. The FT-IR spectra of samples



Fig S5. TEM images of Al:STO (a) and Zr,Al:STO (b)



**Fig S6.** (a) TEM image of Pt nanoparticles distribution on Pt/Zr,Al:STO photocatalyst; Inset: the size distribution of Pt nanoparticles. (b) HRTEM image of Pt/Zr,Al:STO.



Fig S7. UV-vis DRS spectra of Zr,Al:STO for  $H_2O_2$  production.



Fig S8.  $H_2$  generation rate of  $Zr_{0.03}Al_x$ :STO (x=0~0.09) in overall water splitting with different Al dopant amount.



Fig S9. UV-vis DRS spectra of samples.



Fig S10. Gas evolution of Zr,Al:STO with different irradiation conditions.



**Fig S11.** High resolution XPS spectra of Ti 2p region in (a) STO; (b) Al:STO and (c) Zr,Al:STO.



Fig S12. EPR (at 123 K) spectra of STO,  $Al_{0.054}$ :STO and  $Zr_{0.03}Al_{0.054}$ :STO.

The signal at g-value of ~2.003 can be ascribed Vo. The EPR result of  $Al_{0.054}$ :STO showed that the concentration of Vo increased than STO. Moreover, the Vo concentration of Zr<sub>0.03</sub>Al<sub>0.054</sub>:STO decreased than Al<sub>0.054</sub>:STO. The tendency is consistent with O 1s XPS measurement. In addition, the signal at g-value of ~2.010 can be attributed to adsorbed oxygen.



Fig S13. Room-temperature EPR spectra of STO and Zr<sub>0.03</sub>:STO



Fig S14. Amorphous surface images of Al:STO (a) and Zr,Al:STO (b).



Fig S15. Bragg positions of the diffraction lines and the Rietveld refinement result.

Atom	X	У	Z	B <sub>iso</sub> (Å <sup>2</sup> )	Occ
Sr1	0	0	0	0.631	1
Ti1	0.5	0.5	0.5	0.470	0.9800
A11	0.5	0.5	0.5	0.470	0.0200
O1	0	0.5	0.5	0.548	1

 Table S1

 Crystallographic parameters of Al:STO from Rietveld refinement <sup>a</sup>

X-ray diffraction pattern:  $R_p$ =7.53%,  $R_{wp}$ =9.68%,  $R_{Bragg}$ =2.02%,  $R_F$ =7.77%. Space group Pm-3m, a=b=c=3.9051 Å, Z=1, calculated density=5.1460 g/cm<sup>-3</sup>.

stallographic	allographic parameters of Zr,AI:STO from Rietveld refinement <sup>®</sup>					
Atom	Х	у	Z	B <sub>iso</sub> (Å <sup>2</sup> )	Occ	
Sr1	0	0	0	0.671	1	
Ti1	0.5	0.5	0.5	0.535	0.981	
Al1	0.5	0.5	0.5	0.535	0.008	
Zr1	0.5	0.5	0.5	0.535	0.011	
01	0	0.5	0.5	0.815	1	

## Table S2 Crystallographic parameters of Zr,Al:STO from Rietveld refinement <sup>b</sup>

X-ray diffraction pattern:  $R_p=9.53\%$ ,  $R_{wp}=11.83\%$ ,  $R_{Bragg}=1.86\%$ ,  $R_F=9.40\%$ . Space group Pm-3m, a=b=c=3.9081 Å, Z=1, calculated density=5.2596 g/cm<sup>-3</sup>.

#### Table S3

Molar ratio of SrTiO<sub>3</sub> photocatalysts determined by ICP-OES

	Zr <sub>0.02</sub> Al <sub>0.054</sub> :STO	Zr <sub>0.03</sub> Al <sub>0.054</sub> :STO	Zr <sub>0.04</sub> Al <sub>0.054</sub> :STO	Zr <sub>0.05</sub> Al <sub>0.054</sub> :STO	Al <sub>0.054</sub> :STO
[Zr]/[Ti]	1.96%	2.62%	3.07%	3.37%	
[Al]/[Ti]	1.91%	1.77%	1.70%	1.70%	2.39%

	Atom 1	Atom 2	Distance (Å)
A1.STO	Sr1	01	2.76135
AI:510	Ti1	01	1.95257
7. 41.870	Sr1	01	2.76347
ZI,AI:510	Til	01	1.95407

# **Table S4**Selected interatomic distances found in Al:STO and Zr,Al:STO