

Supporting Information (6 pages)

Electronic Structure Basis for Enhanced Overall Water Splitting Photocatalysis with Aluminum Doped SrTiO₃ in Natural Sunlight

Zeqiong Zhao,^a Renato V. Goncalves,^{a,b} Sajib K. Barman,^c Emma J. Willard,^a Edaan Byle,^a Russell Perry,^a Zongkai Wu,^a Muhammad N. Huda,^{*c} Adam J. Moulé,^d and Frank E. Osterloh^{*a}

^a Department of Chemistry, University of California, Davis. One Shields Avenue, Davis, CA, 95616, USA. Fax: (+1) 530 752 8995; E-mail: fosterloh@ucdavis.edu

^b São Carlos Institute of Physics, University of São Paulo, PO Box 369, 13560-970 São Carlos, SP, Brazil.

^c Department of Physics, University of Texas at Arlington, Texas 76019, USA

^d Department of Chemical Engineering, University of California, Davis. One Shields Avenue, Davis, CA, 95616, USA

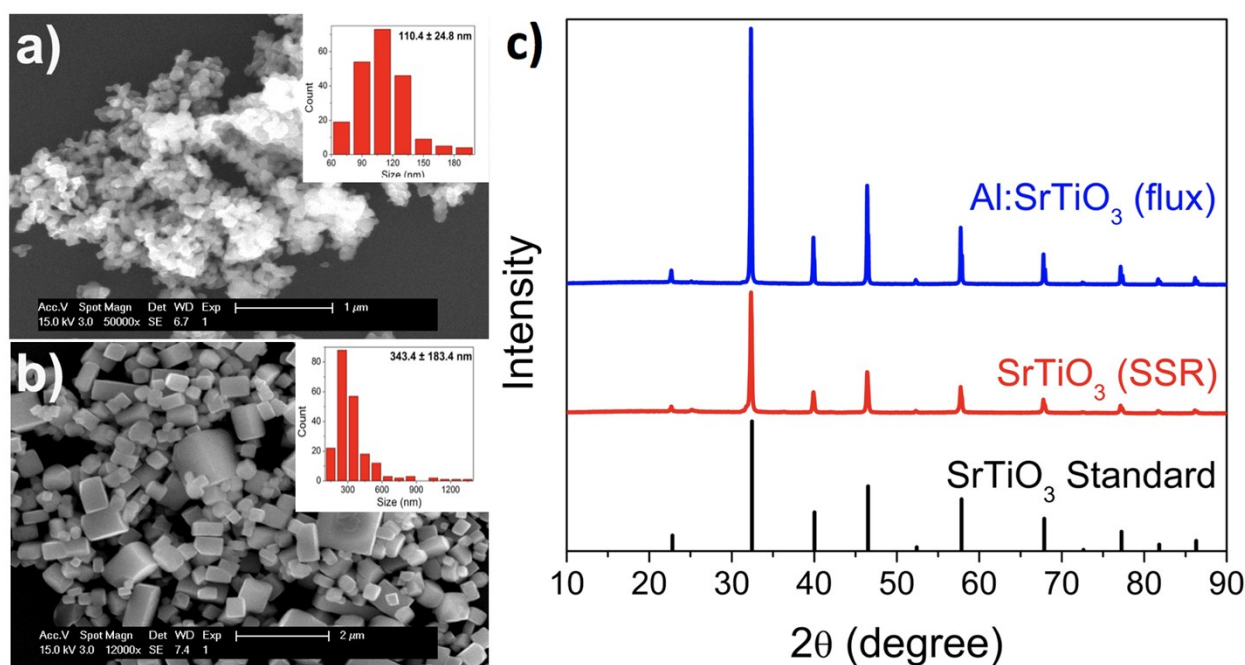


Figure S1. SEM image and size histogram of (a) SrTiO₃ and (b) Al:SrTiO₃. (c) PXRD spectra of SrTiO₃ and Al:SrTiO₃. The reference pattern for SrTiO₃ (JPDF #35-0734) is shown on the bottom. Adapted from Ref. 1 with permission from The Royal Society of Chemistry.

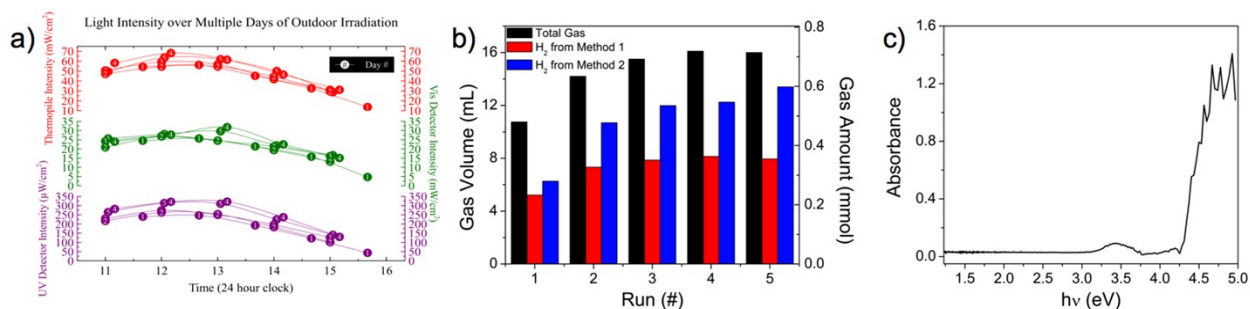


Figure S2. Supporting data for type 1 single bed particle suspension baggie reactor under natural sunlight. (a) Recorded light intensity for every hour with a UV detector (GaN detector, SED (SEL) 365 of 230 to 380 nm range), a thermopile detector (SED 623 of 200 - 4200 nm range), and a visible light detector (GaAsP detector, SED (SEL) 005 of 260-680 nm range) for 5 sunlight irradiation experiments. (b) Generated total gas amount and H₂ gas amount after 4 h sunlight irradiation. After the gas composition is determined by GC, H₂ amount from method 1 is based on the ratio of H₂ to total gas while H₂ amount from method 2 is based on the evolved O₂ to estimate the generated H₂ gas amount after 4 h irradiation. For method 2, O₂ from dissolved air is removed based on the amount of N₂. (c) Absorption spectrum of polypropylene bag.

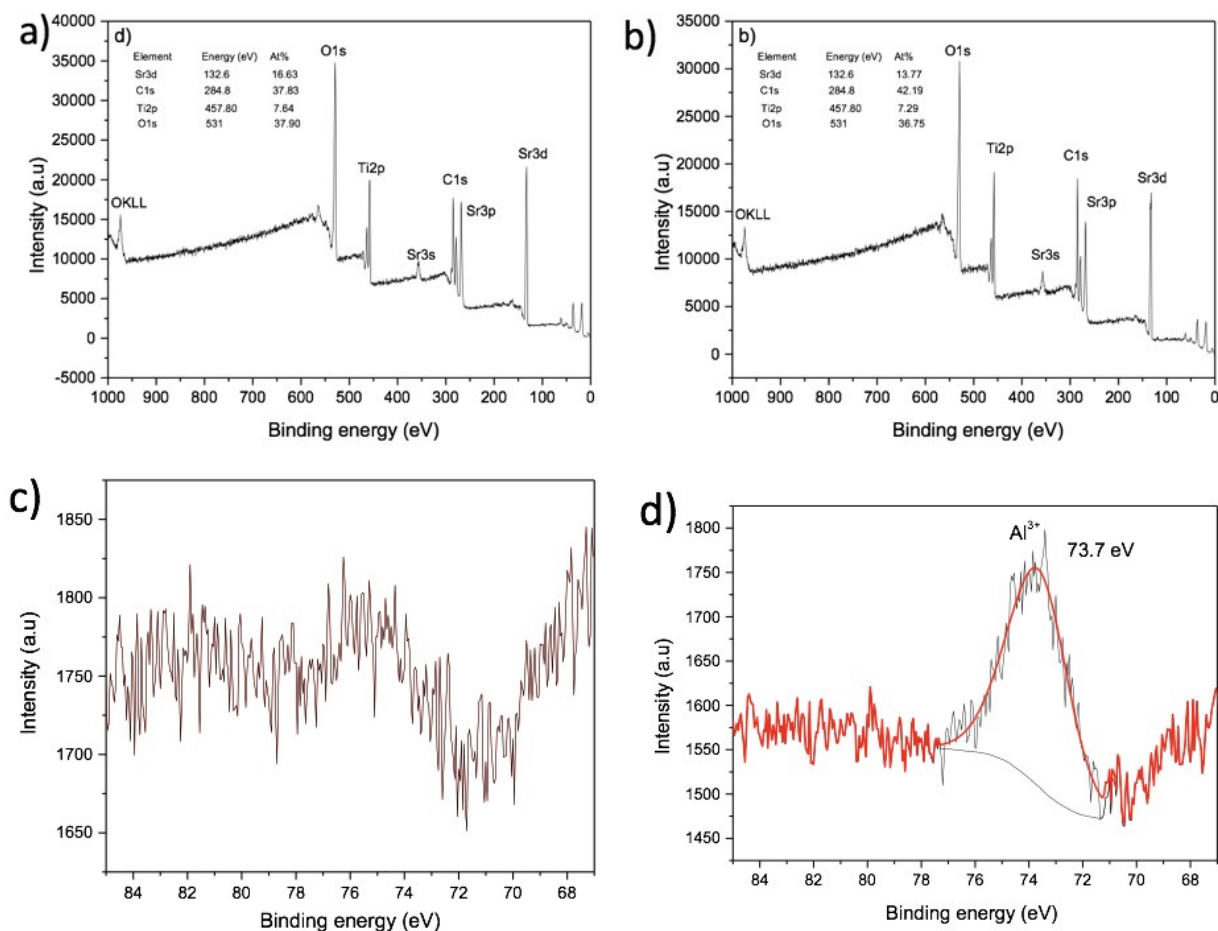


Figure S3. XPS survey spectra for (a) SrTiO₃ and (b) Al:SrTiO₃ and high resolution XPS spectra of Al 2p region in (c) SrTiO₃ and (d) Al:SrTiO₃.

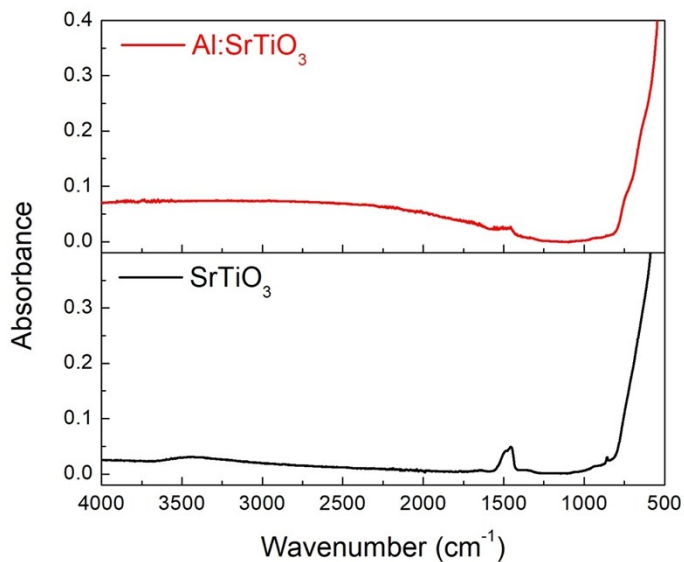


Figure S4. IR spectra of SrTiO₃ and Al:SrTiO₃, showing the broad H-O-H stretching vibration at 3,500 cm⁻¹.

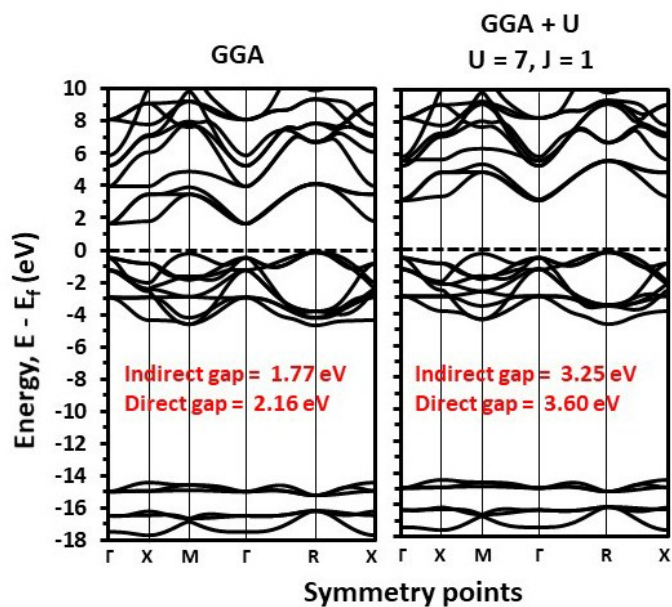


Figure S5. DFT calculated band structures of SrTiO₃ with no defect by GGA method and GGA+U method. The Fermi level (E_f) is set at 0 eV.

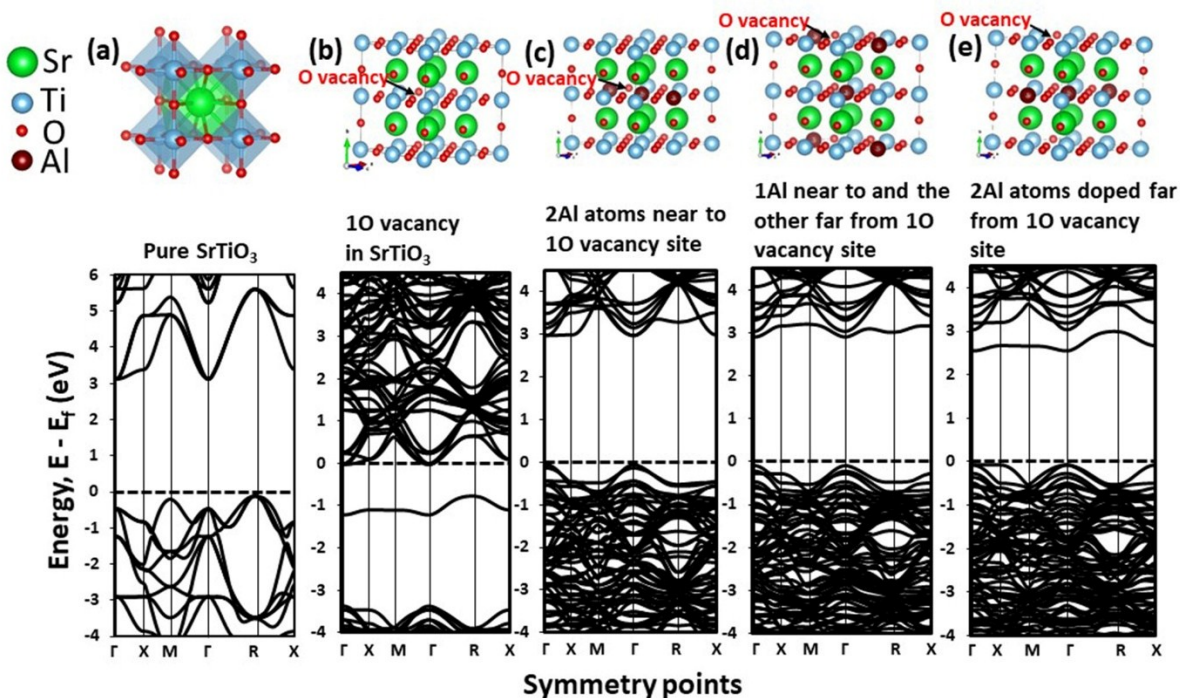


Figure S6. The DFT (GGA+U) electronic band structures of (a) STO with no defects, (b) STO with V_o , (c) 2 Al doped STO with V_o (2 Al close to V_o); (d) 2 Al doped STO with V_o (1 Al close to V_o while 1 Al far from V_o); (e) 2 Al doped STO with V_o (2 Al far away from V_o). The Fermi level (E_f) is set at 0 eV.

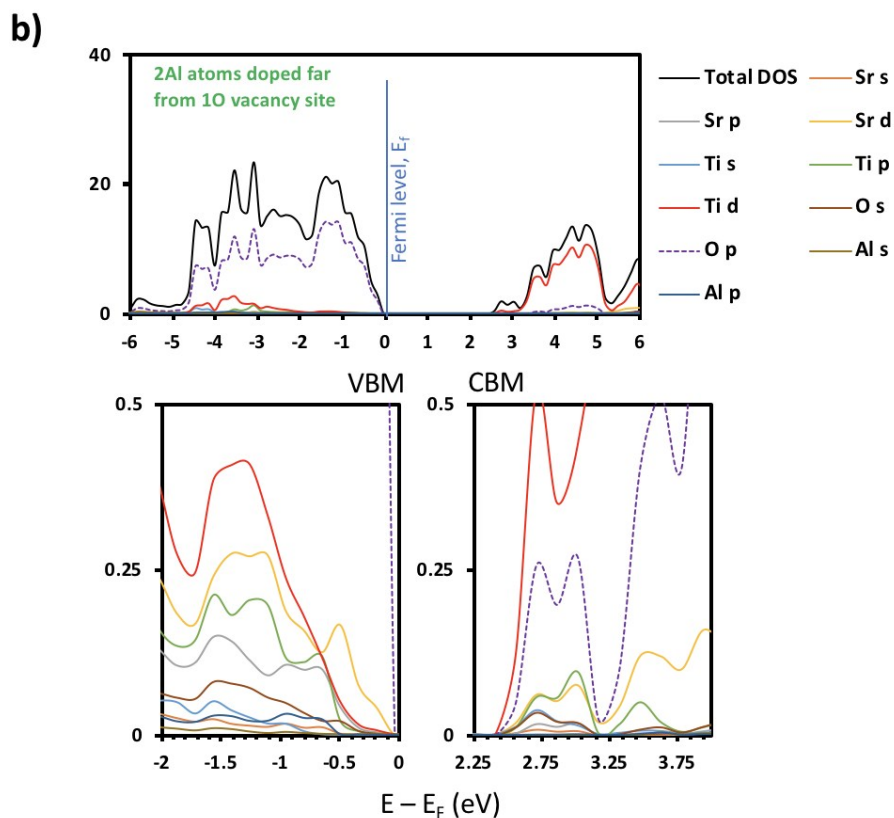
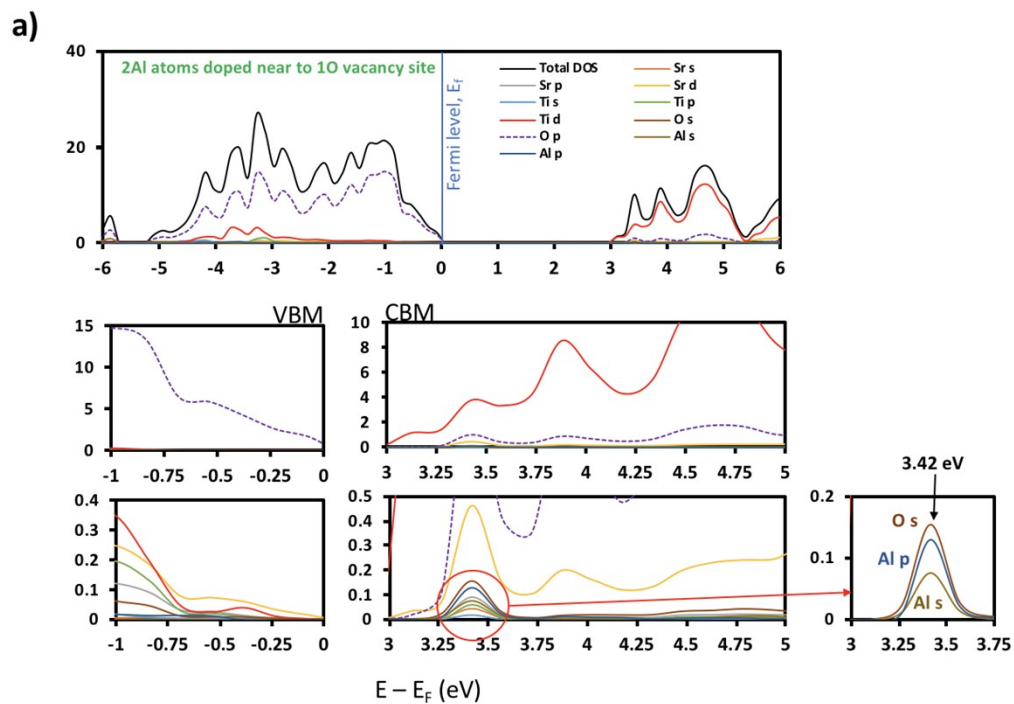


Figure S7. Magnified views of the Density of States plot for a) Al-doped SrTiO₃ (2 Al close to vacancy) and b) for Al-doped SrTiO₃ (2 Al far from vacancy).

Table S1. Summary of 5 experiments for sunlight irradiation and apparent quantum yield (AQY) and stability test of 0.1 wt% Rh, 0.1 wt% Cr, Rh_{2-y}Cr_yO₃ loaded Al:SrTiO₃.

Exp #	1	2	3	4	5	6	7
Light Source	sun	sun	sun	sun	sun	375 nm LED	Xe arc
Light intensity (mW cm ⁻²) /detector	42 / thermopile	48 / thermopile	50 / thermopile	55 / thermopile	54 / thermopile	42 / thermopile	29 / UV
Area (cm ²)	169.7	169.7	169.7	169.7	169.7	2.01	8.0
Gas volume (mL)	10.75	14.2	15.5	16.1	16	-	-
H ₂ evolution rate (mmol h ⁻¹) ^a	0.07	0.12	0.13	0.14	0.15	0.07	0.66
STH (%) ^a	0.06	0.10	0.10	0.10	0.11	-	-
AQY (%)	-	-	-	-	-	14.8%	-

^a The H₂ evolution rate and STH for sunlight irradiated system is obtained based on method 2 (see experimental details).

References

1. Zhao, Z., E.J. Willard, H. Li, Z. Wu, R.H.R. Castro, and F.E. Osterloh, Aluminum enhances photochemical charge separation in strontium titanate nanocrystal photocatalysts for overall water splitting. *Journal of Materials Chemistry A*, **2018**. 6(33): p. 16170-16176.