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Electronic structure basis for enhanced overall water splitting photocatalysis with aluminum doped SrTiO₃ in natural sunlight†

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Overall water splitting with photocatalyst particles presents a potentially cost-effective pathway to hydrogen fuel, however, photocatalysts that can compete with the energy conversion efficiency of photovoltaic and photoelectrochemical cells are still lacking. Recently, Goto *et al.* reported (*Joule*, 2018, 2(3), 509–520) that Al-doped SrTiO₃ microparticles, followed by modification with Rh_{2–y}Cr_yO₃ support overall water splitting with 0.4% solar to hydrogen efficiency and with 56% apparent quantum yield at 365 nm. Earlier, based on transient IR spectroscopy results, the improved activity of Al:SrTiO₃ had been attributed to the removal of Ti³⁺ deep recombination sites by the Al³⁺ ions. Here we use X-ray photoelectron spectroscopy to show that Al³⁺ incorporation not only reduces the Ti³⁺ concentration but also diminishes the n-type character of SrTiO₃ and shifts the Fermi level to more oxidizing potentials. According to DFT, the electronic structure of Al-doped SrTiO₃ depends sensitively on the relative locations of Al³⁺ and oxygen vacancies sites, with Al³⁺ ions next to the oxygen vacancies being most effective at suppressing the sub-band gap states. Reduced hole and electron trapping resulting from the elimination of Ti³⁺ states is confirmed by surface photovoltage spectroscopy and electrochemical scans. These findings not only provide an experimental basis for the superior water splitting activity of Al-doped SrTiO₃, under ultraviolet and solar irradiation, but they also suggest that aliovalent doping may be a general method to improve the solar energy conversion properties of metal oxides. Additionally, overall water splitting with a type 1 single bed particle suspension ‘baggie’ reactor under direct sunlight illumination with 0.11% solar to hydrogen efficiency is also demonstrated for the first time. This provides a proof of concept for one of the models in the 2009 US Department of Energy Technoeconomic analysis for photoelectrochemical hydrogen production.

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Broader context

Water electrolysis provides a pathway to hydrogen as a clean, non-carbon emitting fuel. When coupled to photovoltaic or photoelectrochemical cells, the process can be used to store photovoltaic energy from the sun, thereby creating the basis for a sustainable solar fuel cycle. According to a recent technoeconomic analysis conducted by the U.S. Department of Energy, photocatalysts may be most cost effective and most scalable technology for the water splitting reaction. The problem is that none of the known photocatalysts yet reach their theoretical energy conversion efficiency limit of 14.4%. This is because solar energy conversion with small particles is limited by slow carrier transport, insufficient carrier separation, and fast recombination at the particle surfaces. As Goto *et al.* showed (*Joule*, 2018, 2(3), 509–520), introduction of approximately 1% Al ions into SrTiO₃ can boost the solar to hydrogen conversion efficiency of this material to 0.4%. Here we report the underlying mechanism of the enhancement. Our findings suggest that aliovalent doping may be a general method to improve the photocatalytic properties of metal oxides. We also demonstrate overall water splitting with a type 1 single bed particle suspension ‘baggie’ reactor under direct sunlight illumination for the first time.

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† Electronic supplementary information (ESI) available: SEM images and powder X-ray diffraction patterns, irradiance data and gas evolution data, optical spectra, XPS spectra, DFT calculated band structures, and a movie showing gas evolution from a catalyst suspension in direct sunlight. See DOI: 10.1039/c9ee00310j

Introduction

As a special form of artificial photosynthesis, overall water splitting (OWS) with powdered photocatalysts is potentially a game changing technology for renewable fuel generation from sunlight.^{1,2} A 2009 Technoeconomic analysis by the US Department of Energy predicts that type 1 single bed particle suspension baggie reactors can produce H₂ at a cost of \$1.60 per kg, significantly below the cost of photoelectrochemical approaches.^{2,3} However, while there are many p-type and n-type semiconductors that promote either H₂ or O₂ evolution from water, only a handful of photocatalysts have been shown to coevolve H₂ and O₂ and without any applied electrochemical and chemical bias.^{4–6} Examples of such bias-free OWS photocatalysts include Rh_{2–y}Cr_yO₃/(Ga_{1–x}Zn_x)(N_{1–x}O_x) with an apparent quantum yield (AQY) of 5.9% at 420–440 nm⁷ and the Rh,Lu:SrTiO₃/Mo:BiVO₄ tandem in the photocatalyst sheet (1.1% Solar to Hydrogen Efficiency, STH).^{8,9} Long term stability is key to the usefulness of water splitting devices^{10,11} and therefore the light absorbers must be chosen carefully to avoid photocorrosion. Based on thermodynamics, only metal oxides have intrinsic stability to persist under the corrosive conditions of water electrolysis. However, the large band gap of metal oxide OWS photocatalysts, such as La-doped NaTaO₃ ($E_G = 4.1$ eV, AQY = 56% at 270 nm)¹² and Zn-doped Ga₂O₃ ($E_G = 4.4$ eV)¹³ precludes sunlight driven OWS.^{4,14,15} SrTiO₃ has continued to draw interest as OWS photocatalyst because its relatively narrow 3.2 eV bandgap allows for some sunlight absorption, even though quantum efficiencies for H₂ evolution remained low.^{16–25} Beginning in 2009, the Domen lab and others²⁶ reported that doping of SrTiO₃ with mono-, bi- or trivalent main group element cations (M = Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Mg²⁺, Al³⁺, Ga³⁺ and In³⁺) led to significant OWS improvements^{27–32} when the absorber was combined with the proton-selective reduction catalyst Rh_{2–y}Cr_yO₃.^{33,34} Recently, an AQY of 56% at 365 nm and 0.4% efficient water splitting under sunlight was observed when Al³⁺ was used as a modifier.^{31,35} The activity persisted for over 1000 h.³⁶ It has been speculated that the aliovalent dopant suppresses Ti³⁺ states which are involved in electron-hole pair recombination.²⁷ Indeed, for the Al³⁺ modified material, mid IR transient absorption spectroscopy confirmed extended electron hole carrier lifetimes.²⁹ However, to date, there is no experimental data available on the effect of Al³⁺ on the electronic band structure of the material. In order to close this knowledge gap, we perform here experimental and theoretical studies on the electronic structure of Al-doped SrTiO₃ and on charge carrier separation in the material. According to X-ray photoelectron spectroscopy (XPS), Al³⁺ incorporation suppresses Ti³⁺ states and shifts the Fermi level away from the conduction band edge. Density Functional Theory (DFT) calculations reveal a sensitive dependence of the electronic structure on the proximity between Al³⁺ and oxygen vacancy sites V_O. Complete elimination of sub-band gap states is observed only when the oxygen vacancies V_O are in the coordination sphere of two Al³⁺ ions. Moving one or both Al³⁺ ions further away from the V_O sites leads to the formation of Ti⁴⁺ mid gap states near the vacancies. These {Ti⁴⁺–V_O} oxygen vacancy complexes remain unoccupied by electrons due to the shift

of the Fermi level to more oxidizing potentials. These are responsible, however, for a weak 1.7–3.2 eV feature that is observed in optical absorption spectra of Al-doped SrTiO₃.³⁷ Along with the suppression of the Ti³⁺ states, reduced electron trapping and improved surface photovoltage are observed in electrochemical measurements and surface photovoltage spectra of Al-doped SrTiO₃. These findings provide an experimental basis for the superior water splitting activity of Al-doped SrTiO₃ under UV and solar irradiation.^{31,35} Overall, this work suggests that aliovalent doping with closed shell metal ions may be a general method to control charge trapping sites in metal oxides and to improve their photocatalytic properties.

Experimental section

Titanium(IV) oxide P25 (99.5%, Acros Organics), strontium carbonate (99.9%, Aldrich), strontium chloride hexahydrate (99%, EM Science), rhodium chloride (>99%), chromium(III) nitrate nonahydrate (99%, Acros Organics), alumina crucible (Fisher) were used as received. Water was purified to 18 MΩ cm resistivity by a Nanopure system.

Synthesis of Al:SrTiO₃:³¹ 3.10 g of SrCO₃ was calcined in air at 300 °C for 1 h before use. 1.68 g TiO₂ and 3.10 g SrCO₃ were well mixed by wet grinding with a small volume of added ethanol for 3 times. Afterwards, the mixture was heated at 1000 °C for 10 hours in a covered ceramic crucible. 0.37 g obtained SrTiO₃ was ground with 5.33 g SrCl₂·6H₂O (mole ratio of SrCl₂/SrTiO₃ = 10) for 5 min. The mixture was then heated at 1100 °C for 10 h in a covered alumina crucible. The resulting Al:SrTiO₃/SrCl₂ solid was washed with water until no more white AgCl precipitate formed in rinse solutions upon adding AgNO₃. The overall yield for Al:SrTiO₃ is >90%, based on TiO₂.

Deposition of Rh_{2–y}Cr_yO₃ co-catalyst:^{38–40} 150 mg Al:SrTiO₃ and 4 mL water containing an appropriate amount of RhCl₃ and Cr(NO₃)₃ were placed in a vial inside of a water bath at 70 °C and slowly evaporated under constant stirring. The resulting powder was collected and heated in air at 350 °C for 1 h to produce Rh_{2–y}Cr_yO₃ loaded Al:SrTiO₃ in 95% yield.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were conducted on Philips XL-30 Scanning Electron Microscope and Scios DualBeam Scanning Electron Microscope. Samples were prepared by drop-coating a few drops of the sample suspension onto a silicon wafer followed by drying in air. Powder X-ray diffraction scans were performed using a Bruker D8 Advance Eco with a Cu Kα X-ray radiation and a monochromatic wavelength of 1.5418 Å. UV/vis diffuse reflectance spectra and absorption spectra were recorded on a Thermo Scientific Evolution 220 UV vis spectrometer equipped with an integrating sphere. Surface photovoltage spectroscopy (SPS) measurements were conducted under vacuum (1 × 10^{–4} mBar) using a gold Kelvin probe (Delta PHI Besocke) as the reference electrode. Samples were illuminated with monochromatic light from a 150 W Xe lamp filtered through an Oriel Cornerstone 130 monochromator. The light intensity at the sample was 0.1–0.3 mW cm^{–2}. Spectra were corrected for drift effects by subtracting a dark scan. Particle films were prepared *via* the

following method. First, fluorine-doped tin oxide (FTO) substrates were sonicated sequentially in methanol, acetone and 2-propanol, rinsed with water, and dried under vacuum before use. Gold substrates were sonicated in acetone, soaked in 30% H₂O₂ and 0.1 M KOH solution for 15 min, and then rinsed with water, and dried under vacuum before use. In general, 6 mg Al:SrTiO₃ or SrTiO₃ was suspended in 1 mL water and then sonicated for 3 h. Then 0.1 mL Al:SrTiO₃ suspension was drop coated on 0.8 × 0.8 cm² substrates, followed by heating at 300 °C for 2 h in air. The film thickness was measured with a Dektak 150 profilometer after the SPS measurement.

Chemical surface analysis was performed by X-ray photoelectron spectroscopy (XPS) using a spectrometer (Scienta-Omicron ESCA+) with a high-performance hemispheric analyzer (EAC-2000 sphere) with monochromatic Al K α source ($h\nu$ = 1486.6 eV) radiation as the excitation source. The operating pressure in the ultra-high vacuum chamber (UHV) during the analysis was 10^{−9} Pa. The XPS survey spectra were recorded at constant pass energy of 50 eV with a 0.5 eV per step. The high-resolution core levels and the valence band position spectra were recorded with pass energy of 50 eV with a 0.05 eV per step. To eliminate charging effects, a low energy electron flood gun was used. The positions of the peaks in the spectra were corrected in relation to the binding energy of the carbon peak (C 1s) set at 284.8 eV. Peak fitting of the high-resolution spectra were processed using the CasaXPS software (Casa Software Ltd). A Shirley background subtraction was performed before the curve fitting for all data. Valence band XPS data were calibrated by linear extrapolation of the signal to zero intensity and by equating the zero intensity point to 0 eV binding energy, which is the Fermi level of the sample, by definition.

For electrochemical measurements, thin films of SrTiO₃ and Al:SrTiO₃ microparticles were prepared by drop coating on F:SnO₂ (FTO) substrates and annealing at 500 °C for 2 hours. The working electrode was connected in a 3-electrode configuration with a Pt counter electrode and a saturated calomel reference electrode (SCE). Aqueous electrolyte solution (0.1 M K₂SO₄) were added to the cell and bubbled with N₂ gas to remove all dissolved oxygen prior to scanning. The system was calibrated to vs. NHE using the redox potential of K₄[Fe(CN)₆] at +0.358 V vs. NHE.

Photocatalytic hydrogen and oxygen evolution tests were performed by dispersing 100 mg of the catalysts in 100 mL water in a 165 mL quartz flask connected directly to a Varian 3800 gas chromatograph with a 60/80 Å molecular sieve column and thermal conductivity detector. The catalyst dispersion was sonicated for 15 min and degassed with N₂ for 20 min to remove the residual oxygen gas dissolved in the water. The flask was then purged with argon and the solution mixture was irradiated with a Xe lamp. The light intensity was measured at the flask surface by an International Light IL1400BL photometer equipped with a GaN detector (SED (SEL) 365 with 230 to 380 nm sensitivity). OWS experiments under direct sunlight illumination were conducted using a polypropylene bag of 169.7 cm² surface area mounted on a silver coated metal reflector. The bag was filled with 120 mL of water and 0.300 g of the catalyst powder and then sealed with a septum fitted plastic cap. The bag

was laid flat and exposed to direct sunlight for 4 h periods, after which the evolved gases were measured volumetrically *via* syringe, and the gas composition was determined *via* gas chromatography analysis. About 35% of the evolved H₂ was lost to diffusion through the plastic walls of the bag. Light intensity measurements (ESI†) were conducted every hour using an International Light IL1400BL photometer equipped with a GaN detector (SED (SEL) 365 of 230 to 380 nm range), a thermopile (SED 623 of 200–4200 nm range), and a GaAsP visible light detector (SED (SEL) 005 of 260–680 nm range).

The theoretical part of this work was carried out within the density functional theory (DFT) framework^{41,42} as implemented in the Vienna ab initio simulation package.^{43,44} The projected augmented wave (PAW) method^{45,46} was used for better computational efficiency and the calculations were performed in the generalized gradient approximations (GGA) through the Perdew Burke–Ernserhof (PBE) exchange–correlation.⁴⁷ For simulations, a 40 atom supercell of SrTiO₃ (2 × 2 × 2) is considered in its perovskite structure, which contains 8 unit cells. The size of the supercell remains the same for all total energy and electronic structure calculations. The oxygen vacancy is generated by removing an O atom from its site and doping is achieved by replacing two Ti atoms with Al atoms. All of the structures used in this work were geometrically optimized without any symmetry constraint before calculating the total energy and electronic structure. The kinetic energy cut-off for the plane wave basis set was 500 eV. For ionic relaxation, the force on each ion was set equal to or less than 0.01 eV Å^{−1}. In the electronic self-consistent loop, the allowed error for the global break condition was equal to or less than 1 × 10^{−6} eV. The Brillouin zone was sampled using a 13 × 13 × 13 *k*-grid generated by the Monkhorst–Pack method⁴⁸ for all the supercells. Since GGA underestimates the band gap and since it is well known for transition metals that GGA fails to treat d and f electrons properly, we have adopted the GGA + *U* method for the electronic structure calculations. In this study, the GGA + *U* method was implemented with Dudarev's approach,⁴⁹ with *U* = 7 and *J* = 1 on the Ti d orbital. This choice of *U* and *J* values gives an indirect band gap of 3.25 eV and direct band gap of 3.60 eV for pure SrTiO₃, in good agreement with the experimental band gaps.

Results and discussion

The Al-doped SrTiO₃ perovskite was synthesized as described previously by Ham *et al.*³¹ and its structure type and cubic morphology were confirmed by powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM) (Fig. S1, ESI†).³⁷ According to X-ray fluorescence measurements, Al-doped SrTiO₃ contains 1.2 atom% of Al. Based on the ion radius (54 pm for hexa-coordinated Al³⁺), the Al³⁺ ions mostly likely substitute Ti⁴⁺ ions (61 pm) in the lattice. The active photocatalyst (PC) is obtained after modification of Al-doped SrTiO₃ with Rh_{2−y}Cr_yO₃ cocatalyst (0.1 wt% Rh and 0.1 wt% Cr).⁴⁰ According to energy dispersive X-ray spectroscopy (EDX, Fig. 1c), the co-catalyst is evenly distributed on the Al:SrTiO₃ surface.

Fig. 1 (a) Gas evolution from $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ (0.1 wt% Rh, 0.1 wt% Cr)-loaded Al:SrTiO₃ photocatalyst (PC) suspension in a polypropylene bag after 4 hour direct sunlight irradiation. (b) SEM and (c) EDX results for the particle shown in (b). (d) Solar to hydrogen efficiencies of suspended PC in bag, computed on the basis of detected H₂ amount (method 1) or detected O₂ amount (method 2). For details see Fig. S2 (ESI†). (e) H₂/O₂ evolution from 100 mg PC in 100 mL of pure water under Xe lamp irradiation (29 mW cm⁻² by UV detector, 8 cm² illumination area). (f) UV-vis diffuse reflectance spectra and photos of SrTiO₃ and Al:SrTiO₃. (g) Absorption spectra of flux Al:SrTiO₃ films versus thickness. A linear fit at 3.4 eV (insert) establishes the absorption coefficient $\alpha = 0.297 \mu\text{m}^{-1}$ at 3.4 eV.

Fig. 1a shows a suspension of the catalyst inside of a polypropylene bag exposed to natural sunlight. Gas bubble formation becomes visible within an hour (a time lapse video in ESI†) and continues with rates up to 4 mL per hour. Based on the data in Fig. 1d and Table S1 (ESI†), the solar to hydrogen efficiency under these conditions is estimated as 0.11%. To our best knowledge, this is the first demonstration of sunlight-driven overall water splitting with a type 1 single bed particle suspension baggie reactor.^{2,3} Energy efficiencies of up to 0.4% STH have been measured for fixed bed configurations (panels or sheets) with the Al:SrTiO₃ catalyst.^{31,35,36} The lower efficiency of the suspension is in part due to the optical shading from the polypropylene bag (Fig. S2c, ESI†).

When the experiments are repeated in a closed loop system under monochromatic illumination at 375 nm, stoichiometric H₂/O₂ evolution is observed with an apparent quantum yield (AQY) of 14.8% (Table S1, ESI†). Previously, AQY values of 30–56% at 360 nm (3.44 eV) had been reported for the $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3/\text{Al:SrTiO}_3$ system.^{31,35,36} The lower AQY at 375 nm (3.31 eV) that is observed here is due to the lower optical absorption of the catalyst at this wavelength (Fig. 1f). Under full spectrum Xe illumination (Fig. 1e) the catalyst suspension produces H₂ steadily at a rate of 285 $\mu\text{mol h}^{-1}$ with no decay over 30 hours and a turnover number of 36.5, based on the molar amount of SrTiO₃. Under identical conditions, the hydrogen evolution rate of non-Al-modified $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3/\text{SrTiO}_3$ is only 1 $\mu\text{mol h}^{-1}$. This confirms earlier studies that the improved solar energy conversion ability of Al:SrTiO₃ is correlated with Al content.^{27,31,37}

In order to observe the electronic structure changes brought about by introduction of Al lattice, X-ray photoelectron spectra (XPS) were recorded for SrTiO₃ and for Al-doped SrTiO₃. Fig. 2a shows

the Ti 2p core-level XPS spectrum for non-Al doped SrTiO₃ prepared by solid state reaction. The spectrum is similar to XPS spectra reported in the literature.^{50–52} The doublet at 458.6 and 464.4 eV can be assigned to the Ti 2p_{3/2} and Ti 2p_{1/2} components of Ti⁴⁺. A second doublet at 457.2 and 463.1 eV reveals the presence of Ti³⁺ species in the material.⁵³ Based on the relative peak ratios, 72.8% of titanium is present as Ti⁴⁺ and 27.2% as Ti³⁺. The latter are believed to be mostly at the surface of the particles, as samples of SrTiO₃ with high Ti³⁺ lattice concentration are intensively colored while the SrTiO₃ particles here appear white.⁵² In contrast, the XPS spectrum for Al-doped SrTiO₃ (Fig. 2b) only shows one single spin-orbital doublet feature of Ti⁴⁺ but no discernable contribution of Ti³⁺. This confirms that the introduction of Al³⁺ ions prevents the formation of Ti³⁺ ions in the lattice of SrTiO₃, as hypothesized by Takata *et al.*²⁷ Additionally, incorporation of Al³⁺ ions is found to also modify the high-resolution O 1s region of SrTiO₃ as shown in Fig. 2(c and d). The main peak at 529.8 can be assigned to O²⁻ ions in the lattice, whereas the peak at 531.9 eV has been previously assigned to hydroxyl-groups at the particle surfaces.^{54–56} The small peak at 528.6 eV is tentatively attributed to lattice O²⁻ ions bonded to Ti³⁺ ions in the lattice. This interpretation is supported by the disappearance of the 528.6 eV peak for Al-doped SrTiO₃ in Fig. 2(d), which no longer contains any Ti³⁺. At the same time, the 531.3 eV peak belonging to surface hydroxyl groups is increased to 32% and the 529.2 eV of the lattice O²⁻ ions is decreased to 56%. This suggests an increase of the surface concentration of hydroxyl groups in Al-doped SrTiO₃. To test this assumption, infra-red (IR) absorption spectra were recorded for both compounds (Fig. S4, ESI†). The spectrum of SrTiO₃ does indeed show O–H stretching vibrations from the presence of

Fig. 2 High resolution XPS spectra of Ti 2p region in (a) pure SrTiO_3 and (b) Al:SrTiO₃ and XPS spectra of O 1s region in (c) pure SrTiO_3 and (d) Al:SrTiO₃. All O and Ti peaks move 0.5–0.6 eV to lower binding energy in Al:SrTiO₃. Valence band edge XPS spectra of (e) pure SrTiO_3 and (f) Al:SrTiO₃.

surface adsorbed water or hydroxyl groups, however, these bands no longer exist in the vibrational spectra of Al-doped SrTiO_3 . This means that the increased 531.3 eV signal must be due to other species. Tentatively, we attribute it to the O^{2-} ions bonded to Al^{3+} ions near the surface. This is supported by XPS studies on Al_2O_3 , which show the O 1s peak at 531.8 eV.⁵⁷ The XPS O 1s core spectrum of Al-doped SrTiO_3 also contains a new peak at 533.1 eV (12% of the total) that is attributed to SrCO_3 species, that are produced as a side product during the SrCl_2 flux treatment.^{54,58}

Detailed inspection of the Ti and O core level spectra also reveals a general 0.5–0.6 eV shift of all peaks to lower binding energy. This global shift can be attributed to a change in the charge distribution of the sample, as brought about by a change of the depletion layer.^{59,60} Depletion layers in SrTiO_3 and Al:SrTiO₃ form when the Fermi level of the metal oxide

equilibrates with that of the XPS sample holder.⁶¹ The direction of the signal shift to lower binding energy in Al-doped SrTiO_3 indicates that the Fermi level in Al:SrTiO₃ is more oxidizing than in non-doped SrTiO_3 . As a result, Al:SrTiO₃ on the sample holder is less depleted of electron majority carriers, which agrees with the lower concentration of Ti^{3+} states in Al:SrTiO₃. Analogously, chemically reduced SrTiO_3 samples with higher Ti^{3+} content and more reducing Fermi level produce XPS signal shifts to more oxidizing energy.⁵²

Valence band edge XPS spectra for pure and Al-doped SrTiO_3 are shown in Fig. 2(e and f). In both spectra, the peak around 6 eV is due to ionization of valence band states formed by O 2p and Ti 3d orbital hybridization. Pure SrTiO_3 has a VB edge energy of 1.69 eV, relative to its Fermi level, estimated by linear extrapolation of the peaks to the baseline. For Al-doped SrTiO_3

the VB edge is observed at lower energy (1.30 eV). This 0.39 eV shift in reducing direction corresponds to the shift observed in the Ti and O core level spectra; thus, it is viewed as a result of lower electron depletion in Al-doped SrTiO₃, as discussed above.

The observed changes in Ti³⁺ content and upon Al³⁺ doping can be explained on the basis of defect equilibria in SrTiO₃ (eqn (1)–(4)) that are expressed using the Kröger–Vink notation.^{27,62,63} Thermal annealing of non-doped SrTiO₃ in air or under vacuum is known to produce oxygen vacancies in the lattice according to eqn (1).^{18,64,65} To maintain charge neutrality, the loss of each oxide ion must be accompanied by the formation of two Ti³⁺ ions (eqn (2)). This is the reason for the n-type character of SrTiO₃ and the blue color of vacuum-annealed SrTiO₃.⁶⁶ In Al-doped SrTiO₃, the Al³⁺ ions can substitute for Ti³⁺, reducing the concentration of the latter, and resulting in a decrease of the n-type character of the Al-doped SrTiO₃. Additionally, Al³⁺ can substitute Ti⁴⁺ ions in the lattice, leading to the formation of oxygen vacancies, according to eqn (3). If these formed oxygen vacancies are accompanied by oxygen uptake from the air, according to eqn (4), holes are created and the material becomes p-type.

In order to better understand how the electronic structure of SrTiO₃ is modified by Al³⁺ incorporation, DFT calculations were conducted on SrTiO₃ in the absence and presence of oxygen vacancies and Al³⁺ dopants. The density of states diagram and band structure of pure, defect free SrTiO₃ are shown in Fig. 3a and in Fig. S5 and S6a (ESI†). The results match that of earlier calculations.^{67–69} The conduction band edge is composed mainly of empty Ti 3d orbitals and the valence band edge mainly consists of filled O 2p states. The generalized gradient approximations (GGA)-calculated indirect band gap of 1.77 eV and direct band gap of 2.16 eV are below the experimental values, which is a consequence of the known underestimation of the on-site Coulomb interaction for d and f electrons by GGA-DFT. The application of the Hubbard parameter *U* (*U* = 7 and *J* = 1) fixes this problem and leads to value of 3.25 eV for the indirect gap and 3.60 eV for the direct gap, close to the experimental values seen here and in the literature.¹⁷ The band structure changes when a single oxygen vacancy V_O is added to the 40 atom-supercell, as shown in Fig. 3b and Fig. S6b (ESI†). First, the Fermi level shifts to the conduction band edge, which is due to the creation of two Ti³⁺ ions (see eqn (1) and (2)). Second, new Ti³⁺ states form 0.8–1.3 eV below the SrTiO₃ conduction band edge. Excitation of these states is responsible for the deep blue/black color of vacuum annealed or reduced SrTiO₃,¹⁸ which is associated with a broad optical absorption from 775 nm (1.6 eV) to above 2000 nm (0.62 eV), depending on the presence of other metal impurities.^{64,66} Clearly, the presence of Ti³⁺ states in Al:SrTiO₃ can be ruled out on the basis of the combined DFT, XPS and optical absorption data. As Fig. 3c shows, the Ti³⁺ defect band in SrTiO₃ disappears when

Fig. 3 GGA + *U* projected density of states of (a) pure SrTiO₃, (b) SrTiO₃ with V_O (Sr₈Ti₈O₂₃) and (c–e) Al:SrTiO₃ with V_O (Sr₈Ti₆Al₂O₂₃). For (c), Al³⁺ are close to V_O. For (d), 1 Al³⁺ is close to V_O site while the other is far. For (e), both Al³⁺ are far from V_O. The Fermi level (*E_F*) is set at 0 eV.

two Ti^{4+} sites in the super cell containing the oxygen vacancy are replaced with Al^{3+} ions. Due to the loss of two Ti^{3+} donors, the Fermi level returns to the top of the valence band edge. The added Al^{3+} s and p states are deeply embedded in the conduction band at 0.42 eV above the conduction band edge (Fig. S7, ESI†). According to Fig. 3, the detailed electronic structure of Al-doped SrTiO_3 strongly depends on the distance of the Al^{3+} ions from the oxygen vacancy V_O . If both Al^{3+} ions are next to the oxygen vacancy as in Fig. 3c, the band gap of Al-doped SrTiO_3 resembles that of the undoped, oxygen vacancy-free SrTiO_3 , except for a lower degeneracy of the bands resulting from the lower symmetry of the cell (Fig. S6c, ESI†). As the two Al^{3+} ions are placed farther away from the vacancy, a band gap reduction to 2.5 eV can be observed, which results from lowering the conduction band edge (Fig. 3e and Fig. S6e, ESI†). These new states have mixed contributions from Ti d orbitals and O p orbitals (Fig. S7b, ESI†) and belong to the Ti^{4+} and O^{2-} ions next to the oxygen vacancy. The states from these $\{\text{Ti}^{4+}-\text{V}_\text{O}\}$ vacancy complexes are already observable in the model with only one Al^{3+} near the V_O and one far away from it (Fig. S6d, ESI†), even though in that case, the effect on the band gap of the compound is less significant. The more reducing potential of the Ti^{4+} states in comparison to the Ti^{3+} states in Al-free SrTiO_3 can be understood on the basis of molecular orbital theory. Because the extra electron in the $\{\text{Ti}^{3+}-\text{V}_\text{O}\}$ is located in an antibonding Ti d/O p orbital, it weakens the Ti–O bond and moves the antibonding state energy below that for the $\{\text{Ti}^{4+}-\text{V}_\text{O}\}$ vacancy complex. The new $\{\text{Ti}^{4+}-\text{V}_\text{O}\}$ states in Fig. 3e are likely responsible for the weak absorption at 1.7–3.2 eV that is seen in the optical spectra (Fig. 1f) of Al-doped SrTiO_3 and which causes the pale-brownish appearance of the material (Fig. 1f insert).³⁷ Related states at 1.9–2.6 eV in non-doped SrTiO_3 have been previously attributed to a combination of self-trapped excitons, oxygen vacancies and oxygen vacancy complexes in the lattice and at the surface.^{66,70} Similar states are also seen in the photoluminescence of TiO_2 .⁷¹

In order to obtain information about the carrier dynamics of Al-doped SrTiO_3 , we employ surface photovoltage spectroscopy (SPS) as a sensitive probe of photochemical charge separation.^{23,72–74} In SPS, the surface potential change of an illuminated sample film is monitored with a vibrating Kelvin probe.^{75,76} SPS data for SrTiO_3 and Al: SrTiO_3 particle films on Au or FTO substrates are shown in Fig. 4a–c. Both samples produce negative photovoltage in agreement with electron movement toward the FTO support and n-type character. The effective band gap can be approximated from a tangential fit of the major photovoltage feature.⁷⁷ This yields 3.0 eV for SrTiO_3 and 2.9 eV for Al doped SrTiO_3 , slightly below the optical band gap. The sub-band gap photovoltage in the 2.0–3.0 eV interval is attributed to excitation of surface defects in both samples.⁷⁶ Both compounds reach their maximum photovoltage at 3.4–3.5 eV, just above the optical absorption edge. The voltage is also film thickness-dependent and reaches –3.3 V for a 6.5 μm thick Al: SrTiO_3 particle film (Fig. 4c). This optimum thickness agrees well with the optical absorption depth $2/\alpha$ of the material at 3.4 eV (Fig. 1g). For films thinner than $2/\alpha$, light

absorption limits the photovoltage, while for films thicker than $2/\alpha$, electron transport to the FTO limits the voltage. The data suggests that the electron diffusion length is enhanced in Al: SrTiO_3 over that in the non-doped material, for which the photovoltage maximum is lower (–2.4 V) and occurs for a thinner film (2.6 μm). Interestingly, for the thinnest Al: SrTiO_3 films a small positive photovoltage is seen also (Fig. 4b). This signal inversion is attributed to the formation of a space charge layer at the Al: SrTiO_3 /Au interface, similar to CdSe particle films⁷⁸ or for polyhexylthiophene films.⁷⁹ The fact that this feature only occurs in the Al: SrTiO_3 film suggests that the space charge width is increased as expected from the lower free electron density (Ti^{3+} content).

Based on the energy diagram in Fig. 4d photovoltage generation in Al-doped SrTiO_3 involves two separate charge carrier transfer processes. One is electron injection from the conduction band of SrTiO_3 into the FTO substrate and the second is hole injection from the SrTiO_3 valence band into surface states. Combination of both processes enables a theoretical photovoltage of $-1.5 \text{ V} + (-1.4 \text{ V}) = -2.9 \text{ V}$. The larger experimental value of –3.3 V for Al: SrTiO_3 suggests the presence of an additional photovoltage generating component, likely linked to the oxidation of trace organic impurities at the crystal surface. In combination with strongly reducing species, surface photovoltage values exceeding the band gap of the absorbers are frequently observed.²³ Fig. 4e also shows transient photovoltage experiments with 3.4 eV illumination. Photovoltage generation for Al: SrTiO_3 is nearly fully reversible on the 15 min timescale, while photovoltage generation for SrTiO_3 is only 20% reversible, on the basis of the residual voltage after 30 min. The residual photovoltage for SrTiO_3 is attributed to hole trapping at Ti^{3+} sites in the SrTiO_3 lattice and at the surface. The much lower residual photovoltage for Al: SrTiO_3 agrees with the reduction of hole trapping states in the material.

Electrochemical measurements on non-illuminated SrTiO_3 and Al: SrTiO_3 particle films immersed in 0.1 M aqueous K_2SO_4 electrolyte are shown in Fig. 4f. Anodic currents above +2.0 V and below –1.5 V are assigned to the oxidation and reduction of water respectively. The oxidative small peak at –0.4 V is assigned to oxidation of titanium hydrides formed at –1.5 V.⁸⁰ Additionally, SrTiO_3 shows a reductive peak at –1.0 V (see magnified plot in insert) which is assigned to the reduction of surface Ti^{4+} states. The absence of this peak in Al: SrTiO_3 further indicates that Al^{3+} doping in Al: SrTiO_3 reduces the formation of Ti^{3+} under cathodic bias. Additionally, the anodic current onset for Al: SrTiO_3 is shifted approximately 0.2 V towards less oxidizing potential. This suggests that hole transport is improved in Al: SrTiO_3 , which would agree with the lower n-type character as observed in the XPS data in Fig. 2 and as predicted by eqn (4).

Fig. 5 summarizes the energy diagrams of non-doped SrTiO_3 and Al-doped SrTiO_3 under illumination. Before Al^{3+} incorporation, each oxygen vacancy in SrTiO_3 is associated with two Ti^{3+} states 0.8–1.3 eV below the conduction band. The Ti^{3+} ions are deep electron traps that promote rapid Shockley Read Hall recombination with the photoholes.^{81,82} This reduces the steady state hole concentration under illumination and with it

Fig. 4 Surface photovoltage spectra of (a) SrTiO_3 and (b) Al:SrTiO_3 on Au substrate with different thickness. (c) Thickness dependence of maximum photovoltage at 3.4 eV for SrTiO_3 on Au and Al:SrTiO_3 on FTO. (d) Energy diagram for SrTiO_3 on FTO during SPS measurement. (e) Transient photovoltage with temporary 3.4 eV illumination for SrTiO_3 and Al:SrTiO_3 films on Au substrate. (f) Cyclic voltammetry scans for non-illuminated SrTiO_3 and Al:SrTiO_3 films in 0.1 M aqueous K_2SO_4 (insert: cathodic scan from 0 V to -1.3 V and back).

the driving force for OWS. The introduction of Al^{3+} eliminates the Ti^{3+} recombination states, which enables prolonged lifetimes of photoholes and electrons, as observed in transient IR spectra.²⁹ This improves the photovoltage of the compound and promotes the water splitting reaction. The DFT results show that complete elimination of sub-bandgap states occurs only when the Al^{3+} ions are close to the oxygen vacancies in the compound.

When the Al^{3+} ions are more than a few atoms away from the V_O center, new Ti^{4+} states approximately 0.5–1.0 eV below the conduction band appear in Al:SrTiO_3 . Theoretically, these Ti^{4+} states are expected to trap electrons and holes and diminish the photocatalytic activity of SrTiO_3 . However, this is not observed in the water splitting tests or in the electrochemical or surface photovoltage experiments. One reason is that the Ti^{4+} sites are further away from the mid-band gap position than the Ti^{3+} sites

in non-doped SrTiO_3 (see Fig. 3). States close to the mid-band gap position are most detrimental to recombination because they are equally accessible to electrons and holes. Secondly, the incorporation of Al^{3+} reduces the free electron concentration in Al -doped SrTiO_3 , evident from the 0.5 eV Fermi energy shift seen in the XPS and VB-XPS data. The combination of the E_F anodic shift of 0.5 eV with the Ti^{4+} cathodic shift of ~ 0.3 eV reduces the electron concentration n_T in the Ti^{4+} sub-band gap states by 14 orders of magnitude (at room temperature) based on eqn (5).^{81,82}

$$n_\text{T} = N_\text{T} \exp\left(\frac{E_\text{T} - E_\text{F}}{kT}\right) \quad (5)$$

Here, n_T is the trapped electron concentration, N_T is the density of trap states, E_T is the trap state energy, and E_F is the Fermi level. This reveals that a significant improvement of the

Fig. 5 Schematic energy diagrams for SrTiO_3 and Al:SrTiO_3 , illustrating the effect of Al^{3+} on Ti^{3+} sites and on electron/hole recombination.

photocatalytic activity of Al-doped SrTiO_3 can be attributed to the reduced n-character of the compound. This reduced n-type character also widens the depletion layer of the material, as evident in the surface photovoltage spectrum, and as demonstrated recently for Mg-doped SrTiO_3 ,²⁶ thus improving minority carrier extraction from the compound.

Conclusion

In summary, we use X-ray photoelectron spectroscopy and density functional theory results to understand the mechanism by which aliovalent doping of Al^{3+} into SrTiO_3 increases the OWS activity of the material by a factor of ~ 300 . Incorporation of Al^{3+} into the lattice not only eliminates deep Ti^{3+} recombination sites, as previously suggested by Takata *et al.*,²⁷ but also lowers the Fermi level by approximately 0.5 eV, making the compound less n-type. The detailed effect of Al^{3+} depends sensitively on the relative location to the oxygen vacancies. If the V_O site is surrounded by fewer than two Al^{3+} ions, shallow Ti^{4+} acceptor states are formed near the vacancy. These $\{\text{Ti}^{4+}-\text{V}_\text{O}\}$ vacancy complexes are responsible for the weak optical absorption of Al:SrTiO_3 , which gives rise to its pale-brown color. However, because of the lower Fermi level, these Ti^{4+} states are not permanently populated by electrons and thus only mildly promote electron-hole recombination. This is confirmed by the enhanced reversibility of the surface photovoltage and by electrochemical scans. These changes explain the vastly improved overall water splitting activity of aliovalent doped SrTiO_3 , as observed here and by the Domen group.^{27,31,35} Separately, our work also provides the first example of a type 1 single bed particle suspension ‘baggie’ reactor for overall water splitting under natural sunlight illumination. With Al-doped $\text{SrTiO}_3/\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ as a photocatalyst the device achieves a solar to hydrogen efficiency (STH) of 0.11%. This experimentally verifies one of the model assumptions of the 2009 US Department of Energy technoeconomic analysis for

photoelectrochemical hydrogen production. With its 3.2 eV band gap, the solar to hydrogen STH efficiency of SrTiO_3 is fundamentally limited to 2.5%, but values of up to 14.4% STH are theoretically possible by using metal oxides with band gaps near the 2.0–2.5 eV optimum for a single absorber, if ways can be found to overcome the carrier lifetime limitations of these materials.^{83–87} The results of this work suggest that aliovalent doping may be a one way to achieve this goal with metal oxides.

Conflicts of interest

There are no conflicts of interest to declare.

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