Boosting photocatalytic water oxidation reactions over strontium tantalum oxynitride by structural laminations

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ABSTRACT

Perovskite oxynitrides often own a poor photocatalytic activity under normal conditions, being incommensurate to their strong visible light absorbance. This is particularly true for $SrTaO_2N$ which undergoes self-oxidative decompositions even under protection of a hole scavenger. In this work, we laminate the crystal structure of $SrTaO_2N$ by inserting extra layers of SrO to form a Ruddlesden-Popper (RP) compound Sr_2TaO_3N. This structural modification not only improves the light absorption of $SrTaO_2N$ but also effectively suppresses the defect formation such as Ta^{4+} species etc. More importantly, Sr_2TaO_3N is able to drive photocatalytic water oxidation reactions under visible light illumination ($\lambda \geq 420\,nm$) without the aid of a cocatalyst and self-oxidative decompositions found for $SrTaO_2N$ are largely inhibited. Further analysis suggests that the presence of extra SrO layers positively shifts the valence band edge and stabilizes N species in the structure according to Pauling's second rule. Theoretical calculations indicate that Sr_2TaO_3N has typical 2D charge transportation properties which are associated with the structural laminations. Its conduction band minimum (CBM) and valence band maximum (VBM) are found to be located within TaN_2O_2 square planes which favors efficient charge transportations.

1. Introduction

The fossil-fuel based economy of our modern society is essentially not sustainable, not only because of a rapid depletion of fossil fuel reservoirs but also from environmental considerations [1–4]. An attractive strategy to release us from fossil fuel reliance is to build a hydrogen-based energy infrastructure that is clean and renewable without sacrifice from environmental degradations [5,6]. Photocatalytic water splitting into hydrogen and oxygen on particulate semiconductors, driven by solar insolation, offers an ideal scenario to this strategy as water is a recyclable product of hydrogen and solar energy is inexhaustible in nature and widely accessible all over the world [7–19]. However, most semiconductor photocatalysts that are thermodynamically viable for water splitting own a band gap too large to fit the solar spectral range, being inappropriate for this purpose [20–22]. More importantly, complete water splitting is generally hampered by the sluggish water-oxidation reactions which involve the participation of four holes and four electrons and are energetically and mechanistically cumbersome [23–27]. Therefore, searching/developing photocatalytic materials/systems that are sensitive to a large portion of solar photons as well as active to water-oxidation reactions is a prerequisite to realize solar hydrogen production from water. In this

regard, great attention has been paid to metal nitrides and oxynitrides not only because of their proper band gap ($\sim 2.0\,eV$) that can harness a significant portion of solar spectrum but also due to their intriguing photocatalytic activity towards water oxidation [28–31]. For instance, Ta_3N_5 is sensitive to photons as far as $600\,nm$ and exhibit superior efficiency for oxygen production from water under appropriate conditions [24,32,33]. Nevertheless, a number of perovskite oxynitrides ($LaTiO_2N$ [34,35], AMO_2N (A = Ca, Sr and Ba; M = Nb and Ta) [29,36–38], $LaMON_2$ (M = Nb and Ta) [39]) demonstrate poor photocatalytic activities under normal conditions, being incommensurate to their substantial visible light absorption. Interfacial or bulk defects produced during material synthesis (high temperature and in the presence of ammonia) are believed to be responsible for their poor performance [34,40–42]. Recent efforts on defects management by doping or interfacial treatment have gained some success in improving their photocatalytic performance yet still bear the risks of introducing additional defects which might be detrimental to the activity [24,26,27,43]. In this work, we developed a new method to improve the photocatalytic performance of perovskite oxynitrides by structural laminations, i.e. inserting extra layers of SrO into $SrTaO_2N$ to form Ruddlesden-Popper (RP) compound Sr_2TaO_3N. $SrTaO_2N$ generally owns the poorest photocatalytic activity among perovskite series

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$ATaO_2N$ (A = Ca, Sr and Ba) [36] and is suffered by self-oxidative decomposition even under the protection of an electron donor [37,38]. Laminating the crystal structure of $SrTaO_2N$ substantially extends its light absorption, reduces the defect levels, stabilizes the compound and boosts the photocatalytic oxygen production from water.

2. Experimental

2.1. Material synthesis

$SrTaO_2N$ and its laminated counterpart Sr_2TaO_3N were synthesized by nitridizing appropriate metal oxide precursors. These precursors were prepared by standard polymerized complex (PC) method: proper amounts of strontium nitrate (SCR, 99.5%), tantalum pentachloride (Aladdin, 99.99%), citric acid (Aladdin, 99.5%) and ethylene glycol (Aladdin, GC grade) were dissolved in 5 mL anhydrous ethanol (Aladdin, 99.9%) to form a transparent solution. The solution was magnetically stirred at 423 K for 3 h and 573 K for another 3 h to promote polymerization. The resultant brown resin was transferred into alumina crucibles and calcined at 823 K for 20 h in order to remove organic species. White powders were produced after calcination and were further nitridized in a tube furnace. The nitridation was performed at 1273 K for 20 h under continuous flow of ultrapure ammonia gas (Jiaya Chemicals, 99.999%). Typical gas flow rate was set at 400 mL min^{-1}.

2.2. Materials characterization

Phase purity and crystal structure of sample powders were examined by X-ray powder diffraction (XRD) techniques on a Bruker D8 Focus diffractometer. Incident X-ray radiation were Cu $K_{\alpha 1}$ ($\lambda = 1.5406$ Å) and Cu $K_{\alpha 2}$ ($\lambda = 1.5444$ Å). Typical step size for signal collection was 0.01° and a duration time of 10 s at each step. Crystal structure analysis and simulation was performed using General Structure Analysis System (GSAS) software package for Rietveld refinement [44]. The morphology of the samples was inspected under a field emission scanning electron microscope (Hitachi S4800) and a transmission electron microscope (JEOL JEM-2100). Diffuse reflectance spectra were collected using a UV–vis spectrometer (JASCO-V750) and were analyzed using JASCO software suite. $BaSO_4$ was used as a non-absorbing reference material. Surface state of sample powders was analyzed by X-ray photoelectron spectroscopy (XPS) technique (AXIS Ultra DLD, monochromatic Al K_α X-ray source). All binding energies were adjusted according to adventitious C 1s peak (284.7 eV) [45]. The nitrogen content in sample powders was determined by thermogravimetric analysis (TGA) (SETARAM, Labsys evo DSC). Surface areas were examined by using a Micromeritics instrument TriStar 3000 and were calculated using the Brunauer-Emmett-Teller (BET) model. Mott-Schottky analysis was performed on a Zahner electrochemical workstation with a three-electrode configuration setup. The working electrode was fabricated by electrophoretic deposition method: two pieces of fluorine doped tin oxide (FTO) glass (30 × 10 mm) were immersed in 50 ml acetone solution containing 40 mg sample powders and 10 mg iodine. The two pieces of glass were kept in parallel to each other with a separation distance of 10 mm and conductive sides faced inward. A constant bias (30 V) was applied to the pair of glass for 3 min under potentiostatic control (Keithley 2450 Source Meter). The prepared electrode was then calcined at 473 K in air for 10 min to remove absorbed iodine. Pt foil (10 × 10 mm) and Ag/AgCl electrode were used as counter and reference electrodes respectively. Aqueous K_3PO_4/K_2HPO_4 (0.1 M, pH = 7.95) solution was used as an electrolyte and a buffer.

2.3. Photocatalytic activity

Photocatalytic activities of freshly prepared samples were evaluated by monitoring the O_2 evolution in the presence of sacrificial agent under visible light illumination ($\lambda \geq 420$ nm). The experiments were carried out in a top-irradiation-type reactor connected to a gas closed circulation and evacuation system (Perfect Light, Labsolar-IIIAG). In a typical experiment, 50 mg sample powders was dispersed into a 100 mL silver nitrate aqueous solution (0.025 M) containing 50 mg La_2O_3. The suspension was then sealed in the reactor and subjected to evacuation for the removal of gas dissolved. Silver nitrate (0.025 M) or sodium persulfate (0.05 M) aqueous solution was used as an electron scavenger to promote the water oxidation reactions and La_2O_3 was introduced to control the pH of the solution. CoO_x was used as a cocatalyst to facilitate water oxidation reactions and was loaded onto sample powders by simply mixing method: proper amounts of CoO were ground with sample powders and the admixtures were calcined at 673 K in N_2 for 1 h. SEM-EDS and TEM analysis confirms the homogeneous distribution and firm anchorage of CoO_x onto the surface of sample powders (Fig. S5). A 300 W Xeon lamp (Perfect Light, PLX-SXE300) was used as the light source, which is coupled with a UV cutoff filter ($\lambda \geq 420$ nm) to generate visible light. Water jacket was used to stabilize the reactor temperature around 293 K. The gas within the reactor was sampled by an on-line gas chromatograph (TECHCOMP, GC7900) containing a thermal conductivity detector (TCD) (5 Å molecular sieve columns and Ar carrier gas).

2.4. Theoretical calculations

Theoretical calculations were carried out using density functional theory (DFT) which is implemented through the Vienna Ab initio Simulation Package (VASP) [46]. The Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional within the generalized gradient approxiamtion (GGA) [47] and the projector augmented-wave pseudopotential were applied for calculations [48]. A 2 × 2 × 1 supercell ($a = b = 8.1$ Å, $c = 12.6$ Å, $\alpha = \beta = \gamma = 90°$) with tetragonal symmetry was built for simulation of Sr_2TaO_3N. N atoms were set to be randomly located at the equatorial positions of TaO_4N_2 octahedrons with *cis*-type arrangements. All geometry structures were fully relaxed until the forces on each atom are less than 0.01 eV/Å. Static calculations were done with a 7 × 7 × 4 Monkhorst-Pack *k*-point grid [49].

3. Results and discussions

3.1. Phase purity and crystal structure

The crystal structure of perovskite metal oxynitrides AMX_3 (A = Ca, Sr, Ba, La and Eu; M = Nb, Ta and Zr; X = N/O) has been an intriguing topic for both experimental and theoretical studies [50]. A wealth of important properties such as optical, photocatalytic, dielectric and magnetoresistive properties etc. have been found to be strongly correlated with local anion ordering within the perovskite lattice [51–54]. The general findings are the covalency driven *cis*-type arrangement of N in MX_6 octahedrons and the formation of disordered zigzag -M-N-chains along perovskite network [50]. This leads to the segregation of N atoms into two-dimensional (2D) planes within the perovskite lattice for $SrTaO_2N$ where inequivalent O and $O_{0.5}N_{0.5}$ anion sites appear in the *ab* plane. An orthorhombic supercell ($2a_p \times 2a_p \times 2a_p$) with space group *Fmmm* is found to be most appropriated to describe the crystal structure of $SrTaO_2N$ (Glazer notion $a^\circ b^\circ c^-$) [55]. Our Rietveld refinement using space group *Fmmm* converges with better *R*-factors and χ^2 ($R_p = 4.18\%$, $R_{wp} = 5.67\%$, $\chi^2 = 1.456$) compared to those using space group *I4mcm* ($R_p = 6.05\%$, $R_{wp} = 4.50\%$, $\chi^2 = 1.654$) (Fig. S1) which has been adopted by other research groups [56,57]. The refined unit cell parameters are tabulated in Table 1. The inequivalent O and $O_{0.5}N_{0.5}$ anion sites within $SrTaO_2N$ structure can be easily distinguished (Fig. 1a). Previous report has pointed out that such a *cis*-type configuration in MX_6 octahedrons origins from the high tendency for d° transition metal ions to maximize $M(d_\pi)$-$X(p_\pi)$ covalency (here Ta($5d_\pi$)-