Efficient Water Splitting over Perovskite-type Oxynitride Photoanodes Absorbing a Wide Range of Visible Light

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Abstract: Water splitting using photoelectrodes absorbing a wide range of visible light is attractive for harvesting a large portion of solar spectrum but very challenging because narrowing the band-gap energies of semiconductors lowers the driving force for photoreactions. Herein we report photoactive perovskite-type oxynitrides exhibiting the photoexcitation above 600 nm for water oxidation. Improving the crystallinity of oxynitrides both in the bulk and on the surface and suppressing the reduction of B-cite cations during the synthesis of $AB(O,N)_3$ are critical for water oxidation activity.

Keywords: Water oxidation, Oxygen evolution, Photocatalysts.

1. Introduction

The n-type perovskite oxynitrides, designated $AB(O,N)_3$ (A=La, Ca, Sr and Ba, B=Ti, Ta and Nb), are very interesting because the band-gap energies can be tuned by different combinations of elements at the A and B sites. These oxynitrides absorb a wide range of visible light above 600 nm as shown in Figure 1, expectable theoretically high solar-to-hydrogen (STH) conversion efficiency. In addition, their band-gap positions straddle water redox potentials so that these semiconductors may enable photoelectrochemical (PEC) water splitting without input of electric energy. However, the PEC water splitting using perovskite oxynitrides except $LaTiO_2N$ (~600 nm) has rarely been studied and remains relatively inefficient.[1, 2]

The low photoactivity was mainly because of poor crystallinity of the oxynitrides and generation of defects or impurities in the surface after nitridation, which enhance recombination of photoexcited holes and electrons during the PEC water oxidation. In fact, the presence of B species, which are easily reduced for nitridation because of their high electronegativities, promotes the formation of defect sites, e.g., Nb^{4+} or Nb^{3+} in $ANbO_2N$. Also, the absence of facile, stoichiometric oxide precursors (with Ba/B ratio of 1) for nitridation to $BaBO_2N$, leads to low crystallinity of the oxynitrides. Herein we report an effective synthesis route of oxynitrides, such as nitridation using different starting oxides and subsequent annealing, to increase the degree of crystallinity and as well to suppress the generation of surface defects for high PEC water oxidation activity.

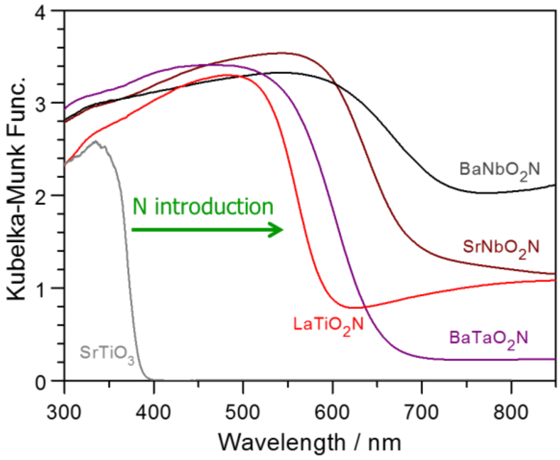

Figure 1. UV-vis DRS spectra of perovskite oxynitride photocatalysts, ABO_2N (A=La, Sr and Ba and B=Ti, Ta and Nb).

2. Experimental

ACO_3 (A=Ba, Sr) and B_2O_5 (B=Ta, Nb) were blended and calcined in air at different temperatures, 1423, 1573 K for 30 h to obtain $A_5B_4O_{15}$. Additionally, the mixtures of $A_5Nb_4O_{15}$ with powdered Nb were calcined under sealed evacuated quartz ampules at 1423 K for 48 h, to synthesis cubic-perovskite $ANbO_3$. The different oxide precursors were nitrided in several nitridation conditions under NH_3 flow with 250 mL min^{-1}. The products were washed with copious amounts of distilled water and dried naturally. Subsequently, the resulting, as-prepared oxynitrides were annealed under different gas atmospheres such as NH_3 and Ar. For PEC measurements, the particulate oxynitride photoanodes were prepared by a particle transfer method.[3]

3. Results and discussion

Perovskite-type $ANbO_2N$ were synthesized by a typical thermal ammonolysis using crystalline, cubic-perovskite oxides $ANbO_3$ (Nb^{4+}) different from facile oxides $A_5Nb_4O_{15}$ (Nb^{5+}).[4] Also, the nitridations of starting oxides with various A/Nb ratios were carried out to determine the effect of different oxide precursors on physical properties of the oxynitrides and the resulting PEC activity. The nitridation of stoichiometric, identical perovskite $ANbO_3$ to $ANbO_2N$ was completed by no structural transition, and this synthesis route understandably induced a preparation of high crystalline $ANbO_2N$. The resultant $ANbO_2N$ photoanodes presented enhanced photocurrent under simulated solar irradiation.

In addition, the annealing of perovskite $BaBO_2N$, prepared from nitridation of Ba-rich oxides $Ba_5B_4O_{15}$, was carried out at Ar and NH_3 atmospheres. The annealing treatments were very effective at improving the surface crystallinity of amorphous, as-prepared oxynitrides, shown in Figure 2. Also, the synthesis route composing of moderate-nitridation and additional annealing suppressed the generation of surface defects. As a result, the particulate $BaNbO_2N$ photoanode, absorbing visible light up to 740 nm, exhibited a remarkably improved photoactivity of 5.2 mA cm^{-2} at 1.23 V_{RHE} under AM 1.5G sunlight.

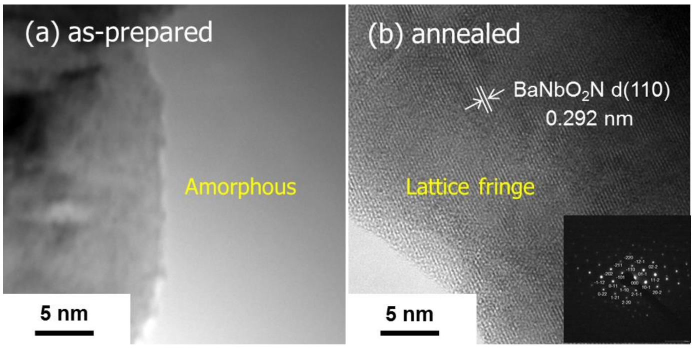

Figure 2. HRTEM images of $BaNbO_2N$ particles (a) as-prepared by the nitridation at 1173 K for 20 h and (b) subsequently annealed in a Ar flow. SAED patterns in (b) indicate diffraction of $BaNbO_2N$ along the [110] zone axis. (a) was reprinted from ref. 4.

4. Conclusions

High crystallinity of semiconductor is a prerequisite for high photoactivity because it influences the charge separation efficiency during photoreactions. However, the synthesis of $AB(O,N)_3$ to exclusively improve its bulk crystallinity led to limited PEC activity. Most effectively, the high crystallinity of oxynitrides not only in the bulk but on the surface, accompanied by supressing the generation of the surface defects, is a determinant factor for achieving high solar-driven water splitting. Detailed characterizations of the prepared, perovskite-type $AB(O,N)_3$ and their photoactivities will be discussed in the presentation.

References

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