

# Efficient Solar Water Splitting on Particulate Perovskite-type Oxynitride Photoanodes

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The n-type perovskite oxynitride semiconductors designated AM(O,N)<sub>3</sub> (A=La, Ca, Sr and Ba, M=Ti, Ta and Nb) have a very interesting structure because their band gap energies can be tuned by employing different combinations of elements at the A and M sites. These oxynitrides are able to absorb a wide range of visible light above 600 nm, as shown in Figure 1 and exhibit theoretically high solar-to-hydrogen (STH) conversion efficiency. In addition, their band gap positions straddle a water redox potential region so that these compounds may allow photoelectrochemical (PEC) water splitting with no input of electric energy. However, the PEC water splitting of Ta or Nb-based perovskite oxynitrides except Ti at M site has rarely been studied and remains relatively inefficient.<sup>[1,2]</sup>

The low PEC water oxidation activity was mainly due to poor crystallinity of oxynitrides and the generation of surface defects during long nitridation of oxide precursors to enhance it, which led to recombination sites of photoexcited holes and electrons. The presence of Nb species, which are more easily reduced than Ta species for nitridation, would promote the formation of much larger defect sites such as Nb<sup>4+</sup> in ANbO<sub>2</sub>N. In a case of BaMO<sub>2</sub>N, the absence of facile stoichiometric oxide precursor with Ba/M ratio of 1 for nitridation, also leads to low crystallinity of oxynitrides, resulting in a limitation of photoactivity. Thus, the effective synthesis way of oxynitrides to increase the degree of crystallinity and as well to suppress the generation of surface defects should be suggested for high PEC water splitting activity.

Herein we investigated the nitridation from different starting oxides and subsequent post treatment for active oxynitrides in PEC water

splitting. ANbO<sub>2</sub>N were synthesized from cubic-perovskite oxides ANbO<sub>3</sub> (Nb<sup>4+</sup>), different from a facile oxide A<sub>5</sub>Nb<sub>4</sub>O<sub>15</sub> (Nb<sup>5+</sup>), by a typical thermal ammonolysis.<sup>[3]</sup> The nitridation of identical perovskite and stoichiometric ANbO<sub>3</sub> to ANbO<sub>2</sub>N was completed by no structural transition, and this synthesis route understandably induced a preparation of high crystalline ANbO<sub>2</sub>N. The resultant ANbO<sub>2</sub>N photoelectrodes exhibited clearly improved mA/cm<sup>2</sup> level PEC water oxidation under simulated solar irradiation (AM1.5G) and a faradaic efficiency close to unity.

In addition, BaMO<sub>2</sub>N was nitrided from a facile Ba<sub>5</sub>M<sub>4</sub>O<sub>15</sub> or mixtures of BaCO<sub>3</sub> and M<sub>2</sub>O<sub>5</sub> with Ba/M ratios of above 1. It was an effective way to suppress the formation of surface defects during high temperature nitridation. Subsequently, the post-annealing of BaMO<sub>2</sub>N under different gases was attempted to modify surface property of oxynitrides. More detailed characteristics and photoactivities for the prepared perovskite AMO<sub>2</sub>N will be reported in the presentation. It will be also discussed a critical factor in oxynitride synthesis to be considered for efficient solar-driven water splitting.

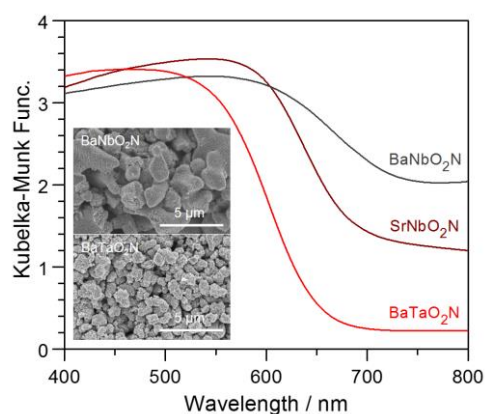


Figure 1. UV-vis spectra and SEM images of perovskite-type oxynitride photocatalysts, AMO<sub>2</sub>N (A=Sr, Ba; M=Ta, Nb).

## REFERENCES

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