

# Flux Synthesis of Layered Perovskite Oxyiodide Photocatalyst for Visible-Light-Driven Water Splitting

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## Significance and Relevance

We report a novel solution-based synthetic approach, the flux method, for the Sillén–Aurivillius layered perovskite oxyiodide Bi<sub>4</sub>NbO<sub>8</sub>I. The flux method provides well-crystalized plate-like particles, improving charge carrier transport property and photocatalytic water oxidation activity compared to the sample prepared via the conventional solid-state reaction (SSR). Surface modification further exploits the flux sample's superior bulk property, achieving an apparent quantum efficiency (AQE) of 8.8% for sacrificial O<sub>2</sub> evolution at 405 nm, the highest value reported for oxyiodide photocatalysts.

Preferred and 2<sup>nd</sup> choice for the topic: "Photocatalysis and photoelectrocatalytic approaches, solar energy utilization" preferred or "H<sub>2</sub> storage and transportation, green H<sub>2</sub> production, hydrogen vectors" Preferred presentation: Oral preferred or Short Oral

## Introduction and Motivations

Sillén–Aurivillius layered perovskite oxyiodides, such as  $Bi_4NbO_8I$ , have recently emerged as a new class of materials for visible-light-driven water splitting photocatalysis, owing to their narrow band gaps and high photocatalytic activities.<sup>1-3</sup> However, their synthesis has been limited to conventional SSR, hindering us from fully exploiting the material's potential.

## **Results and Discussion**

 $Bi_4NbO_8I$  (Figure 1) samples were synthesized using both the conventional SSR method and the flux method, with  $Bi_3NbO_7$  and BiOI as precursors. For the flux synthesis, we employed an alkali metal iodide (eutectic mixtures of CsI and KI) as a molten salt to create an I-rich environment. Chloride salts used as a flux resulted in the chloride counterpart,  $Bi_4NbO_8CI$ , even with BiOI used as a precursor, highlighting the necessity of an iodidebased flux to maintain I-rich conditions. After calcining the precursor with the molten salt in an evacuated quartz tube, the salts were washed away to obtain the product.

While the SSR sample consists of an agglomeration of irregularly shaped particles (Figure 2a), the flux synthesis resulted in plate-like particles (Figure 2b). In addition, the product exhibits a single-crystalline nature, as revealed by the



**Figure 1** Crystal structure of Sillén–Aurivillus phase Bi<sub>4</sub>NbO<sub>8</sub>I.

transmission electron microscopy (TEM) image and the corresponding selected area electron diffraction (SAED) patterns (Figures 2c and 2d).

The band gap of Bi<sub>4</sub>NbO<sub>8</sub>I samples prepared using the flux method was estimated to be 2.45 eV from the absorption edge of 506 nm, identical to that of the SSR sample.<sup>3</sup> The dynamics of photogenerated carriers in Bi<sub>4</sub>NbO<sub>8</sub>I were investigated by time-resolved microwave conductivity (TRMC) measurement.<sup>4</sup> The TRMC signal corresponds to the product ( $\varphi \Sigma \mu$ ) of the charge carrier generation efficiency  $\varphi$  and the sum of charge carrier mobilities  $\Sigma \mu$ , and the decay profile reflects the carrier lifetime. The flux sample exhibited over three times higher intensity and a longer carrier half-



lifetime ( $\tau_{1/2}$ ) than that of the SSR sample (Figure 3a). These results show that the flux sample is superior in carrier transport properties to the SSR one, which can be attributed to its high crystallinity (Figure 2d).

Photocatalytic water oxidation activity was investigated in the presence of an electron acceptor (Ag<sup>+</sup>). As shown in Figure 3b, the optimized IrO<sub>x</sub>-loaded flux sample presented a superior activity to that of the SSR one. The enhanced carrier transport properties of the flux-synthesized sample (Figure 3a), along with its higher surface area (Figures 2a and 2b), can be the improvement factors. The AQE for sacrificial O<sub>2</sub> evolution reached 8.8% at 405 nm, which is the bestreported performance for oxyiodides. Moreover, we demonstrated the visible-light Z-scheme water splitting using Bi<sub>4</sub>NbO<sub>8</sub>I as an O<sub>2</sub> evolution photocatalyst (Figure 3c).

a SSR 1.0 m<sup>2</sup> g<sup>2</sup> 1 µm c d d 040 200 nm 200 nm b flux 37 m<sup>2</sup> g<sup>2</sup> -500 nm -5

Figure 2 SEM images of  $Bi_4NbO_8I$  samples prepared via (a) the flux method and (b) SSR method. (c) TEM image, and (d) the corresponding SAED pattern of the flux-synthesized sample.

The present synthetic method for

oxyiodides and the provided high-quality microcrystalline particles offer a useful playground for designing and modifying the particles for more efficient water-splitting. We also believe that this flux synthesis approach is applicable to a variety of functional iodine-based materials, including other Sillén–Aurivillius phases, paving the way for oxyiodides as high-performance functional materials.



**Figure 3** (a) TRMC transient decay profiles of pristine Bi<sub>4</sub>NbO<sub>8</sub>I samples prepared via the flux method and SSR method. (b) Time courses of O<sub>2</sub> evolution over pristine and IrO<sub>x</sub>-loaded Bi<sub>4</sub>NbO<sub>8</sub>I samples prepared via the flux method and SSR method in an aqueous AgNO<sub>3</sub> solution under visible light irradiation. (c) Time courses of H<sub>2</sub> and O<sub>2</sub> evolution over a mixture of RuO<sub>x</sub>/SrTiO<sub>3</sub>:Rh and IrO<sub>x</sub>/(Fe,Ru)O<sub>x</sub>/Bi<sub>4</sub>NbO<sub>8</sub>I in an aqueous Fe(NO<sub>3</sub>)<sub>3</sub> solution under visible light irradiation.

## References

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