

Behavior of Photogenerated Charge Carriers in BiVO₄ Based Heterojunctions

Chandana Sampath Kumara Ranasinghe¹
Akira Yamakata*¹,

¹ Toyota Technological Institute, Japan

*E-mail: yamakata@toyota-ti.ac.jp

Photocatalytic water splitting using solar radiation is one of the sustainable methods to produce H₂ gas. For this purpose, n-type BiVO₄ (band gap 2.4 eV) has gained much attention due to its activity as a visible active photocatalyst. The photocatalytic activity can be drastically enhanced by making heterostructures with SnO₂ or CoO_x [1, 2].

Basic knowledge of charge transfer processes in these heterostructures is necessary to develop more efficient systems. In this work, we applied the transient absorption spectroscopy (TAS) to study the charge carrier dynamics in these heterostructures. For this experiment, BiVO₄, SnO₂/BiVO₄ and SnO₂/BiVO₄/CoO_x thin-film heterostructures were prepared by high-temperature spray pyrolysis deposition. TA spectra were measured in visible to mid-IR region by exciting the samples using 480 nm laser pulses (7 mJ per pulse, 6 ns duration, 1 Hz) [3].

First, we have examined the photoelectrochemical activity of the fabricated electrodes (Fig. 1). By the illumination of BiVO₄ electrode with 455 nm light, anodic current was observed at > 0.3 V vs. Ag/AgCl. This anodic current is ascribed to the water oxidation, and it was increased by 4 and 5 times by fabricating the SnO₂/BiVO₄ and SnO₂/BiVO₄/CoO_x, respectively.

Then, the behaviors of charge carriers at these heterojunctions are studied. The transient absorption spectra of BiVO₄ measured from 20000-1000 cm⁻¹ are shown in Fig. 2. The spectra exhibited three absorption features: strong absorption at 20000-18000 cm⁻¹, very broad absorption at 18000-7000 cm⁻¹ and 7000-1000 cm⁻¹. According to our previous studies [3], these absorptions are assigned to trapped holes, deeply trapped electrons/holes, and trapped electrons, respectively.

We further examined the decay processes of electrons and holes by probing the intensity changes at 2000 (Fig. 3A) and 19800 cm⁻¹ (Fig. 3B), respectively. The lifetime of electrons becomes longer by fabricating the SnO₂/BiVO₄ heterostructure on the BiVO₄ layer. The deposition of CoO_x on BiVO₄/SnO₂ further decelerates the decay of electrons. These results suggest that SnO₂ and CoO_x effectively prolong the lifetime of electrons excited in BiVO₄. In the case of trapped holes probed at 19800 cm⁻¹, the number of surviving holes increased in SnO₂/BiVO₄ compared to BiVO₄. However, it decreased by loading CoO_x on SnO₂/BiVO₄. The enhancement of both the electrons and holes in SnO₂/BiVO₄ suggests that the electron-hole separation is enhanced by forming the heterostructure, and the favorable band alignment allowing electron transfer from BiVO₄ to SnO₂ would be responsible. However, loading of CoO_x on SnO₂/BiVO₄ further elongated the lifetime of electrons but accelerated the decay of holes. CoO_x can capture holes effectively [3], and hence further enhances the charge separation. This effective charge separation is responsible for the enhancement of the photoelectrochemical activity. The detailed results will be presented at the conference.

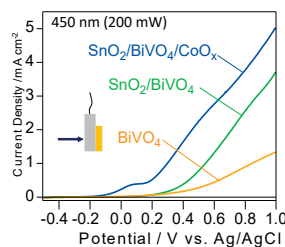


Fig. 1: Photoelectrochemical activity of photoanodes

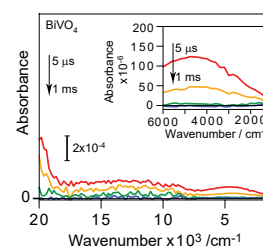


Fig. 2: TA spectra of BiVO₄ by 480 nm (7 mJ) excitation

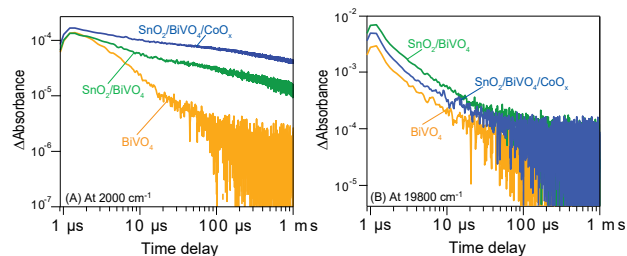


Fig. 3: Decay of charge carriers in BiVO₄, SnO₂/BiVO₄ and SnO₂/BiVO₄/CoO_x at (A) 2000 cm⁻¹ and (B) 19800 cm⁻¹

REFERENCES

- [1] Y. Liang *et al.*, J. Phys. Chem. C, 115 (2011) 17594.
- [2] Chang *et al.*, J. Am. Chem. Soc., 137 (2015) 8356.
- [3] A. Yamakata *et al.*, J. Phys. Chem. C, 118 (2014) 23897.