

Structure transformation of BiOCl as photocatalyst to reduce oxygen in photofuel cell

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1 Introduction

We developed a photofuel cell (PFC) comprising photocatalysts (TiO₂ and Ag–TiO₂) to photooxidize water and photoreduce O₂, respectively. Schottky barrier between TiO₂ and Ag nanoparticle at the cathode rectified the cell current [1].

In this study, n-type semiconductor TiO₂ and p-type semiconductor BiOCl were used on an anode and a cathode to improve the performance of PFC by facilitating charge transfer at the interface between photocatalyst and substrates in solution.

The structure transformation during O₂ reduction on BiOCl coated on the cathode was investigated by means of Bi L₃-edge XAFS spectroscopy.

2 Experiments

BiOCl was synthesized by solvothermal method. The synthesized BiOCl powder were set under Ar and irradiated under UV-visible light for 19 h. Separately, synthesized BiOCl on ITO film was immersed in HCl solution of pH 2.0 in PFC. It was under O₂ atmosphere and irradiated under UV-visible light in total for 2.5 h, and then exposed to air.

Bi L₃-edge XAFS spectra were measured at 290 K in transmission mode on beamline NW10A and 7C. The samples were thoroughly mixed with boron nitride and pressed as disk. Instead, some samples were in Pyrex glass cell equipped with polyethylene naphthalate film window, purged with Ar, and sealed with a fire.

3 Results and Discussion

Bi L₃-edge EXAFS curve fit analysis for as-synthesized BiOCl indicated interatomic distances of Bi-O and Bi-Cl to be 0.244 nm and 0.307 nm, respectively (Table 1a). These interatomic distances are almost identical with reported values in reference (0.231 nm and 0.307 nm [4]) (Table 1f). As synthesized BiOCl comprises BiO⁺ layers and intercalated Cl⁻ anions.

The coordination number (*N*) for interatomic pair of Bi-O of BiOCl sample irradiated under UV-visible light for 19 h & Ar decreased from 4.0 to 1.9. On the other hand, *N* value for Bi-Cl negligibly changed from 4.0 to 3.7 (Table 1b). This change

suggested that O vacancy in BiOCl under Ar and UV-visible irradiation. Bismuth atoms that lost neighboring lattice O may form shorter bond with Cl: 0.276 nm in comparison to 0.307 nm for complete BiOCl crystalline (Table 1b).

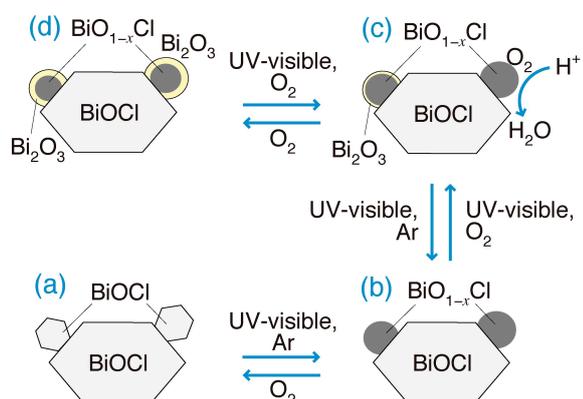
The *N* values of Bi-O for as-synthesized BiOCl (4.0) increase to 5.1 after irradiation under O₂ and UV-visible light. On the other hand, the *N* values of Bi-Cl for as-synthesized BiOCl decrease from 4.0 to 3.1 (Table 1c). The interatomic distances of Bi-O and Bi-Cl were nearly constant at 0.244–0.247 and 0.301–0.307 nm, respectively (Table 1c). These results suggested the partial formation of Bi₂O₃.

Table 1. The curve-fit analysis result of Bi L₃-edge EXAFS for BiOCl

sample	Bi-O	Bi-Cl	Bi-Cl	Bi-Bi	Bi-Bi
	<i>R</i> (nm)				
<i>N</i>					
(a)	0.244	0.307			
As synthesized	(±0.002)	(±0.011)			
	4.0	4.0			
	(±0.7)	(±1.7)			
(b)	0.241	0.276			
In Ar and UV-visible, 19 h	(±0.015)	(±0.021)			
	1.9	3.7			
	(±0.9)	(±0.2)			
(c)	0.247	0.301			
After PFC test in HCl (pH 2.0) for 5h, then exposed to air	(±0.012)	(±0.009)			
	5.1	3.1			
	(±1.6)	(±1.7)			
(d)	0.2330				
Bi ₂ O ₃ [2]	5				
(e)		0.2500			
BiCl ₃ [3]		3			
(f)	0.2314	0.3071	0.3500		
BiOCl [4]	4	4	1		
(g)				0.3071	0.3529
Bi metal [5]				3	3

These results suggested structure transformation for BiOCl as illustrated in Scheme 1. When as synthesized BiOCl was irradiated by UV-visible light, a part of BiOCl crystallines was transformed into BiO_{1-x}Cl species (Scheme 1a, b). The black BiO_{1-x}Cl species should contribute to photocatalytic

O₂ reduction by increasing visible light absorption and also forming electron trapping state below conduction band of BiOCl crystalline (Scheme 3c). The BiO_{1-x}Cl species was stabilized by wrapping with Bi₂O₃ when exposed to air (Scheme 3d).



Scheme 1. Proposed structure transformation of BiOCl.

References

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