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Monitoring of active site in BiOCl used on photocathode at pH 1.0–2.0

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1 Introduction

Photocatalytic solar cell (PC-SC) that enables the electromotive force of as high as 2.11 V was recently reported using photocatalysts on both electrodes [1]. The cell power of PC-SC is presently limited by the rate of oxygen reduction reaction that takes place on the photocathode. The oxygen reduction reaction proceeds in combination with protons and electrons.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (1)$$

Based on the equation 1, the reaction is advantageous to proceed at lower pH. However, the stability and reactivity of BiOCl at pH lower than 2 are rarely reported. Therefore, the active site of BiOCl immersed in HCl of pH at 1–2 was monitored by means of Bi L_3-edge EXAFS.

2 Experimental Section

Bismuth L_3-edge EXAFS spectra were obtained at 290 K in transmission mode on beamline NW10A and 9C. The Bi compounds were thoroughly mixed with boron nitride (BN) and pressed to form disks. Samples were placed in Pyrex glass cell equipped with a Kapton film window (Dupont, Wilmington, DE, USA; 50 μm thick) for X-ray transmission and a polyethene terephthalate film window (Teijin, Japan, G2; 50 μm thick) for both UV–visible light and X-ray transmission, filled with HCl aqueous solution (pH 2.0–1.0).

Bi L_3-edge absorption energy was calibrated to 13 426 eV for the spectrum of a Bi metal powder diluted with BN.

The EXAFS data were analysed using the Athena and Artemis package. Curve-fitting analyses were performed for the inversely Fourier-filtered angular wavenumber $(k)^3$-weighted EXAFS χ function both in k- and interatomic distance (R) spaces using amplitude and phase-shift parameters theoretically generated using FEFF version 6L for the crystal structure of BiOCl. The R values and its associated coordination numbers (N) for Bi···Bi, Bi–O, and Bi–Cl pairs were set to 0.3887 nm with an N value of 4, 0.2316 nm with an N value of 4, and 0.3059 nm with an N value of 4 and 0.3500 nm with an N value of 2. The experimental data was Fourier-filtered in the k-range between 30 and 130 nm^{-1}. We assumed that the many-body reduction factor was identical for the sample and theoretical model.

3 Results and Discussion

The N values of Bi-O and Bi-Cl at pH 1.78 and 15 min and 60 min and at pH 1.00 and 15 min are listed in Table 1b–d. Figure 1 shows Fourier transform at each condition.

Table 1. Curve-Fitting Results of Bi L_3-Edge EXAFS for BiOCl immersed in HCl Solution at pH 2.0–1.0

Entry	pH	Bi–O		Bi–Cl	
		N	R (nm)	N	R (nm)
a	2.00	4.0 ± 0.5	0.232 ± 0.001	4.0 ± 1.3	0.323 ± 0.003
b	1.78 (15 min)	4.3 ± 0.7	0.231 ± 0.001	3.8 ± 1.4	0.323 ± 0.003
c	1.78 (60 min)	4.1 ± 0.7	0.232 ± 0.001	2.8 ± 0.9	0.324 ± 0.017
d	1.00 (15 min)	4.4 ± 0.3	0.227 ± 0.001	2.6 ± 0.8	0.337 ± 0.018
BiOCl		4	0.2316	4	0.3059
				2	0.3500
Bi_2O_3		5	0.2330		
$BiCl_3$				3	0.2500

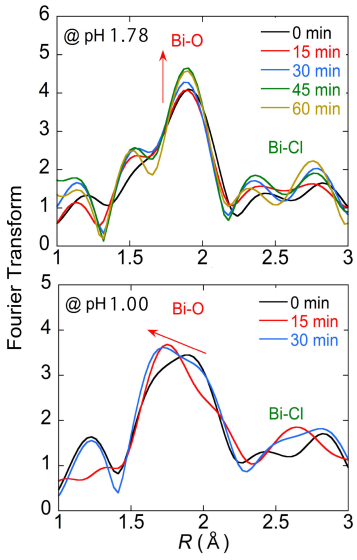

Figure 1. Fourier-transform of Bi L_3-edge EXAFS for BiOCl at pH 1.78 (Top) and pH 1.00 (Bottom).

Based on these results, the following reaction partially proceeded.

$$3BiOCl + HCl \rightarrow Bi_2O_3 + H^+ + BiCl_4^- \quad (2)$$

Bi_2O_3 is poor for photocatalysis and this reaction was disadvantageous as on photocathode in SC. In contrast, the Bi–Cl coordination was retained at pH 1.78 and 15 min (3.8, Table 1b). At pH 1.78, the W_{max} value of SC increased by 40% compared to that at pH 2.0 [2]. At pH 1.78 and 60 min and at pH 1.00 and 15 min, the W_{max} value of SC decreased drastically.

References

(1) K. Urushidate, S. Matsuzawa, K. Nakatani, J. Li, T. Kojima, and Y. Izumi, *ACS Sustainable Chem. Eng.* **6**, 11892–11903 (2018).
(2) K. Urushidate, J. Li, K. Hara, T. Kojima, and Y. Izumi, *ACS Sustainable Chem. Eng.* **8**, 1406–1416 (2020).

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