

# Site Structure of $\text{BiO}_{1-x}\text{Cl}_{1-y}$ Photocathode in Photofuel Cell that Uses Acidic Water as a Fuel

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In-situ site structure of photocathode comprising bismuth compound in photofuel cell was successfully clarified using Bi  $L_{3}$ -edge EXAFS.

## 1 Introduction

The ex-situ structure of photocathode bismuth oxychloride ( $\text{BiOCl}$ ) in photofuel cell was reported in Photon Factory Activity Report 2013 [1]. The photofuel cell in this study is very unique that uses acidic water as a fuel [2]. Herein, the structure of  $\text{BiOCl}$  was studied under in-situ condition of photofuel cell [3].

## 2 Experimental Section

$\text{BiOCl}$  was synthesized via the solvothermal procedure reported in reference 3. A  $\text{BiOCl}$  film was set in the HCl solution (pH 2.0) for cathode of a photofuel cell [2, 3] equipped with polyethylene naphthalate (Q51-16, Teiji-Dupont) window for X-ray beam and UV-visible light irradiations.

Bismuth  $L_{3}$ -edge EXAFS spectra were obtained at 290 K in the transmission mode. On the beamline, the  $\text{BiOCl}$  photoelectrode film was irradiated by UV-visible light for 60 min. The behavior of the Bi sites was monitored also after the light was off.

## 3 Results and Discussion

The  $\text{BiOCl}$  film immersed in HCl aqueous solution (pH 2.0) irradiated by UV-visible light was analyzed (Table 1a). The color of the film was light gray. The coordination number ( $N$ ) of both Bi-O and Bi-Cl decreased from 4.0 to 2.2 and from 4.0 to 3.1, respectively. Taken the fit errors into account, the oxygen vacancy could be formed.

**Table 1:** The curve-fit analysis result of Bi  $L_{3}$ -edge EXAFS for  $\text{BiOCl}$

Sample	Bi-O      Bi-Cl		Goodness of fit
	$R$ (nm)		
	$N$		
	$\Delta\sigma^2$ ( $10^{-5}$ nm <sup>2</sup> )		
(a)	0.250 ( $\pm 0.001$ )	0.329 ( $\pm 0.012$ )	$1.4 \times 10^5$
In HCl (pH 2.0), O <sub>2</sub> gas, & UV-visible, 35 min	2.2 ( $\pm 0.2$ )	3.1 ( $\pm 0.7$ )	
	1.4 ( $\pm 0.5$ )	2.2 ( $\pm 1.7$ )	
	0.247 ( $\pm 0.001$ )	0.331 ( $\pm 0.012$ )	
(b)	4.2 ( $\pm 0.6$ )	4.6 ( $\pm 1.9$ )	$3.2 \times 10^5$
Sample a, 12 min after UV-visible was off	6.0 ( $\pm 1.4$ )	5.7 ( $\pm 1.8$ )	

Then, UV-visible light was turned off. A Bi  $L_{3}$ -edge EXAFS spectrum was obtained at 12 min in the dark. The shape of EXAFS oscillation was similar to that for the sample irradiated by UV-visible light, but the reduced amplitude in the whole spectrum region irradiated by light seemed to recover to the level for the as-synthesized fresh  $\text{BiOCl}$  sample. In fact, the  $N(\text{Bi-O})$  and  $N(\text{Bi-Cl})$  values recovered to 4.2 and 4.6 (Table 1b), respectively, similar to that for as-synthesized  $\text{BiOCl}$  (4.0) [1, 3]. Thus, the O and Cl vacancy formed in HCl aqueous solution irradiated by UV-visible light is suggested to be transformed to the original  $\text{BiOCl}$  crystalline state soon after the light was turned off.

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## References

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## Research Achievements

- (1) 出願番号：特願2014–242685  
発明者：泉 康雄、小倉優太  
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出願人：千葉大学  
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- (2) 出願番号：特願2013–211926  
発明者：泉 康雄、小倉優太、藤嶋幸子  
発明の名称：燃料電池

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