

Transformation of Silver Site over TiO₂ Effectively Used on the Photocathode of Solar Cell

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1 Introduction

High-voltage type solar cell (SC) as high as 2.11 V was recently reported using photocatalysts on both electrodes [1]. Water mediates the redox reactions on both electrodes, and it is essential how to collect light-excited electrons and transfer them to O₂ molecules on the photocathode. We applied O vacancy site of BiOCl [2,3] and silver nanoparticle dispersed on TiO₂ for the electron collect & transfer [4]. The transformation of Ag site on TiO₂ was tentatively investigated using Ag K-edge extended X-ray absorption fine structure (EXAFS), but the sample was as disk [4] not film on electrode. In this report, an Ag–TiO₂ film was formed on indium tin oxide (ITO)/Pyrex and the Ag site transformation was monitored by Ag K-edge EXAFS.

2 Experimental Section

Silver K-edge EXAFS spectra were measured at 290 K in the fluorescence mode in the Photon Factory on beamline NW10A [4]. A Si(3 1 1) double-crystal monochromator and a Pt-coated focusing cylindrical mirror were inserted into the X-ray beam path. Piezo transducer was used to detune the X-ray intensity to two thirds of the maximum to suppress higher harmonics. The Ag K-edge absorption energy was calibrated to 25516.5 eV [5] using the X-ray spectrum of a Ag metal foil.

A film of Ag (3.0 wt %)-TiO₂ photocatalyst (2.0 mg) was formed on an ITO/Pyrex glass plate and was measured using a Lytle detector. First, the sample was in air, then immersed in HCl aqueous solution of pH 2.0 under N₂ atmosphere using a sealable thin transparent plastic bag. Next, the sample in HCl aqueous solution was irradiated by UV–visible light from a 500-W xenon arc lamp (Ushio) at the beamline for 40 min. Finally, the light was turned off and the sample cell was purged with O₂, then with air.

Thus obtained XAFS data were analyzed using the XDAP software package. Multiple-shell curve-fit analyses were performed for the Fourier-filtered *k*³-weighted EXAFS data in *k*- and *R*-space using empirical amplitude and phase-shift parameters extracted from the EXAFS data for Ag metal foil, Ag₂O, and AgCl powders. The interatomic distance (*R*) and its associated coordination number (*N*) for the Ag–Ag, Ag–O, and Ag–Cl pairs were set to 0.2889 nm with the *N* value of 12, 0.2044 nm with the *N* value of 2, and 0.2775 nm with the *N* value of 6.

3 Results and Discussion

Ag K-edge EXAFS spectra were measured under various conditions related to cathodic conditions in SC and were analyzed by curve fitting (Figure 1). For as-prepared Ag–TiO₂ film, the Fourier-filtered *k*³-weighted EXAFS χ -function was fit with two shells of Ag–O and Ag–Ag at 0.2080 and 0.2850 nm. The associated *N* values were 2.6 and 0.41, respectively, demonstrating predominant Ag₂O phase. The latter contribution was regarded as inert metallic Ag nanoparticles formed on specific part on TiO₂ [4]. The ratio of inert Ag⁰ was significantly lower for film sample based on the *N* value (0.41) in comparison to 2.0 for disk sample measured under similar conditions [4].

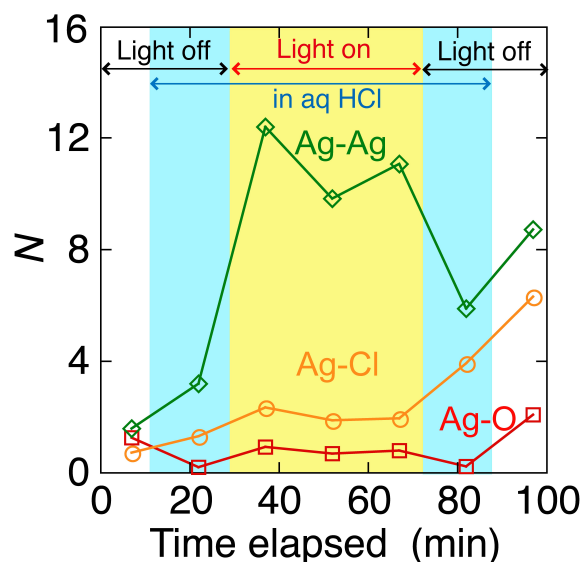


Figure 1. The change of coordination number (*N*) for Ag–O, Ag–Cl, and Ag–Ag interatomic pair of Ag (3.0 wt %)-TiO₂ photocatalyst pasted on ITO/Pyrex electrode based on Ag K-edge EXAFS. Under air, in HCl aqueous solution and N₂, under irradiation of UV–visible light, and under dark and O₂ or air.

Next, the Ag–TiO₂ film on ITO/Pyrex plate was immersed in HCl solution under N₂ atmosphere. The *N* values based on curve fitting analysis became 0.2, 2.9, and 0.7 for Ag–O, Ag–Cl, and Ag–Ag at 0.2069, 0.2661, and 0.2875 nm, respectively. Thus, Ag₂O nanoparticles under air reacted with HCl to form AgCl. This reaction was confirmed also by cyclic voltammetry for disk sample [4]. In contrast, for film sample in this study, the *N* value for Ag–Ag pair increased from 0.41 to 0.7

(Figure 1) while the value negligibly changed from 2.0 to 1.5 for disk sample [4]. We suspect the reduction from $\text{Ag}^{\text{I}}\text{Cl}$ to Ag^0 (0.22 V @standard hydrogen electrode) by the defect site of TiO_2 .

Then, the film of Ag-TiO_2 photocatalyst was irradiated by UV-visible light. The N value for Ag-Ag dramatically increased to 9.8–12.4 (Figure 1) demonstrating photoreduction of $\text{Ag}^{\text{I}}\text{Cl}$ to Ag^0 and possibly corresponding amount of water was oxidized to O_2 . The remained Ag-O and/or Ag-Cl coordination suggested Ag_2O and/or AgCl core and reduced metallic Ag^0 shell structure.

After the light was turned off, the N values for Ag-O , Ag-Cl , and Ag-Ag did not change either under O_2 (@82 min) or under air (@97 min), indicating the stability of Ag^0 nanoparticles as film of Ag-TiO_2 over ITO electrode.

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