

EXAFS Analyses of Photofuel Cell Catalysts Free from Platinum

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Fuel cell is a key technology in the hydrogen energy society in near future. However, major part of fuel cells uses platinum and thus they are not sustainable. For this aim, we have investigated photofuel cells consisting of two photocatalysts [1] free from Pt. In this report, silver species on Ag–TiO₂ photocatalysts were preliminarily studied by EXAFS that are used on photocathode instead of Pt catalysts.

2 Experiments

Ag–TiO₂ photocatalyst was prepared by an incipient impregnation of silver nitrate with TiO₂ powder (P25, Degussa). After the calcination of the obtained powder at 673 K, the color was white. The color changed to purple under ambient air at 290 K for 1 day.

Our photofuel cell utilizes hydrochloric acid solution as electrolyte. Corresponding to the condition, the prepared Ag–TiO₂ purple powder was immersed in HCl solution at the pH of 4–2. The color changed to yellow within 5 s.

Our photofuel cell generates electricity irradiated under UV-visible light. Under the irradiation, the yellow color quickly changed to ochre (within 10 s). In this report, these color changes were monitored using Ag K-edge EXAFS in relation to the photoreduction active sites of Ag–TiO₂.

3 Results and Discussion

The Ag K-edge EXAFS spectrum for calcined and stored sample in ambient air is shown in Fig. 1A. Two peaks were observed at 0.18 and 0.26 nm (phase shift uncorrected; Fig. 1A2) in the Fourier transform (FT) and the curve fit analysis suggested the interatomic pair of Ag and O at 0.23 nm and interatomic pair of Ag and Ag at 0.29 nm (Fig. 1A4). Thus, the exterior of as-prepared Ag nanoparticles were oxidized to Ag₂O.

Immersed in HCl solution, there peaks appeared at 0.15, 0.20, and 0.26 nm (phase shift uncorrected) in the FT of EXAFS. The curve fit analysis suggested the interatomic pairs of Ag and O, of Ag and Cl, and of Ag and Ag at 0.20, 0.26, and 0.28 nm, respectively. Thus, a part of external Ag₂O layers turned to AgCl.

Then, when the Ag–TiO₂ photocatalyst was irradiated by light, two interatomic pairs of Ag and O and of Ag and Ag appeared, but the latter was dominant (Figure 1C4). Thus, AgCl and/or Ag₂O of Ag–TiO₂ sample was transformed to metallic Ag⁰ due to photogenerated electrons. The metallic Ag⁰ sites oxidized again under O₂ when light was turned off (Figure 1D4, Figure 2).

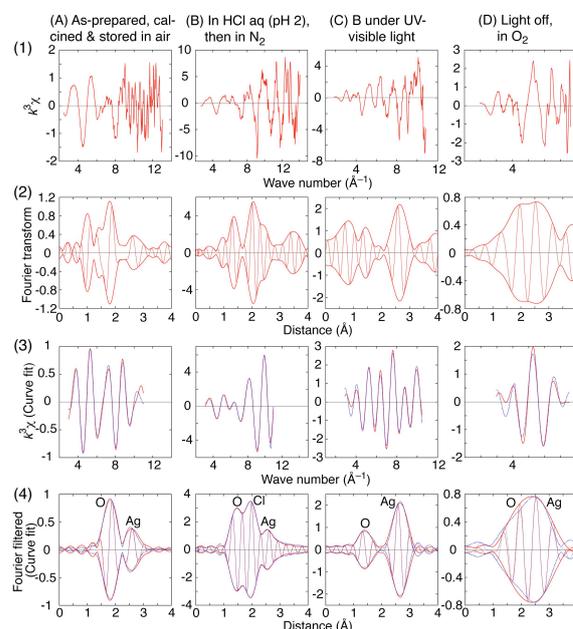


Fig. 1. Ag K-edge EXAFS spectra for as-prepared Ag–TiO₂ (3.0 wt% Ag) (A), A was immersed in HCl solution of pH 2.0 and then under N₂ (B), B was irradiated under UV-visible light (C), and light was turned off and C was under O₂ (D). (1) the $k^3\chi$, (2) its associated FT, and (3, 4) best-fit results. Red line: experimental, blue line: calculated. Solid line: magnitude, dotted line: imaginary part in (2, 4).

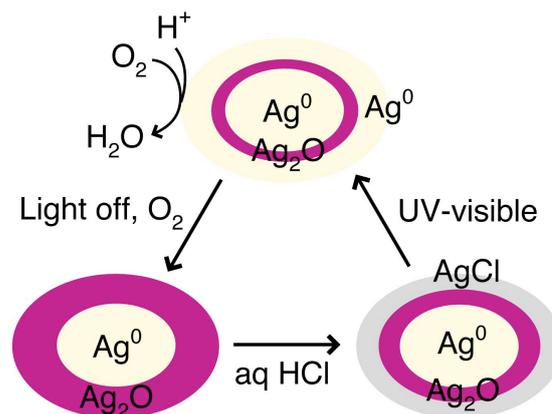


Fig. 2. Transformation of Ag active sites on Ag–TiO₂ photocatalyst.

Reference

[1] Y. Ogura and Y. Izumi, *Japanese Patent* 2012–254796, 2012–223765.

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