

Snapshots of Metal Nanoparticles Generated on TiO₂ Photocatalyst: *In Situ* Time-Resolved Energy-Dispersive X-Ray Absorption Fine Structure Analysis

A photocatalytic system qualifies as a candidate for an environmentally friendly chemical process under ambient condition using solar light. It is well known to utilize a TiO₂ photocatalyst for the oxidative decomposition of pollutants and poisonous and hazardous organic compounds. Since 1970s, a noble metal was often loaded onto a TiO₂ photocatalyst as a modifier to enhance photocatalytic activity. The photodeposition method enables the easy loading of various metal species as cocatalysts on semiconductor photocatalysts because the introduction of a photocatalyst and a metal precursor into an aqueous solution involving alcohol as a sacrificial reagent and the illumination of this suspension with a light source. Time-resolved energy-dispersive XAFS (DXAFS) [1,2] analysis is an up-to-date method for rapidly observing the structural changes of various materials *in situ*. Recently, some groups have reported DXAFS studies on kinetics and dynamics of catalysis with several synchrotron radiation sources in the world. However, the DXAFS analysis has not been applied to photocatalytic reactions involving photodeposition, although several *ex situ* and *in situ* XAFS studies on the photocatalytic reactions were reported. In this study, we investigated the formation of Rh particles on a TiO₂ photocatalyst under photoirradiation by *in situ* DXAFS analysis at beamline BL28B2 [3].

The photocatalyst used in this study was the anatase phase of TiO₂ calcined in a furnace in air at 673 K for 3 h before photodeposition. The photodeposition of Rh metal particles onto a TiO₂ photocatalyst was carried out in a closed batch system. 0.5 g of TiO₂, 0.8 ml of RhCl₃·3H₂O solution (0.095 mol/L) and 3.2 ml of alcohol were introduced into the reactor made of Pyrex[®] glass with a flat glass ceiling window for illumination after Ar bubbling for 10 min. The amount of residual Rh ions in the filtrate was determined using a sequential inductively coupled plasma (ICP) spectrometer. Rh *K*-edge (around 23.2 keV) X-ray absorption fine structure (XAFS) measurements were performed at beamline BL28B2. The main equipment used for DXAFS spectroscopy at beamline BL28B2 in this study consists of a polychromator, which is set to a Laue configuration with net plane Si(422), and a position-sensitive detector (PSD), which is mounted on a θ - 2θ diffractometer, as shown in Fig. 1. The exposure time

of the PSD was 267 msec per shot. 50 snapshot spectra were accumulated to obtain one spectrum; therefore, we observed a spectral variation every 13.35 s in this study.

Figure 2 shows a series of Rh *K*-edge X-ray absorption near edge structure (XANES) spectra for the Rh species in the presence of TiO₂ as a photocatalyst and methanol as a sacrificial reagent under photoirradiation and references, RhCl₃ in solution as a precursor and Rh foil. The XANES spectra obtained before and after photoirradiation were consistent with those of the RhCl₃ solution and Rh foil as references, respectively. The energy position of the absorption edge consecutively shifted to a low-energy side with an increasing in time for photoirradiation. Accordingly, the evolved electron under photoirradiation was trapped by the Rh trivalent ions adsorbed on the surface and the Rh metal particles deposited on the TiO₂ photocatalyst. In addition, a series of XANES spectra exhibited isosbestic points showing that the transient state between a Rh metal particle and a Rh³⁺ ion cannot be captured in the measurement if any, and we can consider that the spectra consist of simply overlapping spectra of Rh⁰ and Rh³⁺.

Figure 3 shows a series of Fourier transforms (FT) for *k*³-weighted Rh *K*-edge EXAFS spectra of the sample shown in Fig. 2 under photoirradiation. Fourier transformation was performed without phase shift correction. The first shell peak located at 1.73 Å disappeared after photoirradiation and an alternative peak appeared at 2.45 Å. This peak is assigned to the Rh-Rh bond of Rh metal, in comparison with the FT spectrum of the Rh foil as a reference. The peak height linearly increased with photoirradiation time

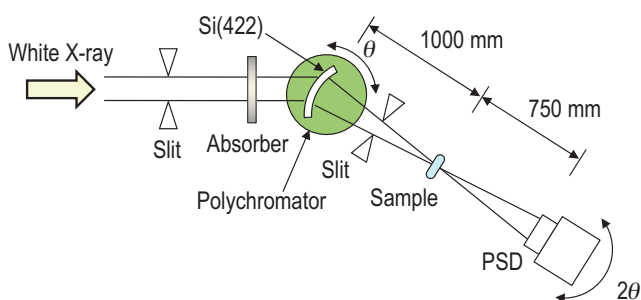


Fig. 1. Schematic view of DXAFS spectrometer for Laue geometry with net plane Si(422).

and saturated after 90 min. This is possibly due to the consumption of all Rh ions in the aqueous solution or the inhibition of Rh metal particle formation. The residual Rh trivalent ions in the filtrate were determined by ICP analysis. There were no ions in the solution in the case of methanol above 90 min of photoirradiation. The amounts of residual Rh trivalent ions linearly decreased with the increasing in photoirradiation time. Accordingly, the formation rate of the Rh metal particles on the irradiated TiO₂ was compatible to the diminution rate of the Rh trivalent ions.

We observed the photodeposition of Rh metal particles onto a TiO₂ photocatalyst from an aqueous solution RhCl₃ as a precursor and alcohol as a sacrificial reagent by *in situ* DXAFS analysis. The Rh trivalent ions are adsorbed on the surface of the TiO₂ photocatalyst, followed by reduction to the Rh metal particles by electron acceptance. The formation rate of the Rh metal particles on the irradiated TiO₂ was closely related to the diminution rate of the Rh trivalent ions. The coordination number of the Rh-Rh bond stopped after 90 min of photoirradiation in the presence of methanol as a sacrificial reagent, suggesting the formation of fine Rh metal particles on TiO₂.

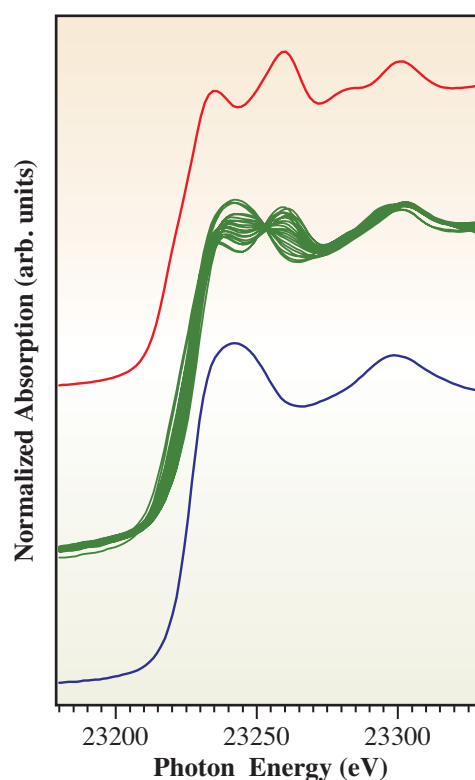


Fig. 2. Series of Rh K-edge X-ray absorption near edge structure spectra for Rh species in TiO₂ as photocatalyst and methanol as sacrificial reagent under photoirradiation (green lines) and references, RhCl₃ in solution as precursor (blue line) and Rh foil (red line).

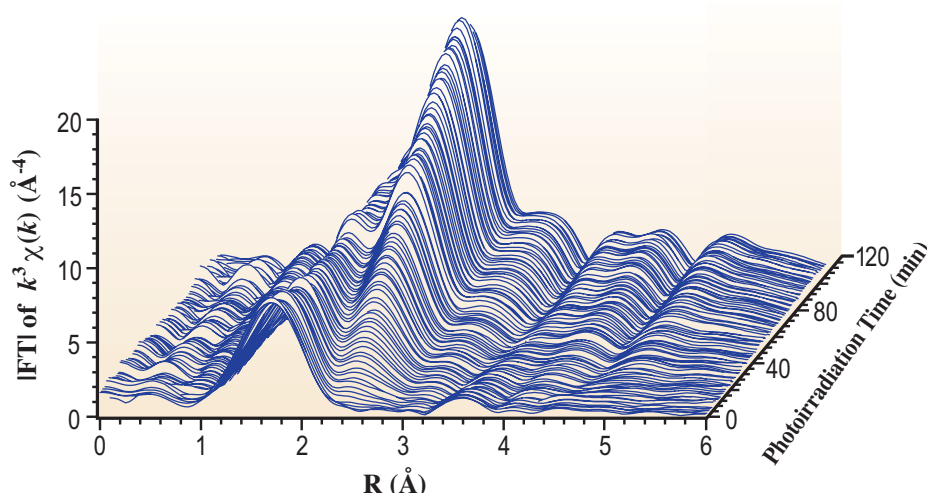


Fig. 3. Series of Fourier transforms (FT) for k^3 -weighted Rh K-edge EXAFS spectra of sample shown in Fig. 2 under photoirradiation.

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