

Monitoring the role of gold combined with ZrO₂ for CO₂ photoconversion irradiated by light

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1 Introduction

The conversion of CO₂ into fuels utilizing sustainable energy sources completes the carbon neutral cycle in an ideal, sustainable society. Solar fuels, in particular, have been identified as promising alternatives to fossil fuels and have thus been widely investigated.¹ However, solar fuel generation from CO₂ is a highly endothermic, unfavorable process, and clarifying a reaction pathway from CO₂ to fuels is essential for making this approach viable and further improvement of catalysts.² ZrO₂ has been shown to successfully promote the photoconversion of ¹³CO₂ into ¹³CO, enabled by both UV light-induced band-gap excitation and heat-induced promotion effects converted from localized surface plasmon resonance (LSPR) via Au doping. The photocatalytic role of Au was clarified using Au L₃-edge EXAFS at KEK.

2 Experimental Section

Au L₃-edge EXAFS spectra were measured at 290 K in transmission mode at the Photon Factory on the NW10A beamline and 9C beamline. On both beamlines, a Piezo transducer was used to detune the X-ray to two-thirds of the maximum intensity to suppress higher harmonics. The Au L₃-edge absorption energy was calibrated at 11 921.2 eV using the spectrum of Au metal. A disk of the Au (5.0 wt %)-ZrO₂ photocatalyst was set in a Pyrex glass reactor equipped with a Kapton film for X-ray transmission and a PET film for both UV-visible light and X-ray transmission. The reactor was filled with 2.3 kPa of CO₂ and 21.7 kPa of H₂. The sample was irradiated with UV-visible light from a 500-W Xe arc lamp through the PET film at the beamline. X-rays transmitted the disk perpendicularly while incident angle of UV-visible light was 45°. For the curve-fit analyses, the empirical amplitude extracted from the EXAFS data for the Au₂O₃ and Au metal was used.³ The Debye temperature [$\theta_{D(\text{Bulk})}$, 165 K] was used for bulk Au while a “surface Debye temperature” [$\theta_{D(\text{Surf}, \perp)}$] of 83 K was used to account for the motion of vertical freedom of translation of fcc Au(1 1 1) or the (1 1 0) surface.

3 Results and Discussion

Light-induced changes in the Fourier transform function of the EXAFS data were quantitatively evaluated. For the Au (5.0 wt %)-ZrO₂ photocatalyst, the N value was 10.8 ± 0.5 before light irradiation (Figure 1A), 10.2–11.1 during light irradiation, and 10.5–11.1 after the light was turned off. Based on the mean particle size range of 4.3 nm obtained for Au in HR-TEM, the dispersion of Au particle was calculated to be 0.31.³

The σ value was calculated to be 0.009 968 nm for Au metal at 290 K using the correlated Debye model² with the ab initio multiple-scattering calculation code, FEFF8, and the Debye temperature for Au (165 K). The initial σ value of 0.010 54 nm for Au (5.0 wt %)-ZrO₂ before light irradiation quickly increased to 0.011 29 nm (10 min light irradiation), remained nearly constant between 0.011 24 and 0.011 34 nm after 70 min of irradiation, and progressively increased to 0.011 40 nm after 110 min of light irradiation (Figure 1B).

Subsequently, this value quickly decreased to 0.010 72 nm after the light was turned off after 120 min of irradiation. The value further decreased gradually to 0.010 55 nm at 190 min, which was essentially the same value as that before light irradiation.

A change in the major peak intensity at 0.24 nm (phase shift uncorrected) was not completely in accord with the change in the σ value during irradiation of UV-visible light for 120 min (Figure 1B, C). The peak intensity progressively decreased during light irradiation for 110 min, whereas the σ value increased only during the first 10 min but essentially remained constant between 10–110 min of light irradiation. The complex correlation was further analysed via log-ratio method analyses.³ The result demonstrated that the combined effects of the $N(\text{Au-Au})$ and σ value changes resulted in a gradual decrease in the peak intensity at 0.24 nm (phase shift uncorrected), i.e. the initial sudden increase of the σ value and subsequent gradual, slow decrease of the N value.

Furthermore, we evaluated the temperature at the Au site based on the σ values. The temperature dependence of σ value is derived from FEFF8 combined with the correlated Debye model for both bulk and surface Au sites using $\theta_{D(\text{Bulk})}$ and $\theta_{D(\text{Surf}, \perp)}$ (Figure 1E-a and b, respectively). We assume preferable exposure of thermodynamically stable fcc(1 1 1) or (1 1 0) face. We also approximated the mean Au nanoparticle temperature as the arithmetic mean temperature based on $\theta_{D(\text{Surf}, \perp)}$ weighted by $1/2 \cdot 1/3D$ [D : dispersion of nanoparticles (0.31), for an effective vertical degree of freedom at a free hemisphere surface] and that based on the $\theta_{D(\text{Bulk})}$ weighted by $(1 - D) + 1/2D + 1/2 \cdot 2/3D$ (bulk site, non-free hemisphere in contact with ZrO₂ and two lateral degrees of freedom at a free hemisphere surface).

As a result, the initial temperature of 295 K before light exposure rose to 316 K after 10 min of irradiation, remained nearly constant between 314 and 318 K after 70 min of irradiation, and progressively increased to 321 K after 110 min of light irradiation (Figure 1B). The temperature quickly dropped to 301 K after the light was turned off. The temperature gradually decreased further to

its initial value before light irradiation (295 K) after 190 min.

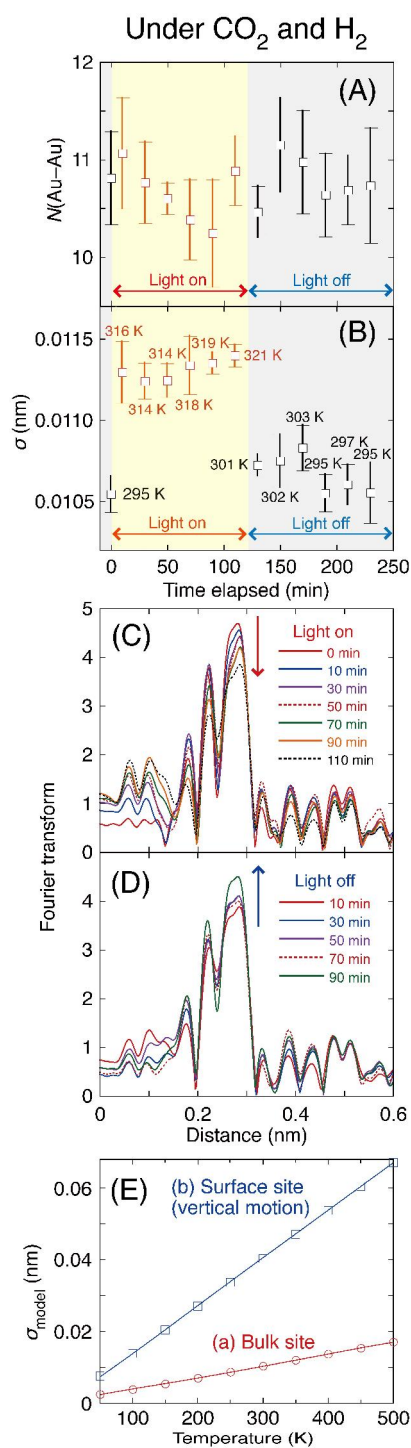


Figure 1. Time course changes of (A) N values, (B) σ values, and (C, D) Fourier transform obtained from k^3 -weighted Au L₃-edge EXAFS χ -function for Au (5.0 wt%)-ZrO₂ under CO₂ (2.3 kPa) and H₂ (21.7 kPa) (C) irradiated by UV-visible light for 120 min followed by (D) dark conditions for 120 min. (E) The correlation between the σ value and temperature for bulk sites (circle, \circ) and surface sites (vertical motion; square, \square) in/on the Au metal generated by the correlated Debye model using an FEFF8 code.

In summary, the contribution of mean 4.3 nm of Au nanoparticles was investigated using in-situ EXAFS. Temperature rise from 295 K to 321 K under the irradiation of UV-visible light and drop to 295 K under dark were directly monitored based on Debye-Waller factor change for Au-Au interatomic pair interference. The lower Debye temperature of Au (165 K) compared to Ag (225 K) resulted in greater heat capacity and the temperature rise via LSPR was smaller, 26 K under CO₂, H₂, and UV-visible light using Au (5.0 wt %)-ZrO₂ in comparison to 106 K under similar conditions using Ag (5.0 wt %)-ZrO₂.² ZrO₂ was effective in promoting both CO and H₂ formation under CO₂, moisture, and UV-visible light conditions, but Au-doped ZrO₂ directed the products toward H₂ production (96%) via a reverse reaction step. During this pathway, a proton is coupled with an electron, and H₂ formation occurs over the Au surface.³

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