Monitoring of Heat via Localized Surface Plasmon Resonance to Convert CO₂ over Silver–Zirconium Oxide

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1 Introduction

Photocatalytic conversion of CO_2 into fuels has been widely investigated to enable carbon-neutral cycle including solar fuel in contrast to irreversible consumption of fossil fuel. Noble metal nanoparticles supported on semiconductor were reported to be efficient for photocatalytic conversion of CO_2 [1], however, the mechanism of enhancement photoreaction over the metal nanoparticles is still unclear. Based on the mechanistic investigation, dual roles of UV–visible light were clarified for the first time using Ag–ZrO_2: (i) charge separation at the band gap and (ii) the heat transformed via localized surface plasmon resonance (LSPR) by using extended X-ray absorption fine structure (EXAFS). The Ag site temperature was monitored via Debye–Waller factor obtained by EXAFS [2].

2 Experimental Section

Silver K-edge EXAFS spectra were measured at 290 K in the transmission mode in the Photon Factory on beamline NW10A, 9C, and 12C. At NW10A, 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 using the X-ray spectrum of a Ag metal foil. A disk (Φ = 10 mm) of Ag (3.0 wt %)–ZrO_2 photocatalyst (125 mg) was set in a Pyrex glass reactor equipped with a Kapton film for X-ray transmission and a polyethylene terephthalate film for both UV–visible light and X-ray transmission filled with 2.3 kPa of CO_2 and 21.7 kPa of H_2 and were measured in the presence/absence of UV–visible irradiation provided by a 500-W xenon arc lamp (Ushio) at the beamline. As control experiments, only visible or infrared light, or under Ar atmosphere were also performed. XAFS data were analyed using the XDAP software package.

3 Results and Discussion

Ag K-edge EXAFS spectra were monitored for Ag (3.0 wt %)–ZrO_2 under CO_2 (2.3 kPa) and H_2 (21.7 kPa) irradiated by UV–visible light at beamline. In the Fourier transform (FT; Figure 1C), a peak due to Ag–Ag interatomic scattering of photoelectrons was predominant at 0.28 nm (phase shift uncorrected), demonstrating that the Ag nanoparticles were exclusively metallic. The FT peak intensity of EXAFS was significantly suppressed as

much as by 31% during the light irradiation of 100 min (Figure 1C). On the contrary, the peak intensity quickly recovered when the light was turned off.
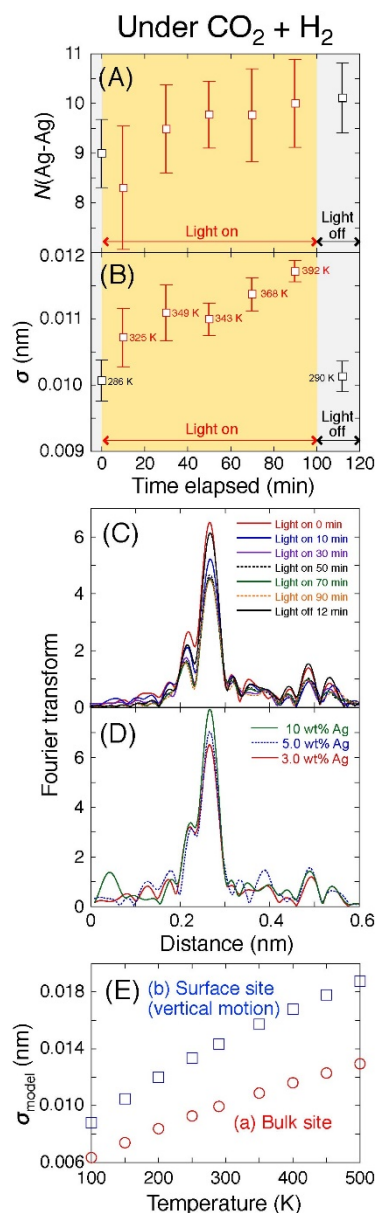
Figure 1. The time-course changes of (A) N and (B) σ values and (C) FT obtained from k^3-weighted Ag K-edge EXAFS χ-function for Ag (3.0 wt %)–ZrO_2 under CO_2 (2.3 kPa) and H_2 (21.7 kPa) irradiated by UV–visible light for 100 min

followed by under dark for 20 min. (D) The change of FT of Ag K-edge EXAFS for fresh Ag–ZrO$_2$: 3.0, 5.0, and 10 wt % of Ag. (E) The correlation between σ value and temperature for bulk sites (circle, ○) and surface sites (vertical motion; square, □) in/on Ag metal generated by the correlated Debye model using a code FEFF8.

Such light-induced change in the FT was quantitatively evaluated by the curve-fit analysis based on plane-wave approximation for amplitude $A_i(k)$, coordination number N_i, interatomic distance R_i, Debye–Waller factor σ_i, backscattering amplitude f_i, and mean free path of photoelectrons λ for shell i using a code XDAP:

$$A_i(k) = \frac{N_i}{kR_i^2}\left|f_i(k)\right|\exp\left[-2\left(\sigma_i^2 k^2 + \frac{R_i}{\lambda}\right)\right], i = Ag \qquad (1).$$

The obtained N value was 9.0 ± 0.7 before light irradiation and did not change significantly during light irradiation (8.3–10.0) and after the light was turned off (10.1±0.7; Figure 1A). Obtained N values of 9–10 correspond to particle size of 2.5–3.7 nm assuming spherical face-centered cubic (fcc) nanoparticle model and the surface dispersion is 0.54–0.36 (mean value 0.45). The σ value was calculated to 0.009 95 nm for Ag metal at 290 K by the correlated Debye model using *ab initio* multiple-scattering calculation code FEFF8 and the Debye temperature for Ag [$\theta_{D(Bulk)}$ 225 K] [3]. The code XDAP provides the experimental difference of σ^2 value from that for Ag metal (model) based on equation 1. Thus-obtained initial σ value 0.010 1 nm for Ag (3.0 wt %)–ZrO$_2$ before light irradiation quickly increased to 0.010 7 nm at 10 min of irradiation and progressively increased to 0.011 7 nm at 90 min of light irradiation (Figure 1B). Then, the value quickly decreased to 0.010 1 nm after the light was turned off at 112 min.

Furthermore, the Ag site temperature was evaluated based on the σ values. The temperature dependence of σ value is supplied using FEFF8 by the correlated Debye model both for bulk and surface Ag sites using bulk and surface Debye temperature (Figure 1E-a and b, respectively). Preferable exposure of thermodynamically stable fcc(1 1 1) face was assumed for latter value [$\theta_{D(Surf, \perp)}$ 155 K]. We also approximated the mean temperature for Ag nanoparticles as the arithmetic mean temperature of that based on $\theta_{D(Surf, \perp)}$ weighted by 1/2·1/3D [D: dispersion of nanoparticles (0.45), for effective vertical degree of freedom at free hemisphere surface] and that based on $\theta_{D(Bulk)}$ weighted by $(1 - D) + 1/2D + 1/2·2/3D$ (bulk site, non-free hemisphere in contact with ZrO$_2$, and two lateral degrees of freedom at free hemisphere surface).

As the result, the initial 286 K before irradiation rose to 325 K at 10 min of irradiation and progressively increased to 392 K until 90 min of light irradiation (Figure 1B). The temperature quickly dropped to 290 K after the light was turned off. Such temperature rise/drop should be due to the heat transformed from LSPR. Quite similarly, the initial temperature increased to 363 K until 90 min of UV–visible light irradiation and quickly dropped to 397 K once the light was off using Ag (5.0 wt %)–ZrO$_2$ sample. The method based on σ value found in this study by EXAFS is very common and directly probe for all nanoparticles to exhibit LSPR, e.g. Au, Ag.

Furthermore, temperature rise/drop was also observed under argon and UV–visible light (367 K at 50 min of light, 302 K at 10 min of light off) [2]. The σ value/temperature negligibly changed up to 329 K when the wavelength of incident light was filtered to be more than 580 nm whereas essentially identical rise/drop to full light (365 K at 90 min, 298 K when light was off) of σ value/temperature was observed when λ was more than 320 nm. The reaction heat did not affect in this study because the reaction to reduce CO$_2$ into CO is endothermic.

In summary, the contribution of mean 2.5–3.7 nm of Ag nanoparticles was investigated using in-situ EXAFS. Temperature rise from 286 K to 392 K under the irradiation of UV–visible light and quick drop to 290 K under dark were directly monitored based on Debye–Waller factor change for Ag–Ag interatomic pair interference. The H$_2$ should be oxidized associated with the reduction of bicarbonate species over ZrO$_2$, but any evidences of available O on Ag were found in this study. Thus, H$_2$ activation is simply over heated Ag surface and the H atoms spill over to bicarbonate species over ZrO$_2$ rather than hot electron injection or plasmonic resonant energy transfer to/with ZrO$_2$.

References
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