Supporting Information

Ag K- and L₃-edge XAFS study on Ag species in Ag/Ga₂O₃ photocatalysts

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Ag K-edge XAFS measurements were carried out at the NW10A station at the Photon Factory in the High Energy Accelerator Research Organization with a Si(311) double-crystal monochromator in the fluorescence mode with a 19 element solid state Ge detector. The intensity of the incident X-ray was measured with a gas-flow type 17-cm ion chamber using a mixture of N₂ and Ar at 50:50. XAFS spectra of Ag foil and Ag₂O powder as reference samples were measured in the transmission mode with gas-flow type 17-cm ion chamber using Ar for the incident X-ray and 31-cm one using Kr for the transmission X-ray.

Figure S1 shows the Ag L₃-edge XANES spectra of 0.1 wt% Ag/Ga₂O₃ (PD) sample, 1.0 wt% Ag/Ga₂O₃ (PD) samples heated in air for 2 h at various temperatures and Ag foil (g). Since both the spectra of 0.1 and 1.0 wt% Ag/Ga₂O₃ (PD) samples were very similar to that of an Ag bulk, the Ag species in these samples were metallic Ag. It was also confirmed that the broad feature shown in the XANES of the 0.1 wt% Ag/Ga₂O₃ (IMP) sample was not due to the low loading amount of Ag.

**Figure S1.** Ag L₃-edge XANES spectra of the 0.1 wt% Ag/Ga₂O₃ (PD) sample (a), the 1.0 wt% Ag/Ga₂O₃ (PD) sample as-prepared (b), the 1.0 wt% Ag/Ga₂O₃ (PD) sample heated in air for 2 h at 473 K (c), 573 K (d), 673 K (e), 773 K (f) and Ag foil (g).

Figure S1 (c-f) shows the Ag L₃-edge XANES spectra of the 1.0 wt% Ag/Ga₂O₃ samples prepared by the PD method, followed by heating in air for 2 h at various temperatures, referred to as Ag/Ga₂O₃ (PD-H). With
increasing the heating temperature, the XANES feature became broad gradually, and at more than 573 K, the spectra were similar to that of the 0.1 wt% Ag/Ga$_2$O$_3$ (IMP) sample. By heating at more than 573 K, Ag particles size decreases and the enhanced interaction with the Ga$_2$O$_3$ surface can be expected. A slight shoulder around 3353 eV suggested that there were oxidized moiety.

Figure S2 shows $k^3$-weighted Ag K-edge EXAFS spectra of the Ag/Ga$_2$O$_3$ and reference samples. Radial structure functions (RSF) were obtained by Fourier transform of the EXAFS in the region of $k = 3.15–11.80$ Å$^{-1}$ as shown in Figure 3 in the main text.

**Figure S2.** $k^3$-weighted Ag K-edge EXAFS spectra of Ag$_2$O (a), the 0.1 wt% Ag/Ga$_2$O$_3$ (IMP) sample (b), the 0.2 wt% Ag/Ga$_2$O$_3$ (IMP) sample (c), the 0.5 wt% Ag/Ga$_2$O$_3$ (IMP) sample (d), the 1.0 wt% Ag/Ga$_2$O$_3$ (IMP) sample (e), the 5.0 wt% Ag/Ga$_2$O$_3$ (IMP) sample (f), the 1.0 wt% Ag/Ga$_2$O$_3$ (PD) sample as-prepared (g), the 1.0 wt% Ag/Ga$_2$O$_3$ (PD-H) sample heated in air for 2 h at 673 K (h) and Ag foil (i).
Curve-fitting was performed to the Fourier-filtered EXAFS including the first and the second coordination shells (R = 1.35–3.35 Å in Figure 3) by using empirical parameters extracted from the XAFS of an Ag₂O (for Ag–O pair) and an Ag foil (for Ag–Ag pair). The results are summarized in Table S1.

| Sample                  | Shell      | CN  | R (Å) | ΔE (eV) | σ(Å) |
|-------------------------|------------|-----|-------|---------|------|
| 0.1 wt% Ag/Ga₂O₃ (IMP)  | Ag–Ag      | 4.3 | 2.89  | −0.5    | 0.064|
| 0.2 wt% Ag/Ga₂O₃ (IMP)  | Ag–Ag      | 6.5 | 2.89  | 1.2     | 0.059|
| 0.5 wt% Ag/Ga₂O₃ (IMP)  | Ag–Ag      | 6.2 | 2.89  | 1.0     | 0.058|
|                         | Ag–Ag      | 4.9 | 3.05  | 6.0     | 0.071|
|                         | Ag–O       | 2.4 | 2.10  | 3.0     | 0.055|
| 1.0 wt% Ag/Ga₂O₃ (IMP)  | Ag–Ag      | 4.6 | 2.89  | 0.0     | 0.055|
|                         | Ag–Ag      | 7.3 | 3.05  | 6.8     | 0.065|
|                         | Ag–O       | 4.0 | 2.11  | 0.5     | 0.055|
| 5.0 wt% Ag/Ga₂O₃ (IMP)  | Ag–Ag      | 10.8| 2.90  | 0.5     | 0.060|
| 1.0 wt% Ag/Ga₂O₃ (PD)   | Ag–Ag      | 11.9| 2.89  | 1.5     | 0.055|
| 1.0 wt% Ag/Ga₂O₃ (PD) heated | Ag–Ag | 7.3 | 2.90 | −0.5 | 0.055|
|                         | Ag–O       | 3.4 | 2.10  | 2.5     | 0.060|
| Ag foil                | Ag–Ag      | 12.0| 2.89  | 0.0     | 0.060|
| Ag₂O                   | Ag–O       | 4.0 | 2.04  | 0.0     | 0.060|

CN: coordination number, R: inter atomic distance, ΔE: edge shift, σ: Debye-Waller factor.

Errors of CN and R are ±14% and ±0.03 Å, respectively.

The average Ag–Ag distance was estimated to be ca. 2.89 Å for the 0.1, 0.2 and 5.0 wt% Ag/Ga₂O₃ (IMP) samples, which was in good agreement with that of the Ag foil. Note that the photocatalytically active Ag clusters formed predominately in the 0.1 wt% Ag/Ga₂O₃ (IMP) sample were metallic. The average coordination number for the Ag–Ag shell (CNₐₐ) for 5.0 wt% Ag/Ga₂O₃ (IMP) was close to that of Ag foil, suggesting the large Ag metal particles, while the CNₐₐ values for the 0.1 and 0.2 wt% Ag/Ga₂O₃ (IMP) samples were 4.3 and 6.5, respectively, which were significantly smaller than that of the Ag foil. The geometrical calculation for the 0.1 wt% Ag/Ga₂O₃ (IMP) sample demonstrated that the Ag species with the CNₐₐ values of 4.3 would be smaller than 1 nm, such as metallic cluster, which was quite consistent with the HAADF-STEM result of this sample. On the other hand, the 0.5 and 1.0 wt% Ag/Ga₂O₃ (IMP) samples had
two types of short (2.89 Å) and long (3.05 Å) Ag–Ag pairs. The latter was longer than that of Ag metal and similar to the Ag–Ag distance (3.03 Å) in AgGaO₂[S1]. The Ag–O pair with 2.10–2.12 Å in length which was longer than those of Ag₂O and AgO and similar to the Ag–O distance (2.10 Å) in AgGaO₂[S1]. These suggest that a part of Ag atoms at the interface between the Ag metal particle and the Ga₂O₃ surface would be in an AgGaO₂-like structure as a result of well interaction with the Ga₂O₃ surface and other part would form Ag metal particles.

In the cases of the 1.0 wt% Ag/Ga₂O₃ (PD) and the 1.0 wt% Ag/Ga₂O₃ (PD-H) samples, the average Ag–Ag distance was estimated to be 2.89 Å for both samples and CNₐg for the former and the latter samples to 11.9 and 7.3, demonstrating that the large Ag metal particles changed to small ones by heating. It is also noteworthy that the Ag–O pair was found only for the 1.0 wt% Ag/Ga₂O₃ (PD-H) sample and the 0.5 and 1.0 wt% Ag/Ga₂O₃ (IMP) samples. Since another Ag–Ag pair of long distance was not recognized for the 1.0 wt% Ag/Ga₂O₃ (PD-H) sample, this Ag–O bond might be formed by the interaction of small Ag metal particles with Ga₂O₃ support.

Reference
[S1] Kandpal H C and Seshadri R 2002 Solid State Sci. 4 1045