

## Supporting Information

### **Photocatalytic reduction of CO<sub>2</sub> with water promoted by Ag clusters in Ag/Ga<sub>2</sub>O<sub>3</sub> photocatalyst**

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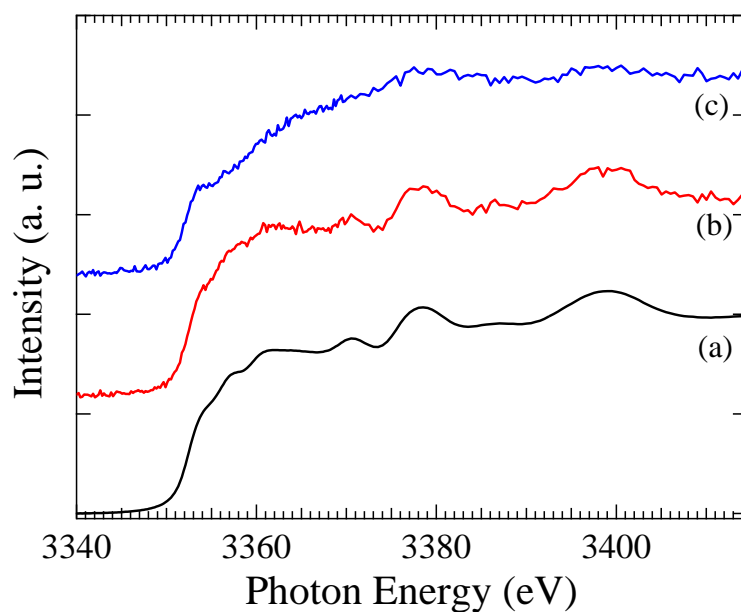


Figure S1. Ag  $L_3$ -edge XANES spectra of an Ag foil (a) and those of 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub>(PD) sample as-prepared (b) and after heating at 673 K for 2 h in air (c).

The 1.0 wt% Ag loaded Ga<sub>2</sub>O<sub>3</sub> (Ag/Ga<sub>2</sub>O<sub>3</sub>(PD)) samples were prepared by photodeposition method. A part of the samples was heated at 673 K for 2 h in air. XANES measurements of the samples were carried out in the same way to Figure 4. As shown in Figure S1, the XANES spectrum of the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub>(PD) sample as-prepared (b) has the feature characteristic of Ag metal (a). On the other hand, XANES spectrum of the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub>(PD) sample heated at 673 K for 2 h in air (c) has the broadening feature similar to that of the 0.1 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> sample discussed in the main text. In our separate TEM measurements, we confirmed that the Ag particle size in the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub>(PD) sample became much smaller as 1-2 nm by the heating and the Ag clusters were highly dispersed on the Ga<sub>2</sub>O<sub>3</sub> surface (Figure S2). Therefore, we concluded that the broadening feature of XANES should originate from the decreased Ag particle size and/or the enhanced interaction between the Ag clusters and the Ga<sub>2</sub>O<sub>3</sub> surface.

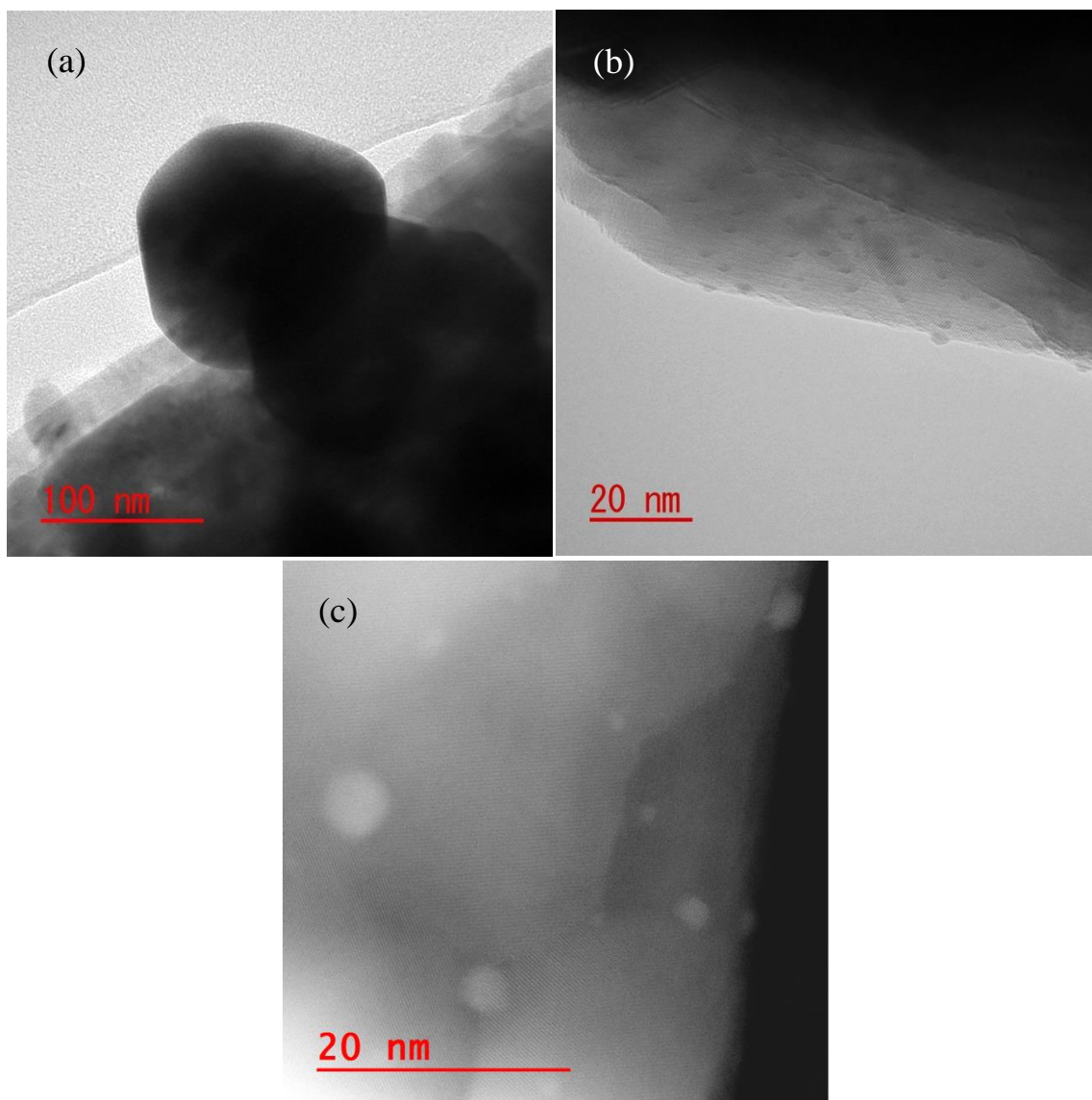


Figure S2. TEM images of the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub>(PD) sample as-prepared (a), heated at 673 K for 2 h in air (b) and HAADF-STEM image of the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub>(PD) sample heated at 673 K for 2 h in air (c).

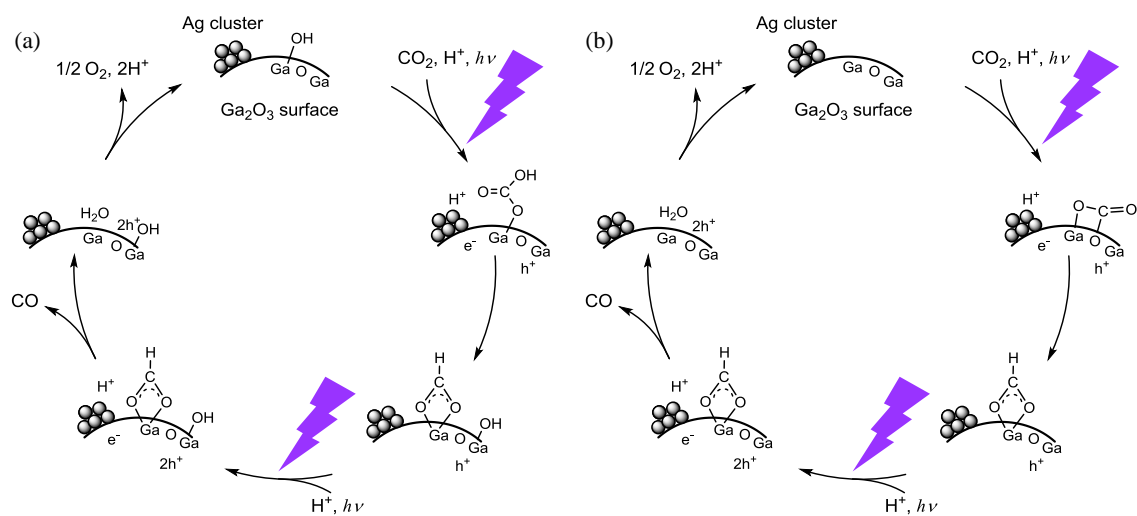


Figure S3. Tentatively proposed reaction schemes for the photocatalytic reduction of CO<sub>2</sub> with water over 0.1 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> sample. These schemes were proposed on the basis of the FT-IR results of this study and our previous study.<sup>1</sup> The reactions start with the adsorption of CO<sub>2</sub> on a surface OH group (a) and on the surface lattice oxygen (b).

## Reference

- 1 M. Yamamoto, T. Yoshida, N. Yamamoto, H. Yoshida and S. Yagi, *J. Surf. Sci. Nanotechnol.*, 2014, **12**, 299.