Effect of Interface Between Ag Nanoparticles and Ga_2O_3 Photocatalysts on Their Photocatalytic CO_2 Photoreduction Activity with Water

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Introduction

Ag nanoparticles (Ag-NPs) deposited on semiconductor photocatalysts are known to enhance CO production in photocatalytic CO_2 reduction with water. This enhancement is partly attributed to charge transfer from the semiconductor to Ag-NPs induced by photoelectron excitation. However, the underlying mechanisms of the charge transfer remain unclear [1]. To experimentally probe the charge transfer, it is essential to monitor changes in the chemical and electronic states of boundaries between Ag-NPs and the semiconductor catalyst under light irradiation. In this study, we have investigated Ag-NPs deposited on gallium oxide (Ag/Ga_2O_3), with using hard X-ray photoelectron spectroscopy (HAXPES) which is suitable to analyze quite localized areas.

Experimental Procedures

Ag nanoparticles (Ag-NPs) were synthesized in NH_3 0.1 mmol/L aqueous solution by a Solution Plasma Process method [2]. The resulting Ag-NPs colloidal solution was added 100 mg of commercial β-Ga_2O_3 powder, dried at 80°C, and subsequently calcined at 450°C for 3 h. The amount of Ag deposited was 0.5 wt% of β-Ga_2O_3. The calcinated sample was irradiated with UV light given by a Xe lamp in pure water and subjected to HAXPES measurements carried out at SPring-8 BL09XU under vacuum using 7940 eV excitation.

Results and Discussion

As shown in Fig. 1, the deposition of Ag-NPs on Ga_2O_3 as a cocatalyst significantly enhanced both the production rate and selectivity of CO in photoreduction of CO_2 with water. Ag/Ga_2O_3 was analyzed by HAXPES to observe XPS spectra of Ag 3p, O 1s, and Ga 4d. Without the UV irradiation, Ag 3p spectra were dominated with the metallic state and Ag-O states, and the calcination increased Ag-O as shown in Fig. 2. After the UV irradiation, the third peak assigned as★ in higher B.E. region became appreciable. New peaks also appeared in the O 1s and Ga 2p core-level spectra. According to previous XAFS studies, the formation of $AgGaO_2$-like structure induced their featured spectra. The third peak that appeared in the HAXPES measurements could be correlated to the formation of interfacial complex oxides [3].

In separately made DOS calculations, such interfacial complex oxide formation could induce hybridized states between Ga 4s-O 1s (conduction band of Ga_2O_3) and Ag 4d, thereby narrowing the Ga_2O_3 band gap. Based on these findings, we have tentatively concluded that the enhanced photocatalytic activity arises from the formation of charge transfer pathways via strong metal–support interaction (SMSI) between Ag-NPs and Ga_2O_3 [4].

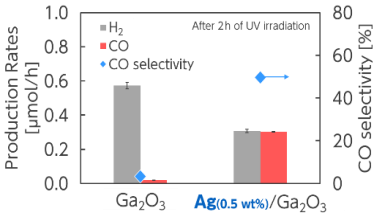

Figure 1 Photocatalytic activity of CO_2 reduction with water for Ga_2O_3 loaded with and without silver nanoparticle loading.

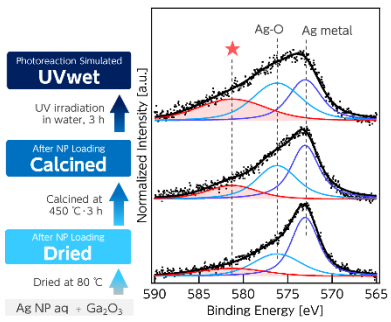

Figure 1 Ag $3p_{3/2}$ spectra of Ag/Ga_2O_3 at each sample condition.

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