BL-9C, BL-12C, AR-NW10A/2021G546

Investigation of stable Ag–Ni–ZrO_2 photocatalyst for sustainable photocatalytic CO_2 reduction into fuels

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1. Introduction

To create a new carbon neutral cycle, Ni–ZrO_2 photocatalyst was investigated to convert CO_2 into methane [1]. The Ni nanoparticles need to be metallic (valence zero) for the best performance, methane formation rate of 0.98 mmol h^{-1} g_{cat}^{-1}. However, a few nanometers Ni particles easily oxidized in air and are difficult to handle in practical applications. In this proposal, secondary metal was deposited to Ni–ZrO_2 and the Ni^0 site was tried to be stable for the sustainable application for CO_2 photocatalytic reduction into fuels.

2. Experimental section

Ni–ZrO_2 photocatalyst was prepared via liquid phase reduction method from $Ni(NO_3)_2$ [1]. Then, Ag was deposited on Ni–ZrO_2 photoelectrochemically. Namely, $Ag(NO_3)$ ethanol solution (50 mmol L^{-1}) was mixed with Ni–ZrO_2 powder and irradiated under UV–visible light for 3–6 h. The suspension was filtered and dried at 373 K. The amount ratio of Ni: Ag used was 1: 10.

3. Results and Discussion

The normalized XANES spectra for Ag–Ni–ZrO_2 photocatalysts that were irradiated under UV–visible light for 3 h and 6 h were compared to those of Ni metal and NiO standard samples (Figure 1). Apparently, Ni sites were oxidized to NiO during drying of Ni^0–ZrO_2 sample obtained via liquid phase reduction. Because the Ni^{II} sites were not reduced under the irradiation of UV–visible light immersed in Ag^+ ethanol solution, we reduced Ag–Ni–ZrO_2 photocatalysts under H_2 at 723 K (Figure 1).

Alternatively, we performed photoelectrochemical deposition of Ag^+ on Ni–ZrO_2 without contact to air during the later stage than liquid phase reduction. In such preparation, Ni sites remained metallic Ni^0 (data not shown).

In this report, the Debye–Waller factor changes for Ag–Ni–ZrO_2 photocatalysts reduced under H_2 at 723 K were monitored by Ni K-edge EXAFS under the irradiation of UV–visible light at beamline (Figure 2). Clearly, Ni sites were quickly warmed by light energy and reached thermal equilibrium while the temperature very quickly dropped to room temperature when the UV–visible light was turned off (Figure 2).

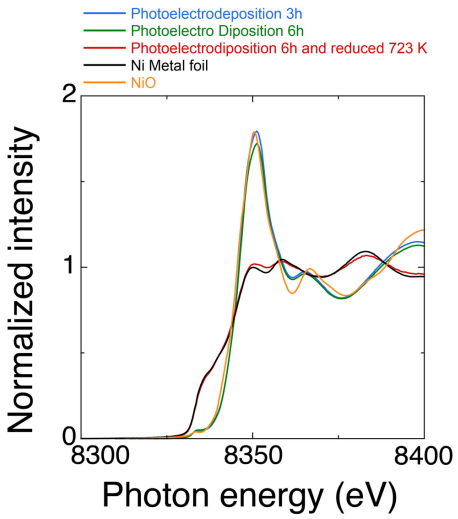

Figure 1. Normalized Ni K-edge XANES spectra for Ag–Ni–ZrO_2 photocatalysts that were irradiated under UV–visible light for 3 h and 6 h and the one irradiated under UV–visible light for 6 h was further reduced under H_2 at 723 K in comparison to standard spectra for Ni metal and NiO.

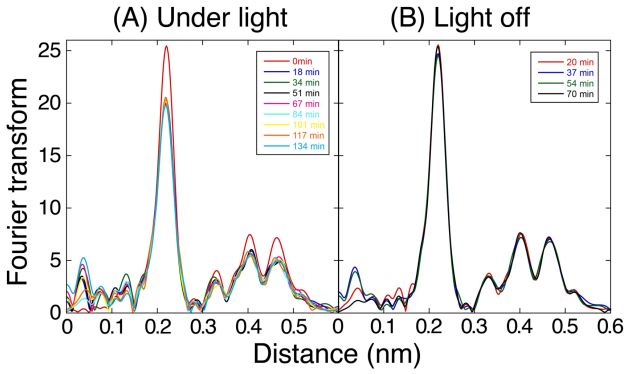

Figure 2. Time course of Co K-edge EXAFS Fourier transform for Ag–Ni–ZrO_2 photocatalysts that were irradiated under UV–visible light for 6 h and then reduced under H_2 at 723 K (A) under UV–visible light irradiation at beamline and (B) UV–visible light off.

Reference

[1] Zhang, H.; Itoi, T.; Konishi, T.; Izumi, Y. Efficient and Selective Interplay Revealed: CO_2 Reduction to CO over ZrO_2 by Light with Further Reduction to Methane over Ni^0

by Heat Converted from Light. *Angew. Chem. Int. Ed.* **2021**, *60*, 9045–9054.

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