

Characterization of Plasmonic Nanoparticles and Dyes Assembled with Layered Double Hydroxides to Promote the Photoreduction of Carbon Dioxide into Fuels

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1 Introduction

The photoreduction of CO₂ to fuels using natural light can contribute simultaneously to reduction of the major greenhouse gas and the development of sustainable energy [1]. Efficient photoreduction of CO₂ into methanol (or CO) was reported using layered double oxides (LDHs) [2–4]. Furthermore, the combination of WO₃ and LDH photocatalysts as a photoanode to oxidize water and a photocathode to reduce CO₂, respectively, was demonstrated [5].

The wide band gap of LDHs is advantageous to reduce high-potential compound, e.g. CO₂. Conversely, wide band gap is also drawback because UV light is required to excite LDHs. In this study, plasmonic nanoparticles of Au and Ag and Cu phthalocyanine were assembled with LDHs to enable CO₂ photoreduction utilizing visible light.

2 Experimental Section

Ag/ZnGa LDH was prepared by ion exchange at 373 K for 15–180 min [6]. The samples were denoted as Ag/ZnGa LDH-15 or Ag/ZnGa LDH-180. Au/ZnGa LDH was prepared by ion exchange and liquid phase reduction using NaBH₄ [6].

CuPcTs/ZnGa LDH was prepared by ion exchange of sodium salt of Cu phthalocyanine tetrasulfonate hydrate (Na⁺₄CuPcTs⁴⁻) with ZnGa LDH [7]. Ag K, Au L₃, and Cu K-edge XAFS spectra were measured in transmission mode at 290 K.

3 Results and Discussion

Ag K-edge XANES spectra for Ag/ZnGa LDH-15 and Ag/ZnGa LDH-180 were depicted in Figure 1A-b and d, respectively. The XANES patterns for these samples were quite similar to that for Ag metal (a) rather than Ag₂O (e). Thus, Ag⁰ nanoparticles were combined with LDH. The metallic Ag⁰ state of Ag/ZnGa LDH-15 negligibly changed after the photocatalytic test in CO₂ and H₂ (Figure 1A-c) in comparison to spectrum b for the as-synthesized sample. Similarly, metallic Au⁰ state of fresh Au/ZnGa LDH unchanged after the photocatalytic test in CO₂ and H₂ (Figure 1B-b, c).

The *k*³-weighted EXAFS function was depicted in Figure 2a for Ag/ZnGa LDH-15 (row 1) and Ag/ZnGa LDH-180 (row 2). The peaks at 0.27 nm (phase shift uncorrected) in the associated Fourier transform (b) were nicely curve-fit by the parameters of Ag–Ag interatomic pair (Figure 2c, d). The *N* value for Ag/ZnGa LDH-15 was 7.6 (particle size ~1.6 nm), significantly smaller than *N* of 10.1 (particle size ~3.7 nm) for Ag/ZnGa LDH-180,

demonstrating the gradual growth of Ag nanoparticles during the synthesis at 373 K.

The *N*(Au–Au) value of 8.3 (particle size ~1.9 nm) for fresh Au/ZnGa LDH (Figure 2, row 3) was consistent with mean particle size of 3.2 nm obtained based on the high-resolution transmission electron microscopy.

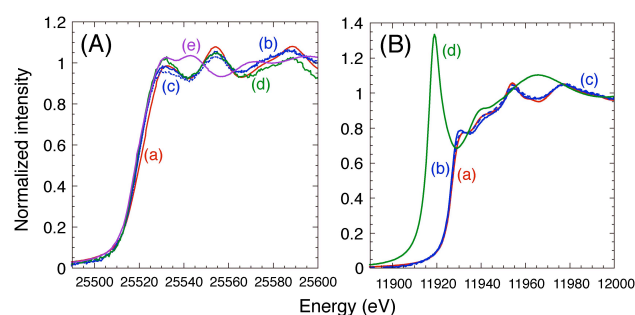


Figure 1. (A) Normalized Ag K-edge XANES spectra for Ag metal (a), Ag/ZnGa LDH-15 (b), sample b after photocatalytic test in CO₂ and H₂ for 5 h (c; dotted line), Ag/ZnGa LDH-180 (d), and Ag₂O (e). (B) Normalized Au L₃-edge XANES spectra for Au metal (a), Au/ZnGa LDH (b), sample b after photocatalytic test in CO₂ and H₂ for 5 h (c; dotted line), and Au₂O₃ (d).

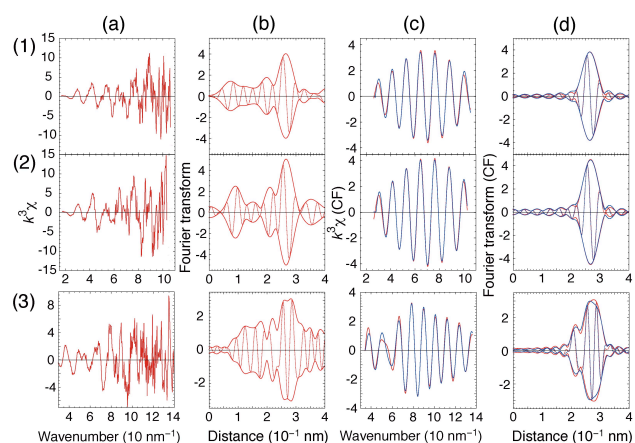


Figure 2. Ag K-edge EXAFS for Ag/ZnGa LDH-15 (1) and Ag/ZnGa LDH-180 (2) and Au L₃-edge EXAFS for Au/ZnGa LDH (3). *k*³-weighted EXAFS oscillation (a), its associated Fourier transform (b), and best-fit results in *k*-space (c) and *R*-space (d).

The XANES spectra for Na⁺₄CuPcTs⁴⁻ and CuPcTs/ZnGa LDH are shown in Figure 3. The spectrum pattern changed negligibly by the dispersion of CuPcTs⁴⁻

over the ZnGa LDH surface as compared with $\text{Na}_4\text{CuPcTs}^{4-}$ crystallines, suggesting that the framework structure of CuPcTs^{4-} was retained upon the dispersion over the LDH surface. In contrast, a sharp shoulder peak at 8988 eV became relatively weaker upon the dispersion over the LDH surface, suggesting the perturbation of LUMO of CuPcTs by the interaction with the LDH.

The EXAFS χ oscillation changed negligibly when $\text{Na}_4\text{CuPcTs}^{4-}$ was dispersed over the LDH surface (Figure 4A). This fact supported the retention of the CuPcTs^{4-} framework over the LDH surface suggested by XANES. The curve-fit results for the Cu–N interatomic pair provided a distance of 0.198 nm (fit error ± 0.011 nm) with a N value of 3.3 (fit error ± 1.3) (Figure 4D, E).

The correlation between characterization by XAFS and the photocatalytic performance of Ag/ZnGa LDH, Au/ZnGa LDH, and $\text{CuPcTs}/\text{ZnGa}$ LDH was discussed elsewhere [6, 7].

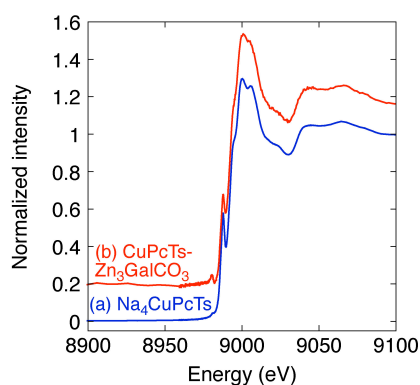


Figure 3. Normalized Cu K-edge XANES spectra for $\text{Na}_4\text{CuPcTs}^{4-}$ (a) and $\text{CuPcTs}/\text{ZnGa}$ LDH (b).

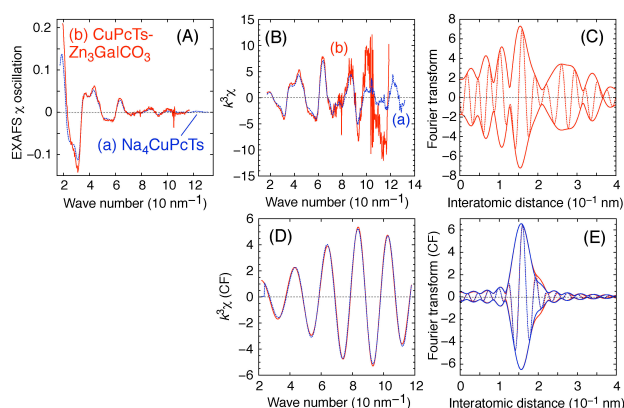


Figure 4. (A) Cu K-edge EXAFS χ oscillation and (B) k^3 -weighted EXAFS χ oscillation for $\text{Na}_4\text{CuPcTs}^{4-}$ (a) and $\text{CuPcTs}/\text{ZnGa}$ LDH (b), (C) its associated Fourier transform, and (D, E) best-fit results in k -space (D) and R -space (E) for $\text{CuPcTs}/\text{ZnGa}$ LDH. Solid line: magnitude and dotted line: imaginary part (C, E). Red (thick) line: experimental and blue (thin) line: fit (D, E).

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