

A copper and chromium based nanoparticulate oxide as a noble-metal-free cocatalyst for photocatalytic water splitting

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Electronic Supplementary Information (ESI)

Experimental section

Materials and reagents

A GaN:ZnO solid solution was prepared according to the method presented in previous papers.^{S1} The production of GaN:ZnO (ZnO/GaN \approx 0.13) was confirmed by powder X-ray diffraction (XRD) and energy-dispersive X-ray (EDX) analysis. The band gap energy was estimated to be ca. 2.7 eV, based on the onset wavelength of the diffuse reflectance spectrum. The specific surface area was measured by nitrogen adsorption at 77 K to be ca. 7–8 m²·g⁻¹.

Cu(NO₃)₂·3H₂O (Wako Pure Chemicals, 99.9%) and Cr(NO₃)₃·9H₂O (Wako Pure Chemicals, 99.9%) were used as precursors for loading the dual-component Cu–Cr cocatalyst. For the measurement of XAFS and XPS spectra, Cu₂O (Wako Pure Chemicals, 99.5%), CuO (Wako Pure Chemicals, 99.9%), Cr₂O₃ (Kanto Chemicals, 98.5%), and CrO₃ (Kanto Chemicals, 98.0%) were used as references.

A mixed oxide of CuCr₂O₄ was prepared as a reference by the polymerized complex method with some modifications.^{S2} First, 1.37 g of Cu(NO₃)₂·3H₂O and 4.54 g of Cr(NO₃)₃·9H₂O were dissolved in 100 mL of methanol (Kanto Chemical, 99.8%). After complete dissolution of the nitrates, 9.49 mL of ethylene glycol (EG) (Kanto Chemicals, 99.5%) and 10.9 g of anhydrous citric acid (CA) (Wako Pure Chemicals, 98.0%) were added to the solution. The solution was then heated overnight at ca. 400 K to promote esterification between EG and CA, yielding a glassy resin. The resin was calcined at ca. 623 K in a mantle heater to complete decomposition. Finally, the resulting black powder was calcined on an Al₂O₃ plate at 1273 K for 2 h in air. The as-synthesized powder was confirmed by XRD to be CuCr₂O₄.

Modification of GaN:ZnO with Cu–Cr cocatalysts

Cu–Cr cocatalysts were loaded onto the as-prepared GaN:ZnO catalyst by impregnation. Briefly, 0.3–0.4 g of GaN:ZnO powder and 3–4 mL of distilled water containing an appropriate amount of Cu(NO₃)₂·3H₂O and Cr(NO₃)₃·9H₂O were placed into an evaporating dish over a water bath. The suspension was stirred using a glass rod to complete evaporation. The resulting powder was collected and heated in air at 473–673 K for 1 h. In this paper, the amount of loaded metals is represented as the metallic content of the cocatalyst.

Photocatalytic reactions

Reactions were carried out in a Pyrex inner-irradiation-type reaction vessel connected to a glass closed gas circulation and evacuation system at room temperature. The reactions were performed in distilled water containing 0.3 g of the cocatalyst-loaded sample. The reactant solution was first evacuated several times to ensure complete air removal, and then irradiated under a 450 W high-pressure Hg lamp via a Pyrex tube as a light filter ($\lambda > 300$ nm). For visible-light experiments, the Pyrex tube was filled with aqueous 2 M NaNO₂ solution to block ultraviolet light ($\lambda > 400$ nm).^{S1} The evolved gases were analyzed by gas chromatography.

Characterization of catalysts

Transmission electron microscopy was conducted using a FEI Tecnai G2 F20 microscope (operating at 200 kV) with a molybdenum mesh sample holder. XAFS measurements were carried out in the BL-9C beamline of the Photon Factory (High Energy Accelerator Research Organization, Tsukuba, Japan) using a ring energy of 2.5 GeV and stored current of ca. 450 mA (Proposal No. 2008G150) for the measurement of Cu–K and Cr–K edge spectra. The X-ray absorption spectra were measured in transmission or fluorescence mode at room temperature with an Si(111) two-crystal monochromator. Data reduction was performed using the REX2000 program (Rigaku Corporation). The Fourier transforms of k^3 -weighted EXAFS spectra were typically in the 3.0–12.0 Å region. The photon energies in the X-ray absorption near-edge structure (XANES) spectra were corrected in reference to copper foil (8980.3 eV) for each sample.

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Electrochemical measurements

Porous GaN:ZnO electrodes were prepared by pasting a viscous slurry onto conducting glass according to a method similar to one we have described previously.^{S3} A mixture of 100 mg of modified GaN:ZnO catalyst (or GaN:ZnO alone without a cocatalyst) powder, 10 μL of acetylacetone (Kanto Chemicals), 10 μL of TritonX (Aldrich, USA), 10 μL of poly(ethylene glycol) 300 (Kanto Chemicals) and 400 μL of distilled water was ground in an agate mortar to prepare a viscous slurry. The slurry was then pasted onto fluorine-doped tin-oxide (FTO) glass slides ($12 \Omega \cdot \text{sq}^{-1}$, transparency 80%, thickness 1 mm; Asahi Glass, Japan) to prepare a $1 \times 4 \text{ cm}^2$ electrode, and the sample was calcined in air at 623 K for 1 h. The as-prepared electrodes were rinsed with pure water to remove residual species (e.g., Cr^{6+}) prior to photoelectrochemical measurements.

Measurements were performed using a conventional Pyrex electrochemical cell with a platinum wire counter electrode and an Ag/AgCl reference electrode under potentiostat control (HSV-100, Hokuto Denko, Japan). Current–voltage curves were measured in an aqueous sodium sulfate solution (Na_2SO_4 , 0.1 M, 100 mL) as a supporting electrolyte. The electrolyte solution was purged with argon prior to the measurements, and was maintained at room temperature by a flow of cooling water during the measurements.

References

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- S2. M. Kakihana and M. Yoshimura, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 1427.
- S3. H. Hashiguchi, K. Maeda, R. Abe, A. Ishikawa, J. Kubota and K. Domen, *Bull. Chem. Soc. Jpn.*, 2009, **82**, 401.

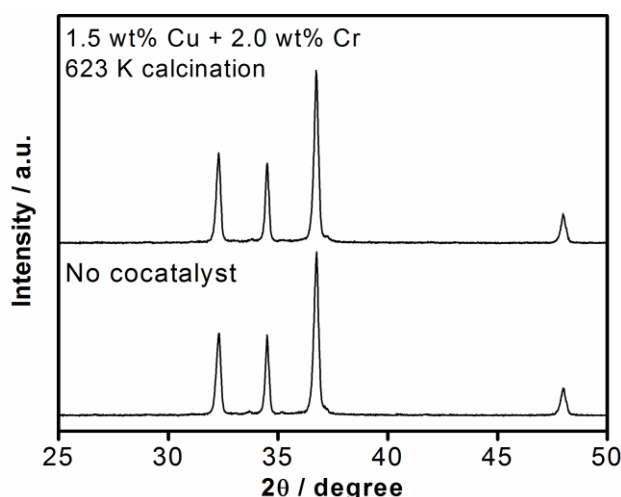


Figure S1. XRD patterns of GaN:ZnO with and without loading 1.5 wt% Cu and 2.0 wt% Cr, followed by calcination at 623 K.

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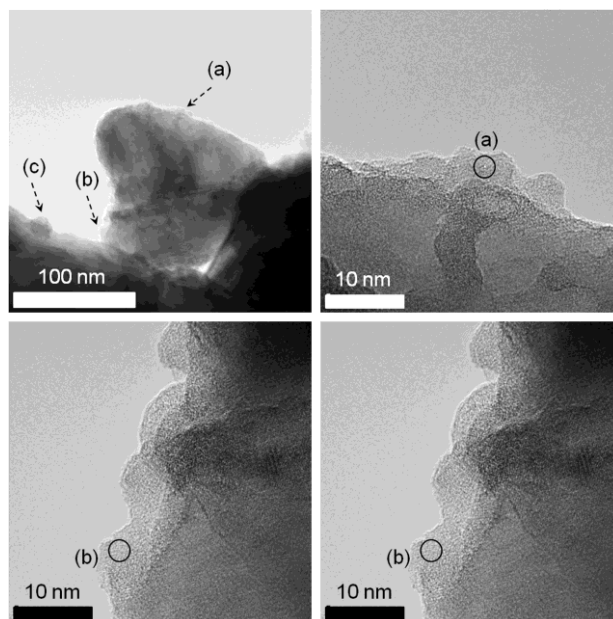


Figure S2. HR-TEM images of GaN:ZnO loaded with 1.5 wt% Cu and 2.0 wt% Cr, followed by calcination at 623 K, and reaction for 5 h under visible light ($\lambda > 400$ nm). Spots of (a) in the panel (A) and (e) in the panel (B) were examined as references, and almost no signals from Cu or Cr could be detected.

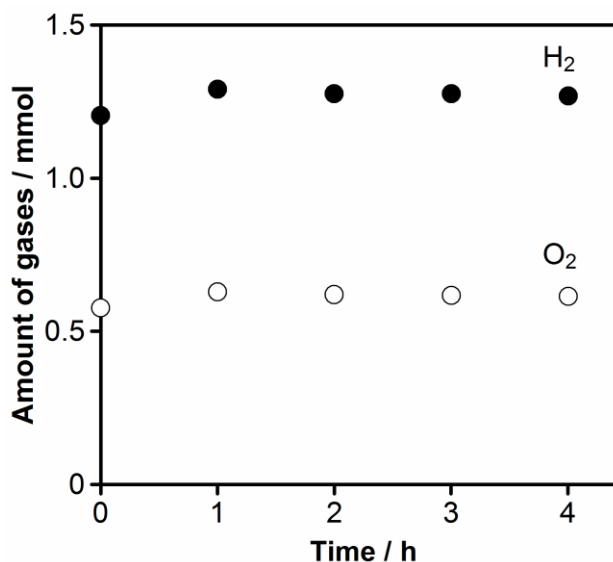


Figure S3. Water formation from H₂ and O₂ in the dark on CuCrO_x/GaN:ZnO. The experiments were carried out in an aqueous suspension of the catalyst using an inner-irradiation-type reaction vessel, connected to a closed-gas circulation system containing a stoichiometric mixture of H₂ and O₂ gases. Reaction conditions: catalyst, 0.3 g; distilled water, 400 mL.

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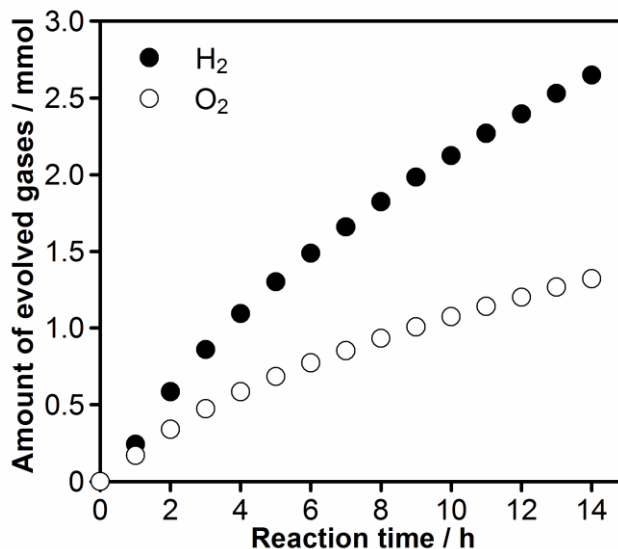


Figure S4. H₂ and O₂ evolution from aqueous K₂CrO₄ solution on CuO/GaN:ZnO under ultraviolet and visible irradiation ($\lambda > 300$ nm). Reaction conditions: catalyst, 0.45 g; aqueous K₂CrO₄ solution (containing 5.0 wt% Cr vs. CuO/GaN:ZnO), 420 mL; light source, high-pressure mercury lamp (450 W); reaction vessel, Pyrex inner-irradiation-type; irradiation wavelength, $\lambda > 300$ nm.

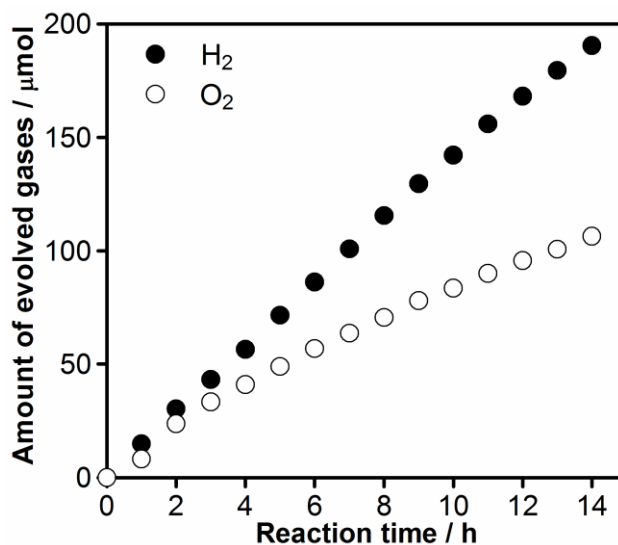


Figure S5. Time course of overall water splitting under visible light over Cr₂O₃-photodeposited CuO/GaN:ZnO. Reaction conditions: catalyst, 0.30 g; distilled water, 400 mL; light source, high-pressure mercury lamp (450 W); reaction vessel, Pyrex inner-irradiation-type with an NaNO₂ solution (2 M) filter; irradiation wavelength, $\lambda > 400$ nm.