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Direct Deposition of Nanoparticulate Rhodium–Chromium Mixed-Oxide on Semiconductor Powder by Band-Gap Irradiation

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Experimental Procedures

Preparation of Semiconductor Powders

$(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ and $(Zn_{1+x}Ge)(N_2O_x)$ were prepared according to the same manner as reported previously (see refs 23b,c and 24). $SrTiO_3$ was prepared by heating a stoichiometric mixture of $SrCO_3$ (Kanto Chemicals, 99.9%) and TiO_2 (Kanto Chemicals, 98.5%, anatase form) powders at 1273 K for 10 h in air. $Ca_2Nb_2O_7$ was prepared by the polymerized complex method reported by Kakihana et al. (M. Kakihana, M. Milanova, M. Arima, T. Okubo, M. Yashima and M. Yoshimura, *J. Am. Ceram. Soc.,* 1996, **79**, 1673.), as follows. To $NbCl_5$ (High Purity Chemicals, 99.9%) dissolved in methanol was added a stoichiometric amount of $CaCO_3$ (Kanto Chemicals, 99.5%). After complete dissolution, ethylene glycol (EG) (Kanto Chemicals, 99.5%) and anhydrous citric acid (CA) (Wako Pure Chemicals, 98.0%) were added, and the solution 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 to afford a black powder, which was further calcined on an Al_2O_3 plate at 923 K for 2 h in air to remove carbon content, and then finally calcined at 1073 K for 2 h in air. β-Ga_2O_3 (High Purity Chemical, 99.9%) was used without further purification. The crystal structure of the semiconductors was confirmed by X-ray diffraction measurements.

Photocatalytic Overall Water Splitting Reactions

Reactions were carried out in an inner irradiation-type reaction vessel connected to a glass closed gas circulation and evacuation system. The reaction was performed in distilled water (360–400 mL) containing 0.15–0.3 g of the catalyst powder. 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 quartz ($\lambda > 200$ nm) or Pyrex ($\lambda > 300$ nm) tube as a light filter. For visible-light experiments, the Pyrex tube was filled with aqueous 2 M $NaNO_2$ solution to block ultraviolet light ($\lambda > 400$ nm). It was confirmed prior to irradiation that no reaction took place in the dark. The evolved gases were analyzed by gas chromatography.

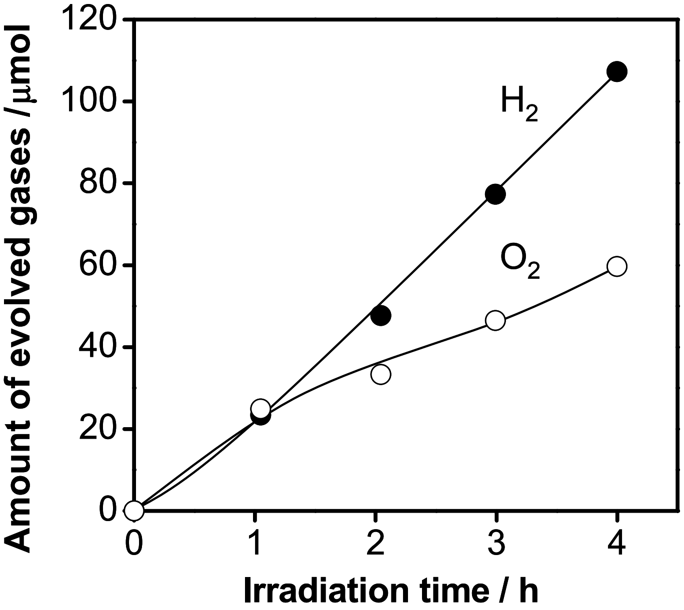

Figure S1. A typical time course of H_2 and O_2 evolution using $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ ($x = 0.12$) from aqueous solution containing $(NH_4)RhCl_6$ and K_2CrO_4 (1 wt % Rh and 1.5 wt % Cr) under visible light irradiation ($\lambda > 400$ nm).

Table S1. Results of TEM-EDS analyses for $Rh_{2-y}Cr_yO_3/(Ga_{1-x}Zn_x)(N_{1-x}O_x)$

Number of samples	Elements / mol.%	
	Rh	Cr
1	53.4	46.6
2	43.4	56.6
3	24.4	75.6
4	40.2	59.8
5	37.4	62.6
6	53.9	46.1
7	55.5	44.5
8	66.0	34.0
9	47.8	52.2
10	47.4	52.6

Preparation conditions: 1 wt% Rh and 1.5 wt% Cr; wavelength of incident light, $\lambda > 400$ nm.