Electronic Supplementary Information

Experimental

$(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ photocatalyst modified with $Rh_{2-y}Cr_yO_3$ cocatalyst was prepared as described in our previous report.[1] Briefly, a mixture of Ga_2O_3 (0.73 g) and ZnO (1.27 g) powders was heated at 1123 K for 8 h and cooled to room temperature under an NH_3 flow (250 mL·min^{-1}). The obtained sample was heated under a N_2O flow (150 mL·min^{-1}) at 773 K for 1 h. The production of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ with wurtzite-type structure at $x \approx 0.18$ was confirmed by powder X-ray diffraction and energy-dispersive X-ray analysis. The bandgap energy of the prepared $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ was estimated, from the onset of the diffuse reflectance spectrum, to be 2.62 eV. The BET specific surface area of the sample was 9.6 m^2g^{-1}. $Rh_{2-y}Cr_yO_3$ was loaded into the prepared $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ photocatalyst as a H_2 evolution cocatalyst by an impregnation method. Photocatalyst powder (0.3 g) and distilled water (3 mL) containing $Na_3RhCl_6·12H_2O$ (Rh 3.0 wt%) and $Cr(NO_3)_3·9H_2O$ (Cr 2.0 wt%) were placed in an evaporating dish on a water bath. The suspension was stirred with a glass rod until it was dry. The resulting powder was heated at 623 K for 1 h in air.

The $Zn:Ga_2O_3$ photocatalyst modified with the $Rh_{2-y}Cr_yO_3$ cocatalyst was prepared according to the literature.[2] A gallium hydroxide precursor was prepared by hydrolysis of $Ga(NO_3)_3$ with aqueous NH_3 at pH 9 followed by calcination at 1273 K for 6 h. The obtained β-Ga_2O_3 was doped with Zn (3 mol%) by an impregnation method using $Zn(NO_3)_2$, and then calcined at 1123 K for 6 h. Finally, $Rh_{2-y}Cr_yO_3$ was loaded into the prepared $Zn:Ga_2O_3$ photocatalyst by an impregnation method (Rh 0.5 wt%, Cr 0.75 wt%).

For the synthesis of $Mg:BaTaO_2N$, $Mg(NO_3)_2·6H_2O$, $BaCO_3$ and Ta_2O_5 were mixed in the ratio of Ba : Ta : Mg = 1 : 0.925 : 0.075 and heated in air at 923 K for 10 min. The obtained

precursor was nitrided under 200 mL min^{-1} of NH_3 flow at 1173 K for 20 h in total with intermittent grinding.

The squeegee method, often used to fix photocatalyst powder onto a conductive substrate for preparing photoelectrodes, was applied to the fabrication of the photocatalyst panels of $Rh_{2-y}Cr_yO_3/(Ga_{1-x}Zn_x)(N_{1-x}O_x)$. A slurry was prepared by mixing 20 mg of photocatalyst with 20 μL of acetylacetone, 20 μL of a surfactant (Triton-X), and 200 μL of distilled water. This slurry was spread onto a glass plate with a glass rod and heated in air at 673 K for 1 h to remove the surfactant. Note that the amount of the photocatalyst was not exactly controlled with this method because a certain amount of slurry remained on the glass rod.

The drop-casting method was also employed for fabricating photocatalyst panels. In this case, the photocatalyst powder (20 mg) was suspended in 200 μL of distilled water with and without 20 mg of nanometer-sized and micrometer-sized silica. After ultrasonication, 20 μL of the suspension was drop-cast on a glass plate, and the droplet was then spread uniformly and dried on a hot plate at 323 K. This process was repeated 10 times.

Photocatalytic water splitting reactions were carried out using a top-irradiation Pyrex glass vessel. A photocatalyst panel containing 20 mg of the photocatalyst was immersed to the bottom of the reactor containing 100 mL of pure H_2O, 10 vol% MeOH, or 0.01 $AgNO_3$ aqueous solution for overall water splitting, hydrogen evolution, or oxygen evolution reactions, respectively. The reaction solution was evacuated to remove air to a sufficient extent. The photocatalyst panel was then illuminated with a 300 W Xe lamp ($\lambda > 300$ nm). For comparison, photocatalyst (20 mg) suspended in distilled water or precipitated at the bottom of the reactor containing distilled water was also illuminated. The evolved gases were analyzed by gas chromatography (Shimadzu, GC-8A with TCD detector and MS-5A column, argon carrier gas).

References

1. K. Maeda, K. Teramura, K. Domen., *J. Catal.*, 2008, **254**, 198.

2. Y. Sakata, Y. Matsuda, T. Nakagawa, R. Yasunaga, H. Imamura, K. Teramura, *ChemSusChem*, 2011, **4**, 181.

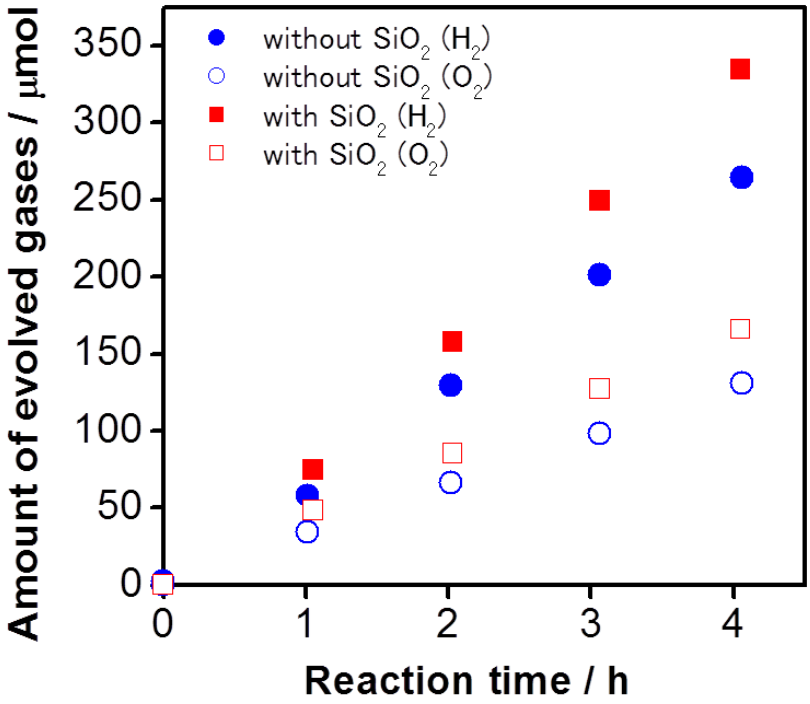

Figure S1. Time course of photocatalytic water splitting using $Rh_{2-y}Cr_yO_3/Zn:Ga_2O_3$ photocatalyst panels with and without nanometer-size SiO_2 for H_2 and O_2 evolution. Reaction conditions: photocatalyst powder, $Rh_{2-y}Cr_yO_3/Zn:Ga_2O_3$ 20 mg; SiO_2, 20 mg; solution, H_2O 100 mL; light source, 300 W Xe lamp (λ > 200 nm); reaction vessel, top-irradiation vessel with a quartz window.

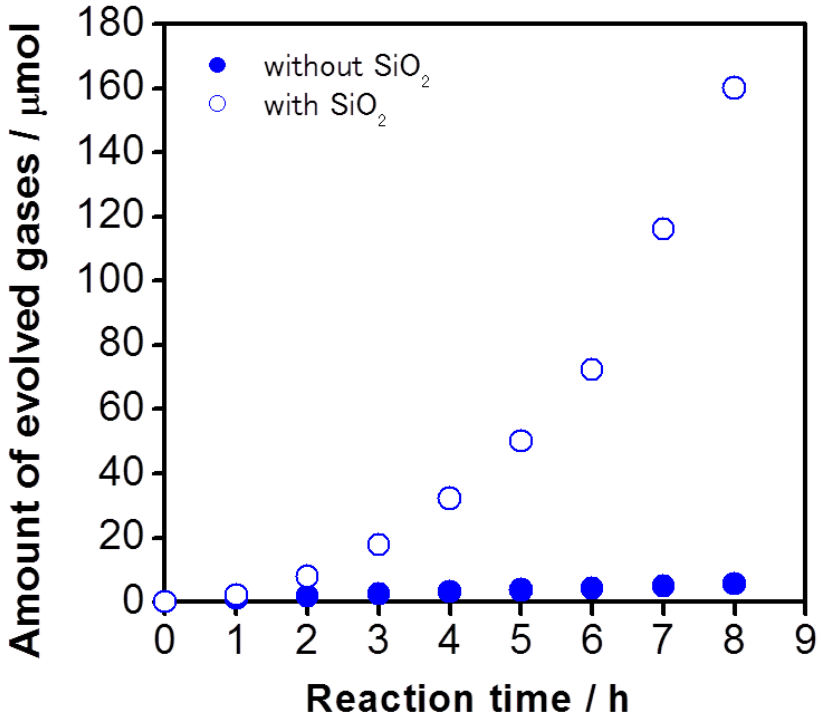

Figure S2. Time course of H_2 evolution using the Mg:$BaTaO_2N$ photocatalyst panel with and without nanometer-size SiO_2. Reaction conditions: photocatalyst powder, Mg:$BaTaO_2N$ 20 mg; SiO_2, 20 mg or none; solution, 10 vol% MeOH aqua solution 100 mL; light source, 300 W Xe lamp ($\lambda > 300$ nm); reaction vessel, Pyrex top-irradiation vessel.

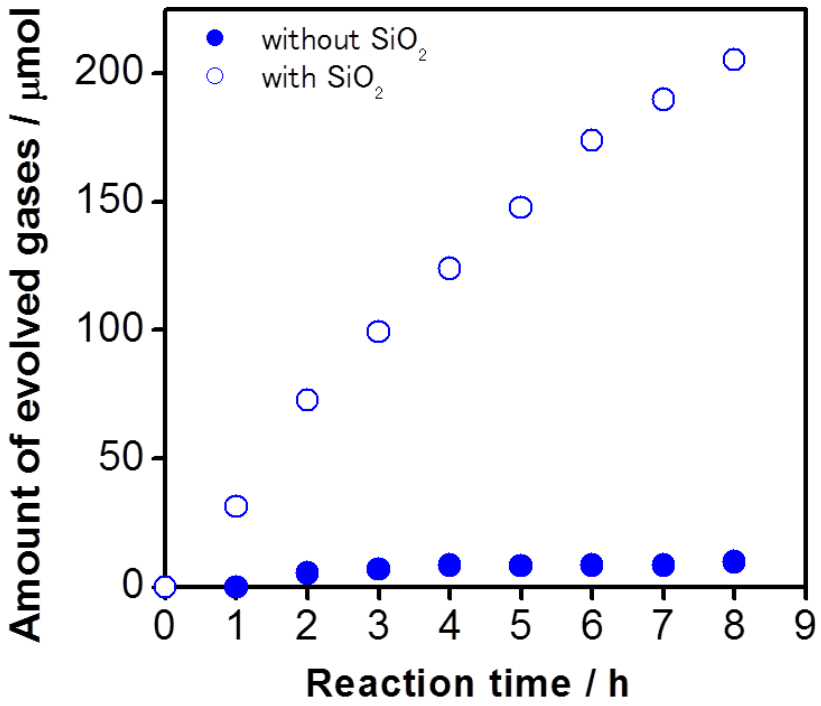

Figure S3. Time course of O_2 evolution using Mg:$BaTaO_2N$ photocatalyst panels with and without nanometer-size SiO_2. Reaction conditions: photocatalyst powder, Mg:$BaTaO_2N$ 20 mg; SiO_2, 20 mg or none; solution, 0.01M $AgNO_3$ aqua solution 100 mL; light source, 300 W Xe lamp ($\lambda > 300$ nm); reaction vessel, Pyrex top-irradiation vessel.

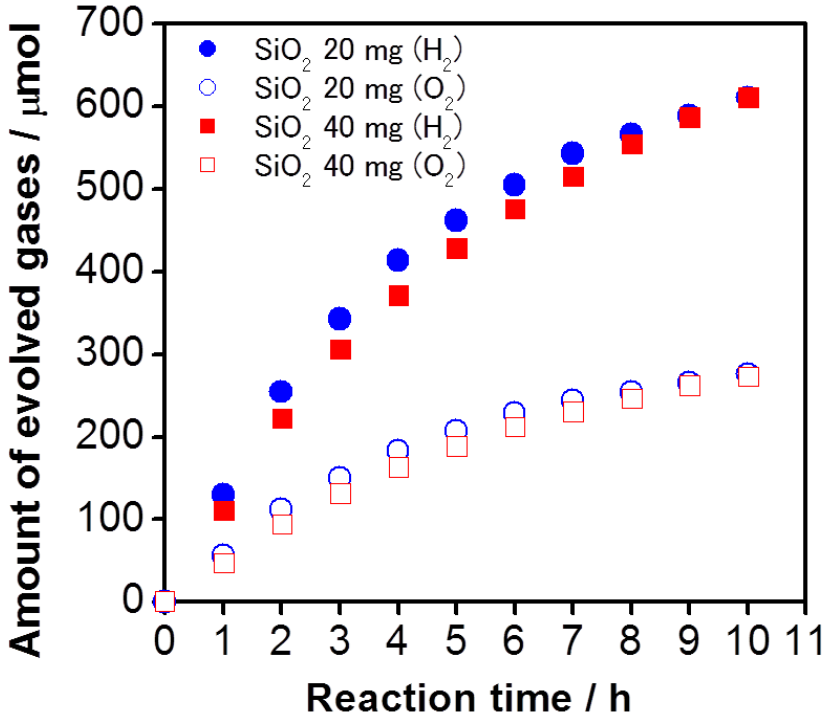

Figure S4. Time course of photocatalytic water splitting using $Rh_{2-y}Cr_yO_3/(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ photocatalyst panels with different amounts of nanometer-size SiO_2. Reaction conditions: photocatalyst powder, $Rh_{2-y}Cr_yO_3/(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ 20 mg; SiO_2, 20 or 40 mg; solution, H_2O 100 mL; light source, 300 W Xe lamp ($\lambda > 300$ nm); reaction vessel, Pyrex top-irradiation vessel.

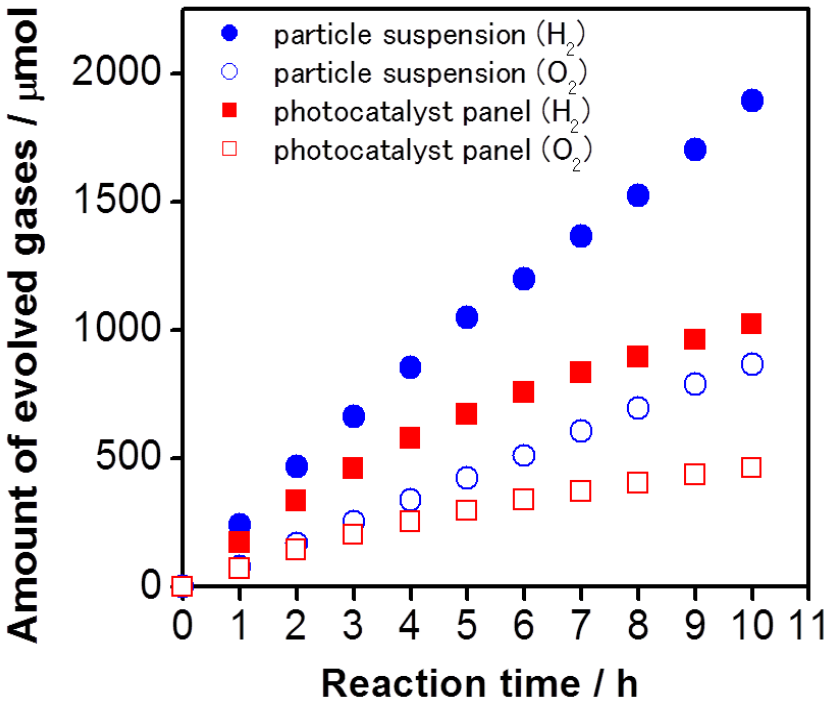

Figure S5. Time course of photocatalytic water splitting using the photocatalyst panel and powder suspension in pH 4.5. Reaction conditions: photocatalyst powder, $Rh_{2-y}Cr_yO_3/(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ 20 mg, micrometer-size SiO_2, 20 mg; solution, H_2SO_4 aqua solution (pH 4.5) 100 mL; light source, 300 W Xe lamp ($\lambda > 300$ nm); reaction vessel, Pyrex top-irradiation vessel.