Electronic Supplementary Information

Experimental

\((\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)\) photocatalyst modified with \(\text{Rh}_{2-y}\text{Cr}_y\text{O}_3\) cocatalyst was prepared as described in our previous report.\(^1\) Briefly, a mixture of \(\text{Ga}_2\text{O}_3\) (0.73 g) and \(\text{ZnO}\) (1.27 g) powders was heated at 1123 K for 8 h and cooled to room temperature under an \(\text{NH}_3\) flow (250 mL·min\(^{-1}\)). The obtained sample was heated under a \(\text{N}_2\text{O}\) flow (150 mL·min\(^{-1}\)) at 773 K for 1 h. The production of \((\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)\) 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 \((\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)\) 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\(^2\) g\(^{-1}\). \(\text{Rh}_{2-y}\text{Cr}_y\text{O}_3\) was loaded into the prepared \((\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)\) photocatalyst as a \(\text{H}_2\) evolution cocatalyst by an impregnation method. Photocatalyst powder (0.3 g) and distilled water (3 mL) containing \(\text{Na}_3\text{RhCl}_6\cdot12\text{H}_2\text{O}\) (Rh 3.0 wt%) and \(\text{Cr(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}\) (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 \(\text{Zn:Ga}_2\text{O}_3\) photocatalyst modified with the \(\text{Rh}_{2-y}\text{Cr}_y\text{O}_3\) cocatalyst was prepared according to the literature.\(^2\) A gallium hydroxide precursor was prepared by hydrolysis of \(\text{Ga(NO}_3\text{)}_3\) with aqueous \(\text{NH}_3\) at pH 9 followed by calcination at 1273 K for 6 h. The obtained \(\beta\)-\(\text{Ga}_2\text{O}_3\) was doped with \(\text{Zn}\) (3 mol%) by an impregnation method using \(\text{Zn(NO}_3\text{)}_2\), and then calcined at 1123 K for 6 h. Finally, \(\text{Rh}_{2-y}\text{Cr}_y\text{O}_3\) was loaded into the prepared \(\text{Zn:Ga}_2\text{O}_3\) photocatalyst by an impregnation method (Rh 0.5 wt%, Cr 0.75 wt%).

For the synthesis of \(\text{Mg:BaTa}_2\text{O}_5\); \(\text{Mg(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\); \(\text{BaCO}_3\); and \(\text{Ta}_2\text{O}_5\) were mixed in the ratio of \(\text{Ba} : \text{Ta} : \text{Mg} = 1 : 0.925 : 0.075\) 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\(_y\)O\(_3\)/(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\(_2\)O, 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


**Figure S1.** Time course of photocatalytic water splitting using Rh$_2$Cr$_3$O$_3$/Zn:Ga$_2$O$_3$ photocatalyst panels with and without nanometer-size SiO$_2$ for H$_2$ and O$_2$ evolution. Reaction conditions: photocatalyst powder, Rh$_2$Cr$_3$O$_3$/Zn:Ga$_2$O$_3$ 20 mg; SiO$_2$, 20 mg; solution, H$_2$O 100 mL; light source, 300 W Xe lamp ($\lambda > 200$ nm); reaction vessel, top-irradiation vessel with a quartz window.
**Figure S2.** Time course of H₂ evolution using the Mg:BaTaO₂N photocatalyst panel with and without nanometer-size SiO₂. Reaction conditions: photocatalyst powder, Mg:BaTaO₂N 20 mg; SiO₂, 20 mg or none; solution, 10 vol% MeOH aqua solution 100 mL; light source, 300 W Xe lamp (λ > 300 nm); reaction vessel, Pyrex top-irradiation vessel.
Figure S3. Time course of O$_2$ evolution using Mg:BaTaO$_2$N photocatalyst panels with and without nanometer-size SiO$_2$. Reaction conditions: photocatalyst powder, Mg:BaTaO$_2$N 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$_y$O$_3$/(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$_y$O$_3$/(Ga$_{1-x}$Zn$_x$)(N$_{1-x}$O$_x$) 20 mg; SiO$_2$, 20 or 40 mg; solution, H$_2$O 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\textsubscript{2-x}Cr\textsubscript{x}O\textsubscript{3}/(Ga\textsubscript{1-x}Zn\textsubscript{x})(N\textsubscript{1-x}O\textsubscript{x}) 20 mg, micrometer-size SiO\textsubscript{2}, 20 mg; solution, H\textsubscript{2}SO\textsubscript{4} aqua solution (pH 4.5) 100 mL; light source, 300 W Xe lamp (λ > 300 nm); reaction vessel, Pyrex top-irradiation vessel.