Photocatalysis

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Photocatalytic Overall Water Splitting Promoted by Two Different Cocatalysts for Hydrogen and Oxygen Evolution under Visible Light**

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Overall water splitting using a particulate photocatalyst and solar energy has attracted significant attention as a potential means of large-scale H_2 production from renewable resources without carbon dioxide emission.[1,2] The reaction occurs in three steps: 1) the photocatalyst absorbs photon energy greater than the band-gap energy of the material and generates photoexcited electron–hole pairs in the bulk, 2) the photoexcited carriers separate and migrate to the surface without recombination, and 3) adsorbed species are reduced and oxidized by the photogenerated electrons and holes to produce H_2 and O_2, respectively. The first two steps are strongly dependent on the structural and electronic properties of the photocatalyst, while the third step is promoted by an additional catalyst (called cocatalyst). Therefore, it is important to develop a photocatalyst and a cocatalyst in harmony.

Recently, our group has focused on active sites for H_2 evolution on the surface of a photocatalyst, because most photocatalysts lack surface H_2 evolution sites.[2b] Using a solid solution of GaN and ZnO (abbreviated GaN:ZnO hereafter) that can harvest visible photons up to ca. 500 nm,[3] chromium-containing transition-metal oxides[4] or noble-metal/chromia (core/shell) nanoparticles (NPs)[5] have been shown to function as H_2 evolution cocatalysts, resulting in efficient water splitting under visible light. Meanwhile, also several sulfides were proposed as efficient catalysts for H_2 evolution,[6] and the role of H_2 evolution cocatalysts has been explored by spectroscopic and electrochemical techniques.[7]

It would be natural to expect that loading both H_2 and O_2 evolution cocatalysts onto the same photocatalyst would improve water-splitting activity, compared to photocatalysts modified with either an H_2 or O_2 evolution cocatalyst.[8] It is easy to imagine how these two different cocatalysts would separately facilitate H_2 and O_2 evolution, thereby promoting overall water splitting in harmony. Unfortunately, no successful and reliable example of this has been reported since the initial reports on photocatalytic water splitting in the 1980s. The actual demonstration of the concept remains a major challenge. Herein, we show a proof-of-concept using GaN:ZnO loaded with Rh/Cr_2O_3 (core/shell) and Mn_3O_4 NPs as H_2 and O_2 evolution promoters, respectively, under irradiation with visible light ($\lambda > 420$ nm).

First, Mn oxide was introduced onto GaN:ZnO, prepared by our previous method,[3] as O_2 evolution cocatalyst. Some Mn oxides have been reported to act as O_2 evolution promoters,[9] and it is well known that a Mn complex is the O_2 evolution center in the photosynthesis of green plants. MnO NPs with a mean size of (9.2 ± 0.4) nm (Figure S1 in the Supporting Information) were adsorbed onto GaN:ZnO. It was revealed by UV/vis spectroscopy that the introduced MnO NPs (ca. 1.0 wt%) were almost quantitatively anchored on the GaN:ZnO surface, based on the change in the absorption band of the MnO NPs (Figure S2 in the Supporting Information). The as-prepared MnO/GaN:ZnO sample was then calcined in air at 673 K for 3 h to remove organic residues. Separate experiments with thermogravimetry, differential thermal analysis (TG-DTA), and X-ray diffraction (XRD) showed that the organic ligands stabilizing the MnO NPs were completely burned off by calcination in air at 673 K, and that calcination of dried MnO NP powder under the above conditions resulted in phase transformation of the MnO into Mn_3O_4 (Figure S3 in the Supporting Information). Transmission electron microscopy (TEM) observation revealed that the particle size of the Mn oxide was maintained, even after calcination (Figure S1 in the Supporting Information). Thus, GaN:ZnO particles were successfully decorated with Mn_3O_4 NPs which were expected to act as water oxidation cocatalysts.

Because GaN:ZnO is an n-type semiconductor, it is possible to monitor the photooxidation reaction occurring on its surface using an electrochemical technique.[10] Under

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intermittent visible light ($\lambda > 420$ nm), the unmodified electrode generated anodic photocurrent based on water oxidation under visible light. With Mn_3O_4 modification, however, this anodic photocurrent increased (Figure S4 in the Supporting Information), although the absolute photocurrent value was relatively low (in the order of several $\mu A\,cm^{-2}$) due primarily to the insufficient quality of the photoelectrode.[10] At zero applied potential (0 V vs RHE), equivalent to the condition in photocatalytic reactions in which no external energy other than visible light is supplied, the Mn_3O_4-modified electrode produced an anodic photocurrent three times that of the unmodified sample. These results indicate that the loaded Mn_3O_4 NPs promoted water oxidation on GaN:ZnO under visible light. On the other hand, Mn_3O_4/GaN:ZnO did not promote H_2 evolution from an aqueous solution containing methanol as an electron donor, indicating that Mn_3O_4 on GaN:ZnO does not host water reduction sites.

Next, we introduced H_2 evolution sites into Mn_3O_4-loaded GaN:ZnO. Because the loaded Mn_3O_4 NPs did not function as electron collectors to host H_2 evolution sites on GaN:ZnO, we employed an in-situ photodeposition method that in principle allows the deposition of NPs on the reduction sites of a given photocatalyst.[11] The H_2 evolution promoter selected was core/shell-structured Rh/Cr_2O_3 NPs, which can readily be introduced on a semiconductor photocatalyst through a stepwise reduction of Rh^{III} ions and Cr^{VI} ions under band-gap irradiation.[5] In this system, the backward reaction over the noble metal (water formation from H_2 and O_2) is prevented by the Cr_2O_3 shell. Specifically, the amorphous Cr_2O_3 shell is permeable to protons and evolved H_2 molecules, but not to O_2.[7] TEM images of GaN:ZnO modified with Mn_3O_4 and Rh/Cr_2O_3 (core/shell) NPs are shown in Figure 1. The observation with energy-dispersive X-ray spectroscopy (EDS) analysis revealed that Rh/Cr_2O_3 (core/shell) and Mn_3O_4 NPs were almost separately loaded on the GaN:ZnO, although part of the Rh cores were aggregated[5] and there was little EDS signal of Rh on Mn_3O_4 NPs (Rh/Mn $\approx$ 0.06–0.07). We thus concluded that Rh/Cr_2O_3 (core/shell) NPs were successfully introduced onto Mn_3O_4/GaN:ZnO without concealing the pre-deposited Mn_3O_4 NPs and changing the original size of about 9 to 10 nm.

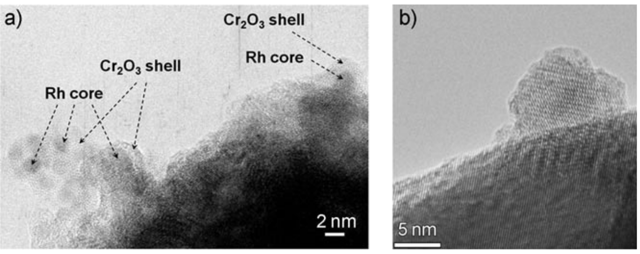


Figure 1. TEM images of GaN:ZnO modified with Mn_3O_4 and Rh/Cr_2O_3 (core/shell) nanoparticles: a) Rh/Cr_2O_3, b) Mn_3O_4.

Figure 2 shows time courses of overall water splitting under visible light ($\lambda > 420$ nm) using differently modified GaN:ZnO catalysts. As reported previously, GaN:ZnO modified with Rh/Cr_2O_3 (core/shell) NPs catalyzed overall water splitting steadily.[5] In contrast, Mn_3O_4/GaN:ZnO did not produce any H_2 or O_2 (data not shown). These results highlight the necessity of loading H_2 evolution sites on GaN:ZnO to achieve overall water splitting. Interestingly, GaN:ZnO modified with both Rh/Cr_2O_3 and Mn_3O_4 exhibited enhanced activity, compared to catalysts modified with either Rh/Cr_2O_3 or Mn_3O_4. The pH value of the reactant solution after reaction for 12 h had not changed noticeably (pH $\approx$ 6). The photocatalytic activity was also found to be dependent on the loading amount of Mn_3O_4. The rates of H_2 and O_2 evolution both increased with increasing Mn loading, reaching a maximum at 0.05 wt%, beyond which the activity began to decrease.

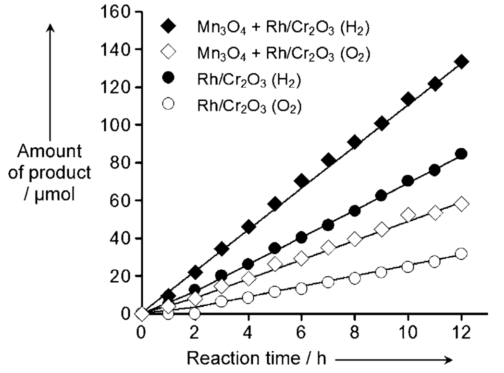
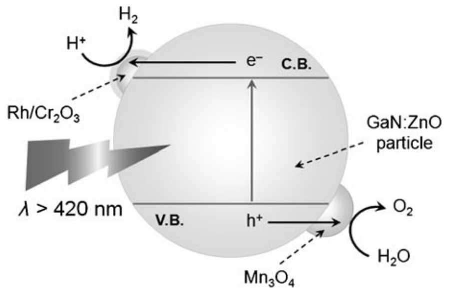


Figure 2. Time courses of H_2 and O_2 evolution using modified GaN:ZnO catalysts under visible light ($\lambda > 420$ nm). Mn loading: 0.05 wt%.

On the basis of the above results, a reaction mechanism for visible-light-driven overall water splitting on this catalyst can be proposed, and is illustrated in Scheme 1. The loaded NPs of Mn_3O_4 function as O_2 evolution sites, as indicated by photoelectrochemical measurements, while Rh/Cr_2O_3 (core/shell) NPs host H_2 evolution sites. With assistance by Mn_3O_4 NPs in O_2 evolution, the photocatalytic activity for overall water splitting by GaN:ZnO modified with core/shell-structured Rh/Cr_2O_3 NPs was improved, compared to analogues modified with either H_2 or O_2 evolution cocatalysts. The present results are in good agreement with our recent kinetic assessment of overall water splitting using GaN:ZnO modi-



Scheme 1. A proposed reaction mechanism for visible-light-driven overall water splitting on GaN:ZnO modified with Mn_3O_4 and Rh/Cr_2O_3 (core/shell) nanoparticles. C.B.: conduction band, V.B.: valence band, e^-: electron, h^+: hole.

fied with Rh-Cr mixed oxide as an H_2 evolution cocatalyst, which suggests that there is room for improvement of water-splitting activity by introducing O_2 evolution sites in addition to H_2 evolution sites.[12] It should also be noted that the present coloading method is applicable to a metal oxide photocatalyst (Figure S5 in the Supporting Information), suggestive of the general utility of this method.

Although the quantum yield of this system was relatively low (ca. 1 %), this is the first demonstration that loading two different kinds of cocatalysts can effectively promote overall water splitting, along with direct evidence of the functionality of each cocatalyst in the reaction. The relatively low activity of the present system can be attributed to the method of cocatalyst modification; specifically, the present photodeposition method causes aggregation of Rh cores.[13] In conclusion, we demonstrated for the first time the validity of modifying a photocatalyst with two different cocatalysts for H_2 and O_2 evolution to improve water-splitting activity under visible light.

Experimental Section

A GaN:ZnO solid solution as a base photocatalyst was prepared according to a previously described method.[3] Briefly, a mixture of Ga_2O_3 and ZnO powders (1.08 g Ga_2O_3 and 0.94 g ZnO) was heated at 1098 K under NH_3 flow (250 mL min^{-1}). After 13 h of nitridation, the sample was cooled to room temperature, maintaining the NH_3 flow throughout. The production of GaN:ZnO (ZnO/GaN $\approx$ 0.13) was confirmed by powder X-ray diffraction and EDX analysis. The band gap energy of the as-obtained GaN:ZnO was 2.68 eV, as estimated from the onset of the diffuse reflectance spectrum.

MnO nanoparticles were prepared according to a method similar to that of Hyeon et al.[14] The procedure involved the preparation of a Mn oleate complex, followed by heating in 1-octadecene. The Mn oleate complex was prepared by heating a mixed solvent of ethanol (30 mL), distilled water (40 mL), and hexane (70 mL) to dissolve $MnCl_2\cdot 4H_2O$ (40 mmol) and sodium oleate (80 mmol) at 343 K under N_2 overnight. The solution was then transferred to a separatory funnel, and the upper organic layer was separated. After evaporation of the solvent, the as-prepared Mn oleate complex (0.4 mmol) was heated in 1-octadecene (10 mL) according to the following procedure: The mixture was heated at 393 K for 1 h under vacuum. Then, the temperature was increased at a ramp rate of 10 K min^{-1} to 573 K. After the mixture was stirred magnetically at 573 K for 30 min, the temperature was lowered to room temperature. The as-obtained product was purified by ethylacetate, and then dispersed in THF. The mean particle size of the as-prepared MnO nanoparticles was (9.2 ± 0.4) nm, according to TEM observation (Figure S1 in the Supporting Information). Using another Mn precursor ($Mn(NO_3)_2\cdot 6H_2O$), the above-mentioned procedure led to a similar result, yielding MnO nanoparticles having a mean size of (8.9 ± 0.5) nm.

The as-prepared GaN:ZnO powder was suspended in THF containing the desired amount of MnO nanoparticles (ca. 1.0 wt % Mn loading). After ultrasonication, THF (5 mL) containing 16-hydroxyhexadecanoic acid (20 μmol) was added to the suspension, which was then stirred for 3 h. This procedure allowed MnO nanoparticles to be adsorbed onto GaN:ZnO almost quantitatively (Figure S2 in the Supporting Information). The MnO-containing GaN:ZnO was then heated in air at 673 K for 3 h (ramp: 5 K min^{-1}) to remove organic residues. This calcination procedure converted MnO into Mn_3O_4 (Figure S3 in the Supporting Information), but the particle size of the Mn oxide remained relatively unchanged (Figure S1 in the Supporting Information).

The Rh/Cr_2O_3 (core/shell) NPs were prepared according to a previous method.[5] The Mn_3O_4-loaded sample (0.13 g) was dispersed in aqueous $Na_3[RhCl_6]$ solution, followed by irradiation by visible light ($\lambda > 420$ nm) for 4 h to reduce Rh^{III} into metallic Rh under air-free conditions. After deposition of Rh and addition of K_2CrO_4 (0.8 mM), the solution was again exposed to visible irradiation ($\lambda >$ 420 nm) for another 4 h to reduce K_2CrO_4 to Cr_2O_3. Irradiation was conducted using a 300 W xenon lamp with a cutoff filter. The loading amounts of Rh and Cr introduced by this procedure were ca. 0.75 and 0.31 wt %, respectively.[5b] The temperature of the reactant solution was maintained at room temperature by a flow of cooling water during the preparation procedure. The final product was washed well with distilled water and dried overnight at 343 K. For comparison, unloaded GaN:ZnO was calcined under the same conditions before modification by Rh/Cr_2O_3 (core/shell) nanoparticles.

Photocatalytic reactions were carried out using the same experimental setup as used for the preparation of Rh/Cr_2O_3 (core/shell) nanoparticles. A reactant solution consisting of 0.1 g of catalyst and 100 mL of pure water was evacuated several times prior to the reaction to ensure that no air remained in the reaction vessel. The evolved gases were analyzed by a gas chromatograph connected directly to the closed gas circulation system.

A porous GaN:ZnO electrode was prepared by pasting a viscous slurry onto conducting glass according to a previously described method.[10] A mixture of 0.1 g of the as-prepared GaN:ZnO powder, 10 μL of acetylacetone (Kanto Chemicals, Japan), 10 μL of TritonX (Aldrich, USA), and 200 μL of distilled water was ground in an agate mortar for preparation of the viscous slurry. The slurry was then pasted onto fluorine-doped tin oxide (FTO) glass slides (12 Ω sq^{-1}, transparency 80 %, thickness 1 mm; Asahi Glass, Japan) to prepare a 1×4 cm^2 electrode, and the sample was calcined in air at 623 K for 1 h. Loading Mn_3O_4 nanoparticles onto the as-prepared electrode was conducted by dropping a required volume of the THF solution containing MnO nanoparticles, followed by calcination in air at 673 K for 3 h to convert MnO into Mn_3O_4. For comparison, an unmodified electrode was also calcined under the same conditions.

Photoelectrochemical measurements were performed using a conventional Pyrex electrochemical cell with a platinum wire as the 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, 0.1M, 100 mL) as the supporting electrolyte. The electrolyte solution was purged with nitrogen prior to the measurements, and was maintained at room temperature by a flow of cooling water during the measurements. A 300 W xenon lamp fitted with a cutoff filter was used as a visible light irradiation source. The effective irradiation area was 1×3.5 cm^2.

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