Noble-Metal/Cr$_2$O$_3$ Core/Shell Nanoparticles as a Cocatalyst for Photocatalytic Overall Water Splitting**

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Catalytic overall water splitting (OWS) in the presence of a semiconductor photocatalyst has been studied extensively as a potential method to supply clean and renewable hydrogen. Although a number of metal oxides have been reported to be active photocatalysts for this reaction, most only function under UV irradiation owing to the large band-gap energy of the materials (> 3 eV).[1] To utilize solar energy to drive this reaction, it is therefore necessary to develop a visible-light-responsive photocatalyst, and numerous attempts have been made in recent years to produce such a material.[2–4] We have reported that certain oxynitrides, such as TaON,[3a] LaTiO$_2$N,[3b] and the $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ solid solution,[4] are promising stable photocatalysts for OWS under visible-light irradiation. Although these oxynitrides exhibit high photocatalytic activity for water oxidation in the presence of an appropriate electron acceptor,[3,4d] their activity for water reduction is approximately one order of magnitude lower than that for water oxidation. An effective modification method to promote the water reduction is therefore required to improve the overall efficiency of these oxynitrides.

Noble metals or transition-metal oxides are often employed as a cocatalyst to facilitate water reduction. Such cocatalysts are typically applied as nanoparticles (NPs) to the catalyst surface by impregnation or in situ photodeposition. In the impregnation method, active species are dispersed randomly on the photocatalyst surface and an activation

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treatment, such as reduction or oxidation, is necessary to obtain high activity.[1,4] This approach appears to be somewhat unsuitable for oxynitrides as they are less thermally stable than the corresponding metal oxides.[5] In contrast, in situ photodeposition allows the cocatalysts to be loaded selectively at reaction sites without the need for an activation treatment.[6] However, most of the cocatalysts suitable for introduction by this method are noble metals (e.g., Rh, Pd, and Pt), which act as a catalyst not only for water reduction but also for water formation from H_2 and O_2, an undesirable backward reaction.[1b] Although Kudo et al. have reported that La-doped $NaTaO_3$ ($NaTaO_3$:La) photodeposited with IrO_2 has a higher photocatalytic activity for OWS than $NaTaO_3$:La alone, it has been confirmed that the loaded IrO_2 functions as a promoter of water oxidation.[1h] A new modification method that realizes a water-reducing cocatalyst without the need for an activation treatment is therefore desirable. Herein, a new strategy for the production of a water-reduction catalyst is proposed. In this approach, cocatalyst NPs consisting of a noble-metal core and Cr_2O_3 shell are prepared for use with the $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ solid solution,[4] and this catalytic system is demonstrated to be effective for visible-light-driven OWS.
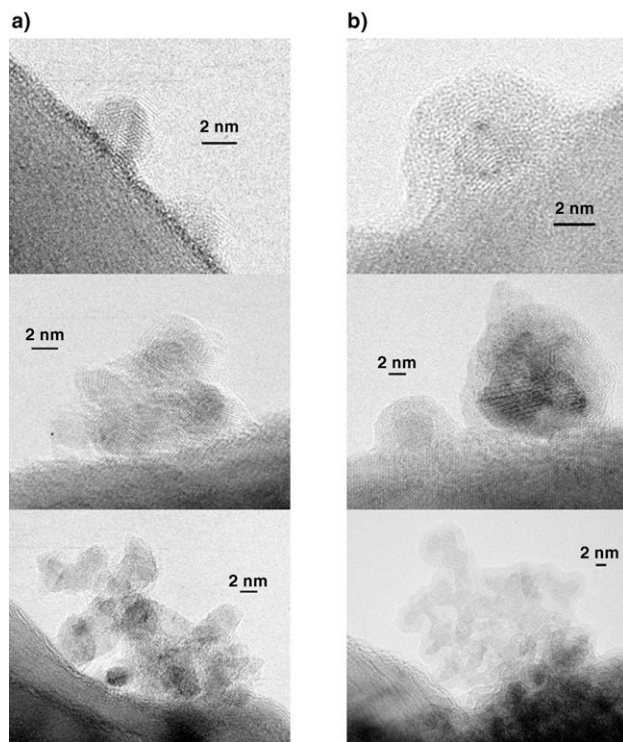
Noble-metal/Cr_2O_3 (core/shell) NPs were prepared by an in situ photodeposition method[6] from a noble-metal complex salt (e.g., $Na_3RhCl_6 \cdot 2H_2O$) and K_2CrO_4 as precursors. Noble-metal NPs were first photodeposited on $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ ($x = 0.12$; represented as GaN:ZnO hereafter), which was prepared by a reported method.[4a,b] Figure 1a shows a high-resolution (HR) TEM image of a catalyst loaded with 1 wt% Rh. The primary particle size of the introduced Rh NPs is 2–3 nm, although some of them aggregate to form larger

secondary particles. The Rh-loaded sample (0.3 g) was then dispersed in an aqueous K_2CrO_4 solution (0.234 mM). After evacuation, the solution was exposed to visible-light irradiation ($\lambda > 400$ nm) for 4 h to reduce K_2CrO_4 to Cr_2O_3.[7] The final product was washed thoroughly with distilled water and dried overnight at 343 K. The HR-TEM images of this sample are shown in Figure 1b, which shows that the Rh NPs have been coated with a shell layer about 2 nm thick to form a core/shell nanostructure. Although some of them form large agglomerates, the shell thickness is almost constant (ca. 2 nm) regardless of the size of the Rh particle. Examining over 50 particles irradiated with visible light in an aqueous K_2CrO_4 solution showed that all the particles had a core/shell structure. It was confirmed by X-ray absorption fine-structure spectroscopy (XAFS) and X-ray photoelectron spectroscopy (XPS) that the core and the shell consist of metallic Rh and Cr_2O_3, respectively.

After shell formation, the particle size distribution (Figure 2b; based on the HR-TEM observations) is shifted to larger size compared with that before shell formation (Figure 2a), which suggests an increase in particle size. The
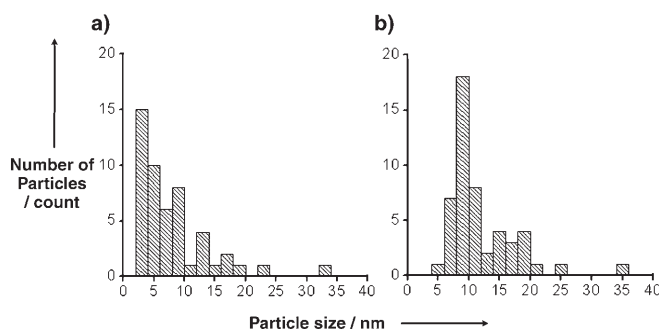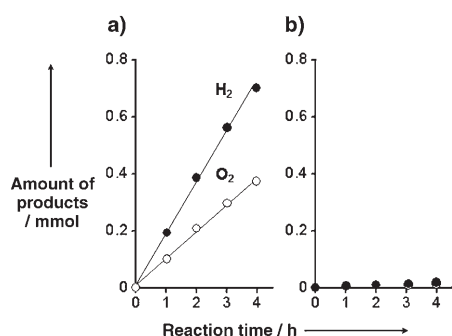

Figure 2. Particle size distribution histograms of Rh-loaded $(Ga_{1-x}Zn_x)$-$(N_{1-x}O_x)$ before (a) and after (b) photodeposition of the Cr shell.

average sizes of 50 different particles of Rh and Rh/Cr_2O_3 were calculated to be about 7.6 and 11.8 nm, respectively. The difference in these average sizes (4.2 nm) is close to twice the Cr_2O_3 shell thickness (ca. 2 nm) surrounding the Rh NPs. This result supports the idea that a Cr_2O_3 shell about 2-nm thick covers all of the Rh NPs, as indicated by the TEM images (Figure 1b).

Rh-loaded GaN:ZnO exhibits little photocatalytic activity for OWS even after extended periods of irradiation, probably because of rapid water formation on the Rh NPs.[1b] However, GaN:ZnO loaded with the Rh/Cr_2O_3 core/shell cocatalyst gives stoichiometric H_2 and O_2 evolution from pure water. A typical time course of OWS on Rh/Cr_2O_3-loaded GaN:ZnO under visible-light irradiation ($\lambda > 400$ nm) is shown in Figure 3a.[8] Both H_2 and O_2 evolve steadily and stoichiometrically as the reaction proceeds, thereby indicating migration of the electrons photogenerated[9] in the GaN:ZnO to the surface of the Cr_2O_3 shell to reduce H^+ to H_2. Addition of the Rh-loaded catalyst to the reactant suspension containing the Rh/Cr_2O_3-loaded catalyst resulted in a marked decrease in the rates of both H_2 and O_2 evolution (Figure 3b). It is thus clear that water formation from H_2 and


Figure 1. HR-TEM images of Rh-loaded $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ before (a) and after (b) photodeposition of the Cr shell.

Figure 3. Time courses of OWS using Rh/Cr$_2$O$_3$-loaded (Ga$_{1-x}$Zn$_x$)-(N$_{1-x}$O$_x$) under visible-light irradiation ($\lambda > 400$ nm). a) 0.15 g of catalyst, b) mixture of 0.15 g of catalyst with 0.15 g of a sample loaded with Rh-NPs. Reactions were performed in pure water (370 mL) with illumination from a high-pressure mercury lamp (450 W) through an aqueous 2 M NaNO$_2$ solution filter.

O$_2$ on unmodified Rh NPs is significant in the OWS reaction and that the suppression of water formation is therefore essential to achieve efficient evolution of H$_2$ and O$_2$ in this system.

The use of other noble metals, such as Ir and Pt, as a core with the Cr$_2$O$_3$ shell in the same manner achieves similar results to those observed for Rh (see Supporting Information, Table S1). This modification method could be applicable to other photocatalysts for OWS, such as SrTiO$_3$ and NaTaO$_3$.

A schematic illustration of the reaction mechanism of OWS on Rh/Cr$_2$O$_3$-loaded GaN:ZnO is shown in Figure 4. As demonstrated above, H$_2$ evolution occurs on the Cr$_2$O$_3$-coated Rh NPs, whereas the impregnation of GaN:ZnO with Cr$_2$O$_3$ NPs alone (3–10 nm) does not promote OWS.[4d] This behavior indicates that Cr$_2$O$_3$ on GaN:ZnO cannot induce the migration of photogenerated electrons from the bulk to the catalyst surface but instead provides sites at which adsorbed protons (H$^+$) are reduced to H atoms by photogenerated electrons to form H$_2$ molecules. H$_2$ evolution also occurs on Rh NPs loaded on GaN:ZnO in the absence of O$_2$,[4e] thus indicating that the electrons photogenerated in the GaN:ZnO bulk by visible-light absorption can indeed migrate to the
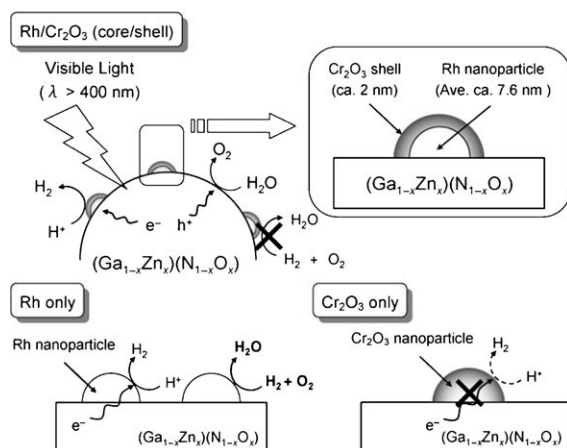
Rh NPs and cause H$_2$ evolution. However, in the presence of O$_2$, this H$_2$ reacts immediately with O$_2$ on the Rh NPs to form H$_2$O as mentioned above. Nosaka et al. have reported that noble metals dispersed on TiO$_2$ can generate an electronic field between the noble metal and the TiO$_2$, thereby promoting electron transfer from the TiO$_2$ to the noble metal.[10] A similar promotion effect on the electron transfer from GaN:ZnO to Rh NPs is therefore expected to occur in the present case. Accordingly, in the Rh/Cr$_2$O$_3$/GaN:ZnO system, the Rh NPs forming the core are considered to play the role of inducing the migration of photogenerated electrons from the GaN:ZnO bulk and the Cr$_2$O$_3$ shell provides an H$_2$ evolution site at the external surface while preventing water formation from H$_2$ and O$_2$ on Rh. Thus, the sandwich structure of Rh/Cr$_2$O$_3$/GaN:ZnO is indispensable for achieving OWS. In photocatalytic OWS, cocatalysts such as NiO$_x$,[1a,c,d,g] RuO$_2$,[1e,f,4a–c] and Rh$_{2-y}$Cr$_y$O$_3$,[4d,e] play at least two roles simultaneously, namely extraction of photogenerated electrons or holes from the photocatalyst bulk and reduction of H$^+$ to H$_2$ or oxidation of H$_2$O to O$_2$ on the cocatalyst surface. In contrast, these two roles are successfully separated in the present core/shell cocatalyst, which is of interest in considering the role of cocatalysts loaded on a photocatalyst.

Another core/shell cocatalyst, namely Ni/NiO core/shell NPs, for photocatalytic OWS has been reported by some of us and applied to many heterogeneous photocatalytic systems.[1a,c,d,g] Compared with Ni/NiO, the present core/shell cocatalyst has several advantages, including the possibility of selectively introducing active species for OWS at the reduction sites of the photocatalyst, the possibility of using various noble metals as the core for extraction of photogenerated electrons from the bulk, and elimination of the need for activation treatment by oxidation or reduction. Although the performance of the present Rh/Cr$_2$O$_3$-loaded GaN:ZnO catalyst is lower than that reported for the Rh$_{2-y}$Cr$_y$O$_3$-loaded catalyst,[4d,e] the present modification method offers a new strategy to create a water-reducing cocatalyst for photocatalytic OWS. This method may also be useful for reducing Cr^{6+} ion pollution in industrial waste water[7] through the use of solar energy as well as hydrogen production by OWS. This possibility is currently under investigation.

Figure 4. A schematic reaction mechanism of OWS on Rh/Cr$_2$O$_3$-loaded (Ga$_{1-x}$Zn$_x$)(N$_{1-x}$O$_x$) and the corresponding processes on supported Rh NPs and Cr$_2$O$_3$ NPs. See text for details.

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