GaN:ZnO Solid Solution as a Photocatalyst for Visible-Light-Driven Overall Water Splitting

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Overall water splitting using a heterogeneous photocatalyst is an attractive solution to supply clean and recyclable hydrogen energy. A number of photocatalysts have been proposed, and some have achieved high quantum efficiencies.[1] However, most of the photocatalysts proposed to date consist of metal oxides and work only in the ultraviolet region. At present, there is a lack of suitable materials with sufficiently small band gap, an appropriate band gap position for overall water splitting, and the stability necessary for practical applications. In general, efficient photocatalytic materials contain either transition-metal cations with a d^0 electronic configuration (e.g., Ti^{4+} and Ta^{5+}) or typical metal cations with d^{10} electronic configuration (e.g., In^{3+} and Sn^{4+}) as principal cation components, the empty d or sp orbitals of which form the bottom of the conduction bands.[1-3] The tops of the valence bands of metal–oxide photocatalysts with d^0- or d^{10}-metal cations usually consist of O2p orbitals, which are located at about +3 eV or higher versus NHE and, as such, produce a band gap too wide to absorb visible light.[4]

The authors reported that some (oxy)nitrides containing d^0 transition-metal cations, such as Ta_3N_5, TaON, and $LaTiO_2N$, are potential photocatalytic materials that meet the three requirements mentioned above.[5-7] However, overall water splitting using such (oxy)nitrides has yet to be accomplished, presumably due to high defect densities in these materials. Recently, we also reported that p-block typical metal nitride, β-Ge_3N_4, combined with RuO_2 nanoparticles functions as a photocatalyst for overall water splitting. The genuine band gap energy of β-Ge_3N_4 is about 3.8 eV, which works only under ultraviolet light.[8]

This paper reports on a new type of oxynitride with a unique composition and structure: a solid solution of GaN and ZnO with a wurtzite-type structure, classified as a material containing d^{10} typical metal cations. A photocatalyst prepared using this new material achieves water splitting into H_2 and O_2 under visible light irradiation.

GaN has a band gap of about 3.4 eV and has been studied extensively for application in light-emitting diodes and laser diodes.[9,10] GaN has been examined as a photoelectrode, and it has been confirmed to have the potential for overall water splitting under UV irradiation.[11-13] ZnO is also a well-known material with a band gap of 3.2 eV and is being examined as light-emitting diode and gas sensors.[14,15] Both materials have wurtzite structures with similar

Table 1. Results of Elemental Analyses

sample	Nitridation condition			Elements (atom %)			
	temp (K)	time (h)	NH₃ flow rate (mL/min)	Ga	Zn	N	O
A[a]	1123	20	250	46.7	3.4	44.8	5.2
B[a]	1123	15	250	43.9	6.4	41.9	7.9
C[a]	1123	5	500	38.3	13.3	32.7	15.7
GaN(HM)[b]	1123	30	250	47.6	d	45.4	7.0
GaN(ref)[c]				48.9	d	50.6	0.5

[a] Prepared from Ga_2O_3 and ZnO (Ga_2O_3:ZnO = 1:2). [b] Prepared from Ga_2O_3. [c] Supplied by Mitsubishi Chemical Co. [d] No data.
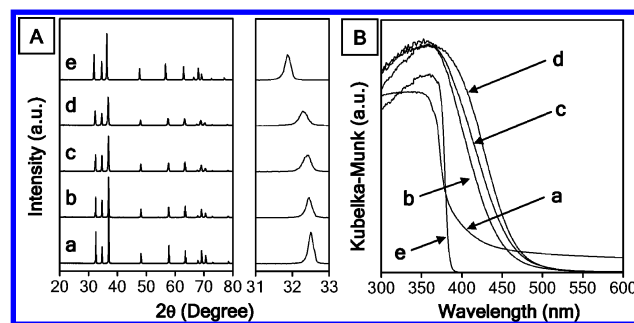
Figure 1. (A) Powder XRD pattern and (B) UV visible diffuse reflectance spectra: (a) GaN (ref), (b) GaN:ZnO (Zn 3.4 atom %), (c) GaN:ZnO (Zn 6.4 atom %), (d) GaN:ZnO (Zn 13.3 atom %), and (e) ZnO.

lattice parameters (GaN: $a = b = 0.319$, $c = 0.519$ nm. ZnO: $a = b = 0.325$, $c = 0.521$ nm).[16,17]

Nitridation of a mixture of Ga_2O_3 (High Purity Chemicals, 99.9%) and ZnO (Kanto Chemicals, 99%) powders (1.08 g of Ga_2O_3, 0.94 g of ZnO) under NH_3 flow (100–500 mL/min flow rate) at 1123 K for 5–20 h resulted in a yellow powder. The elemental analysis of typical samples and a GaN reference is shown in Table 1. In all samples, the ratios of Ga to N and Zn to O were close to 1. Figure 1A shows the powder X-ray diffraction (XRD) patterns of samples with different compositions, along with GaN and ZnO data for comparison. All samples exhibit single-phase diffraction patterns indicative of the wurtzite structure similar to the GaN and ZnO precursors. The position of the d(100) diffraction peak shifted to lower angles (2θ) with increasing Zn and O concentrations.

Figure 1B shows the UV–visible diffuse reflectance spectra of several samples. GaN(ref) prepared from elemental Ga has a long tail in the visible region, which is considered to be attributable to remnant Ga. The absorption edge shifts to longer wavelengths with increasing Zn and O content in the sample. The samples have band gaps smaller than those of the GaN- and ZnO-only materials and

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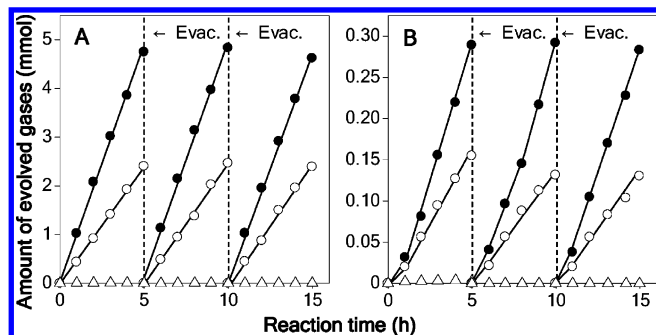⊥ Current address: Kyoto Institute of Technology.

Figure 2. Time courses of overall water splitting under (A) UV irradiation and (B) visible irradiation on RuO_2/GaN:ZnO (sample B; see Table 1). Catalyst (0.3 g); an aqueous solution adjusted to pH 3 by H_2SO_4 (390 cm^3); light source, high-pressure mercury lamp (450 W); inner irradiation-type reaction vessel made of Pyrex: (●) H_2; (○) O_2; (△) N_2.

are estimated to be roughly 2.58 eV for the sample with $x = 0.13$ (see Table 1) based on the UV−visible diffuse reflectance spectrum. Density functional theory (DFT) calculations indicate that the bottom of the conduction band for GaN:ZnO is mainly composed of 4s and 4p orbitals of Ga, while the top of the valence band consists of N2p orbitals followed by Zn3d orbitals. The presence of Zn3d and N2p electrons in the upper valence band provides p−d repulsion for the valence band maximum, which results in narrowing the band gap.[18]

On the basis of the characterization above, it is concluded that the samples prepared from the Ga_2O_3 and ZnO mixture under ammonia flow are solid solutions of GaN and ZnO. Therefore, the ideal composition of the present samples can be expressed as $(Ga_{1−x}Zn_x)(N_{1−x}O_x)$, although the real compositions are somewhat deviated from the ideal one, as shown in Table 1. In this paper, they are termed GaN:ZnO for simplicity. A similar type of solid solution is that between Si_3N_4 and Al_2O_3, $(Si_{3−x}Al_x)(N_{4−x}O_x)$, which is well-known as "SiAlON".[19]

The photocatalytic activity of the as-prepared GaN:ZnO for overall water splitting was negligible. However, the modification of GaN:ZnO with RuO_2 according to our previous method[3,8] resulted in clearly observable H_2 and O_2 evolution. This modification involved the deposition of RuO_2 nanoparticles on the surface of the GaN:ZnO as H_2 evolution sites.[8] On the other hand, both GaN and ZnO showed no activity for overall water splitting. The photocatalytic performance of the RuO_2-loaded GaN:ZnO was found to be strongly dependent on the pH of the aqueous solution. The activity increased as the pH decreased from pH 7, passing through a maximum at pH 3, and then decreasing. In general, (oxy)-nitride materials have an inherent instability in basic media but are stable in acidic media. As a result, the highest activity was obtained at pH 3. Below pH 3, the surface of the catalyst was not completely stable. A typical time course of H_2 and O_2 evolution over RuO_2 (5 wt %)/GaN:ZnO (sample B, Table 1) at pH 3 is shown in Figure 2. Figure 2A shows the time course of H_2 and O_2 evolution under irradiation from a high-pressure mercury lamp (450 W) via a Pyrex glass tube ($\lambda > 300$ nm). H_2 and O_2 evolved steadily and stoichiometrically with no N_2 evolution. After filtering the UV by filling the tube with $NaNO_2$ solution to pass only visible light ($\lambda > 400$ nm), stoichiometric H_2 and O_2 evolution was again confirmed, as shown in Figure 2B. It is considered that in this experiment an emission of a high-pressure mercury lamp at 436 nm mainly contributes to the reaction. It was also confirmed that by using a Xe lamp (300 W) irradiation, the GaN:ZnO photocatalyst works at the wavelength as long as 460 nm. The average apparent quantum efficiency in the range of 300−480 nm was calculated to be 0.14% by using a Si photodiode.

It is known that O_2 evolution occurs over ZnO when employed as a photoanode for water oxidation in a photoelectrochemical cell, and that the ZnO degrades as a result.[20] Therefore, the origin of O_2 evolution over the present catalyst was examined by conducting the photocatalytic reaction in a mixture of $H_2^{16}O$ and $H_2^{18}O$ ($H_2^{16}O/H_2^{18}O = 8.6$). It was confirmed that the ratio of $^{16}O/^{18}O$ in evolved O_2 ($^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$) matched this value of 8.6 within experimental error (± 0.1) over reaction for 16 h, and no differences could be identified in the XRD patterns of the samples before and after the reaction. Furthermore, inductively coupled plasma mass spectrometry confirmed that the solution contained no Zn cations after the reaction. These results indicate that GaN:ZnO functions as a stable visible-light-driven photocatalyst for the overall cleavage of water.

The relatively low quantum efficiency achieved in the present study can be attributed to the high defect density in GaN:ZnO, and the performance of this catalyst can thus be expected to be improved by refining the preparation method. It also appears possible to extend the absorption edge by changing the composition of the (oxy)nitride materials. The present study, therefore, clearly demonstrated the high potential of (oxy)nitrides for overall water splitting using solar energy, which opens the possibility of new non-oxide-type photocatalysts for the solar energy conversion.

Supporting Information Available: Full citation of refs 8 and 14 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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