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.1,2 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.3–5 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.6

The authors reported that some (oxy)nitrides containing d^0 transition-metal cations, such as Ta_2N_5, TaON, and LaTiO_2N, are potential photocatalytic materials that meet the three requirements mentioned above.3–6 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-GeN_4, combined with RuO_2 nanoparticles functions as a photocatalyst for overall water splitting. The genuine band gap energy of β-GeN_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 photocathode, 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 a light-emitting diode and gas sensors.14,15 Both materials have wurtzite structures with similar

Table 1. Results of Elemental Analyses

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nitridation condition</th>
<th>Elements (atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>temp (K)</td>
<td>time (h)</td>
</tr>
<tr>
<td>A’</td>
<td>1123</td>
<td>20</td>
</tr>
<tr>
<td>B’</td>
<td>1123</td>
<td>15</td>
</tr>
<tr>
<td>C’</td>
<td>1123</td>
<td>5</td>
</tr>
<tr>
<td>GaN(HM)</td>
<td>1123</td>
<td>30</td>
</tr>
<tr>
<td>GaN(ref)</td>
<td>1123</td>
<td>30</td>
</tr>
</tbody>
</table>

For A’–C’, GaZnN_2O_4, ZnO:Ga (ZnO:Ga = 1:2), and GaN:ZnO (GaN:ZnO = 1:2), respectively. 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:Ga (Zn 6.4 atom %), (d) GaN:ZnO (Zn 13.3 atom %), and (e) ZnO.

The 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, 99.9%) 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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are estimated to be roughly 2.58 eV for the sample with 

It is known that O2 evolution occurs over ZnO when employed as a photoanode for water oxidation in a photoelectrochemical cell, and that the ZnO degrades as a result. Therefore, the origin of O2 evolution over the present catalyst was examined by conducting the photocatalytic reaction in a mixture of H218O and H216O (H218O/H216O = 8.6). It was confirmed that the ratio of 18O/16O in evolved O2 (16O2, 18O2, and 1618O2) 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.

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