



# WATER SPLITTING BY $d^0$ OR $d^{10}$ PHOTOCATALYSTS

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## ABSTRACT

In this research paper we use  $d$ -block element as catalysts for water splitting and we generate hydrogen as energy molecules. Water splitting to form hydrogen and oxygen over a heterogeneous photo-catalyst using solar energy is a promising process for clean and recyclable hydrogen production in large-scale. However, most of the photo-catalysts 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 photo-catalytic 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  $sp$  orbital's of which form the bottom of the conduction bands.

**Keywords:** Renewable Energy, Co- Catalyst , Photo Catalyst , Oxy-Nitrides , Photochemical Cell

## I. INTRODUCTION

Researchers are intensively investigating photochemical water splitting as a means of converting solar to chemical energy in the form of fuels. Hydrogen is a key solar fuel because it can be used directly in combustion engines or fuel cells, or combined catalytically with  $CO_2$  to make carbon containing fuels. Different approaches to solar water splitting include semiconductor particles as photo catalysts and photo electrodes, molecular donor acceptor systems linked to catalysts for hydrogen and oxygen evolution, and photovoltaic cells coupled directly or indirectly to electro catalysts.

To effectively address the depletion of fossil fuels and the serious environmental problems accompanying their combustion, modern society has been searching for a new form of energy that is clean, renewable, cheap, and a viable alternative to fossil fuels. Recently, much attention has been paid to hydrogen as a next-generation energy carrier, and over the past 3 decades, photo catalytic overall water splitting using solar energy has been studied as a potential method of hydrogen production. Research on such catalysts was triggered by the work of Honda and Fujishima, who demonstrated that overall water splitting can be achieved using a photo electrochemical (PEC) cell consisting of a single-crystalline  $TiO_2$  (rutile) anode and a Pt cathode under ultraviolet (UV) irradiation and an external bias.<sup>1</sup> Since then, a large number of PEC cells have been developed, many of which are designed specifically for the efficient utilization of solar energy. However, due to the lack of suitable photoelectrode materials with appropriate band gap structures and stability, the system proposed to date have been rather complicated, integrated multilayer and tandem systems being examples.<sup>2-4</sup> Overall water splitting for the

production of hydrogen using a particulate photo catalyst, similar in many ways to the photosynthetic reaction, have also been examined since 1980.<sup>5-7</sup> From the viewpoint of large-scale hydrogen production, particulate photo catalyst systems are considered to be advantageous over more complex multilayer or tandem structure devices and have a wider range of potential applications,<sup>8</sup> although a method for separating the simultaneously produced H<sub>2</sub> and O<sub>2</sub> remains to be developed. Thermodynamically, the overall water splitting reaction is an uphill reaction with a large positive change in Gibbs free energy ( $\Delta G^\circ$ ) 238 kJ/mol). Figure 1 shows a schematic illustration of the basic principle of overall water splitting on a heterogeneous photo catalyst. Under irradiation at an energy equivalent to or greater than the band gap of the semiconductor photo catalyst.<sup>1</sup>

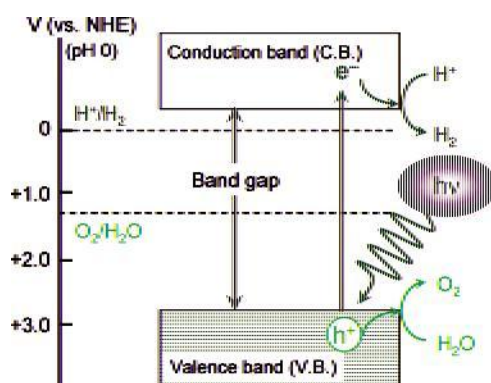


Fig.1. Basic principle of overall water splitting on a heterogeneous photo catalyst.

Table 1. Other metal oxides with d<sup>0</sup> or d<sup>10</sup> electronic configurations, such as V<sup>5+</sup>, Mo<sup>6+</sup>, and Zn<sup>2+</sup>, are also expected to be active as photocatalysts for overall water splitting, although there are, as of yet, no reports on such photocatalysts with reasonable activity. A number of metal oxide photocatalysts have been proposed to date, and some have achieved high quantum efficiencies as high as 30-50%.<sup>15,22</sup> However, the tops of the valence bands of such metal oxide photocatalysts, having d<sup>0</sup> or d<sup>10</sup> metal cations, usually consist of O2p orbitals, which are located at ca. +3 V or higher (vs NHE). Therefore, if the bottom of the conduction band of a given metal oxide is located at a potential more negative than the water reduction potential, the band gap of the material will inevitably becomes larger than 3 eV, rendering the material inactive in the visible-light region.<sup>2</sup>

TABLE 1: Representative Metal Oxide Photocatalysts with d<sup>0</sup> or d<sup>10</sup> Electronic Configuration<sup>a</sup>

d <sup>0</sup> -Type Photocatalysts	
element	photocatalyst
Ti <sup>4+</sup>	TiO <sub>2</sub> , <sup>6</sup> SrTiO <sub>3</sub> , <sup>5,7,9</sup> Na <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub> , <sup>12</sup> BaTi <sub>4</sub> O <sub>9</sub> , <sup>13</sup> K <sub>2</sub> La <sub>2</sub> Ti <sub>3</sub> O <sub>10</sub> <sup>14,15</sup>
Zr <sup>4+</sup>	ZrO <sub>2</sub> <sup>23</sup>
Nb <sup>5+</sup>	K <sub>4</sub> Nb <sub>6</sub> O <sub>17</sub> , <sup>10,11</sup> Sr <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub> <sup>17</sup>
Ta <sup>5+</sup>	K <sub>3</sub> Ta <sub>3</sub> Si <sub>2</sub> O <sub>13</sub> , <sup>16</sup> ATaO <sub>3</sub> (A) Li, Na, K), <sup>18,20</sup> NaTaO <sub>3</sub> :La, <sup>22</sup> BaTa <sub>2</sub> O <sub>6</sub> , <sup>18</sup> RbNdTa <sub>2</sub> O <sub>7</sub> , <sup>19</sup> H <sub>2</sub> SrTa <sub>2</sub> O <sub>7</sub> ·nH <sub>2</sub> O <sup>21</sup>
W <sup>6+</sup>	AMWO <sub>6</sub> (A) Rb, Cs; M) Nb, Ta) <sup>24</sup>

d<sup>10</sup>-Type Photocatalysts

element	photocatalyst
Ga <sup>3+</sup>	ZnGa <sub>2</sub> O <sub>4</sub> <sup>26</sup>
In <sup>3+</sup>	AlInO <sub>2</sub> (A) Li, Na, <sup>28</sup> AlIn <sub>2</sub> O <sub>4</sub> (A) Ca, Sr <sup>25,29</sup>
Ge <sup>4+</sup>	Zn <sub>2</sub> GeO <sub>4</sub> <sup>30</sup>
Sn <sup>4+</sup>	Sr <sub>2</sub> SnO <sub>4</sub> <sup>25</sup>
Sb <sup>5+</sup>	NaSbO <sub>3</sub> , <sup>25,27</sup> CaSb <sub>2</sub> O <sub>6</sub> , <sup>27</sup> A <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub> (A) Ca, Sr <sup>27</sup>

Figure 2, the overall water splitting reaction on a semiconductor photocatalyst 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<sub>2</sub> and O<sub>2</sub>, respectively.

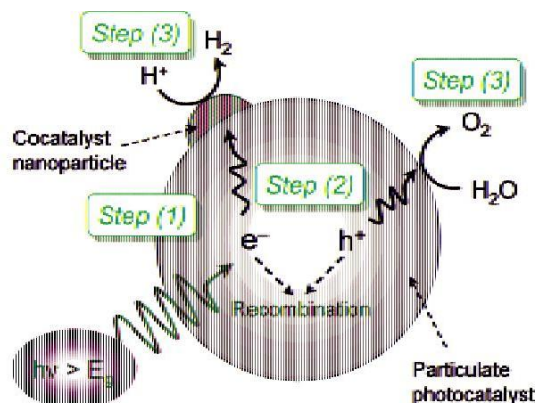


Fig 2. Processes involved in photocatalytic overall water splitting on a heterogeneous photocatalyst.

## II. D<sup>0</sup> ELECTRONIC CONFIGURATION ((OXY)NITRIDES )

Some particulate (oxy)nitrides containing early-transition-metal cations are stable and harmless materials and can be readily obtained by nitriding a corresponding metal oxide powder.<sup>54-62</sup> Figure 7 shows the UV-visible diffuse reflectance spectra for certain (oxy)nitrides containing transition-metal cations of Ti<sup>4+</sup>, Nb<sup>5+</sup>, and Ta<sup>5+</sup> with d<sup>0</sup> electronic configuration. It is apparent that these (oxy)nitrides possess absorption bands at 500-750 nm, corresponding to band gap energies of 1.7-2.5 eV. As expected from DFT calculations, these (oxy)nitrides have band edge potentials suitable for overall water splitting, as revealed by UV photoelectron spectroscopy (UPS) and photoelectrochemical (PEC) analysis.<sup>63</sup> The band structures of Ta<sub>2</sub>O<sub>5</sub>, TaON, and Ta<sub>3</sub>N<sub>5</sub> determined by UPS and PEC analysis are depicted schematically in Figure 8. It is clear that the tops of the valence bands are shifted to higher potential energies in the order Ta<sub>2</sub>O<sub>5</sub> < TaON < Ta<sub>3</sub>N<sub>5</sub>, whereas the potentials of the bottoms of the conduction bands are almost the same. Investigation of the nitridation process for the preparation of



TaON and Ta<sub>3</sub>N<sub>5</sub> from Ta<sub>2</sub>O<sub>5</sub> by X-ray diffraction (XRD) measurements and high-resolution transmission electron microscopy (HR-TEM) have revealed that the solid-state transformation of Ta<sub>2</sub>O<sub>5</sub> reacted with NH<sub>3</sub> to TaON and Ta<sub>3</sub>N<sub>5</sub> is pseudomorphic and topotactic, producing single-crystalline particles of TaON and Ta<sub>3</sub>N<sub>5</sub> with a porous structure from the single-crystalline Ta<sub>2</sub>O<sub>5</sub> particle precursor.<sup>3</sup>

**TABLE 2: Photocatalytic Activities of (Oxy)nitrides with d<sup>0</sup> Electronic Configuration for H<sub>2</sub> or O<sub>2</sub> Evolution in the Presence of Sacrificial Reagents under Visible Light ( $\lambda > 420$  nm)<sup>a</sup>**

photocatalyst	band gap energy <sup>b</sup> eV	activity $\mu\text{mol h}^{-1}$		ref
		H <sub>2</sub> <sup>c</sup>	O <sub>2</sub> <sup>d</sup>	
LaTiO <sub>2</sub> N	2.0	30	41	58
Ca <sub>0.25</sub> La <sub>0.75</sub> TiO <sub>2.25</sub> N <sub>0.75</sub>	2.0	5.5	60	58
CaNbO <sub>2</sub> N	1.9	1.5	46	57
TaON	2.5	20	660	55
Ta <sub>3</sub> N <sub>5</sub>	2.1	10	420	56
CaTaO <sub>2</sub> N	2.4	15	0	62
SrTaO <sub>2</sub> N	2.1	20	0	62
BaTaO <sub>2</sub> N	1.9	15	0	62
LaTaO <sub>2</sub> N	2.0	20	0	57

<sup>a</sup> Reaction conditions: 0.2-0.4 g of catalyst, 200 mL of aqueous solution containing sacrificial reagents, 300 W xenon lamp light source, Pyrex top irradiation-type reaction vessel with cutoff filter. <sup>b</sup> Estimated from onset wavelength of diffuse reflectance spectra. <sup>c</sup> Loaded with nanoparticulate Pt as a cocatalyst; reacted in the presence of methanol (10 vol %) sacrificial reagent. <sup>d</sup> Sacrificial reagent: silver nitrate (0.01 M).

Table 2 lists the photocatalytic activities of d<sup>0</sup> (oxy)nitrides for H<sub>2</sub> or O<sub>2</sub> evolution in the presence of sacrificial reagents. These (oxy)nitrides exhibit relatively high photocatalytic activity for water oxidation to form molecular oxygen under visible irradiation ( $\lambda > 420$  nm), with some exceptions, such as ATaO<sub>2</sub>N (A = Ca, Sr, Ba) and LaTaON<sub>2</sub>. Among this group, TaON achieves the highest quantum efficiency of 34%.<sup>55</sup> It should be noted that water oxidation involving a 4-electron process can be achieved by (oxy)nitrides with high quantum efficiencies, although silver nitrate is used as an electron acceptor in such a system. In contrast, nitrogen-doped TiO<sub>2</sub> displays negligible activity for this reaction under the same reaction conditions.<sup>60</sup> (Oxy)nitrides also produce H<sub>2</sub> from an aqueous methanol solution upon visible irradiation when loaded with nanoparticulate Pt as a cocatalyst for H<sub>2</sub> evolution. However, the activities for H<sub>2</sub> production are about an order of magnitude lower than those for O<sub>2</sub> evolution, although the photocatalytic performance for H<sub>2</sub> evolution is stable. In this context, several new modifications to enhance the H<sub>2</sub> evolution rate of (oxy)-nitrides have been pursued, and it has been found that the photocatalytic activity of TaON for water reduction can be increased markedly by the photodeposition of Ru nanoparticles as H<sub>2</sub> evolution sites.<sup>65</sup> High-pressure treatment of Ta<sub>3</sub>N<sub>5</sub> with NH<sub>3</sub> gas is also effective for enhancing the H<sub>2</sub> evolution activity.<sup>4</sup>



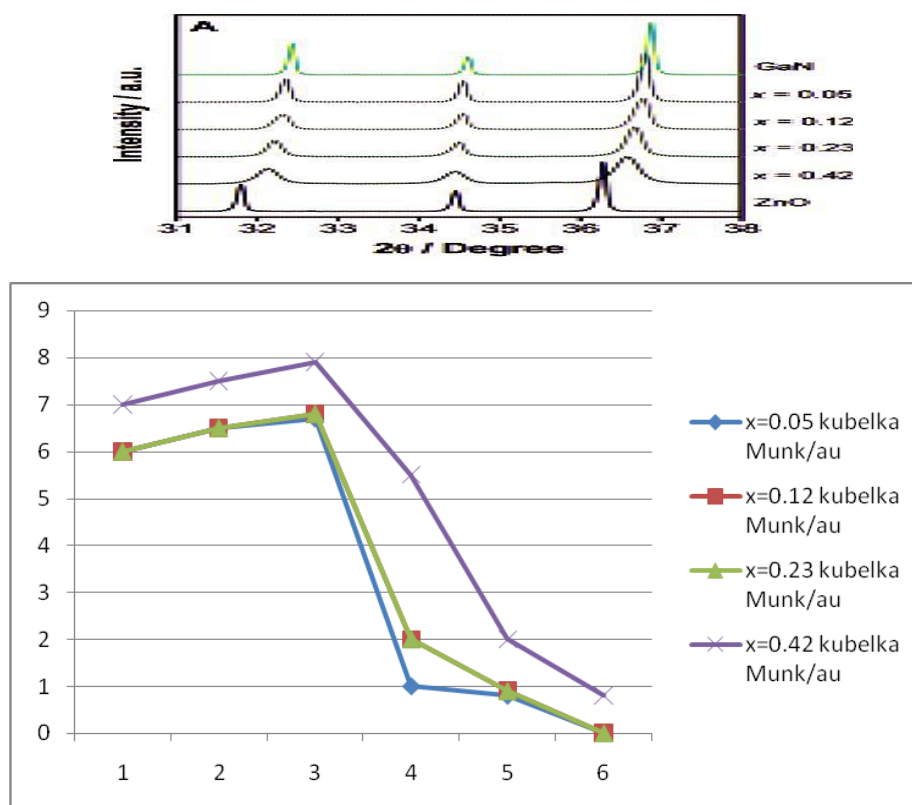
III. D<sup>10</sup> ELECTRONIC CONFIGURATION ((OXY)NITRIDES)

The (oxy)nitride and oxysulfide photocatalysts having the ability to reduce and/or oxidize water under visible light are composed of transition-metal cations of Ti<sup>4+</sup>, Nb<sup>5+</sup>, or Ta<sup>5+</sup> with d<sup>0</sup> electronic configuration.<sup>55-71</sup> From the viewpoint of the electronic band structure, however, d<sup>10</sup>-based semiconducting materials are advantageous over the d<sup>0</sup> configurations as a photocatalyst in that, while the top of the valence band consists of O2p orbitals, the bottom of the conduction band is composed of hybridized s,p orbitals of typical metals.<sup>25-30</sup> The hybridized s,p orbitals possess large dispersion, leading to increased mobility of photogenerated electrons in the conduction band and thus high photocatalytic activity.<sup>25-30</sup> This has stimulated study on (oxy)nitrides or oxysulfides with the d<sup>10</sup> electronic configuration as a photocatalyst for overall water splitting.

**β-Ge<sub>3</sub>N<sub>4</sub>.** As a typical metal nitride with d<sup>10</sup> electronic configuration, *α*-Ge<sub>3</sub>N<sub>4</sub> is synthesized from GeO<sub>2</sub> powder by nitridation under a flow of NH<sub>3</sub> at 1153-1173 K for 10 h.<sup>74-76</sup> The photocatalytic activity of the as-synthesized *α*-Ge<sub>3</sub>N<sub>4</sub> for overall water splitting is negligible. However, when modified with RuO<sub>2</sub> nanoparticles, the material becomes photocatalytically active for the stoichiometric evolution of H<sub>2</sub> and O<sub>2</sub> from pure water. This demonstration of the photodecomposition of water is the first involving a non-oxide photocatalyst. High-pressure treatment of *α*-Ge<sub>3</sub>N<sub>4</sub> with NH<sub>3</sub> gas was found to produce a 4-fold increase in activity by reducing the density of defects.<sup>75</sup> The photocatalytic performance of RuO<sub>2</sub>-loaded *α*-Ge<sub>3</sub>N<sub>4</sub> is strongly dependent on the pH of the aqueous solution, with the activity increasing with decreasing pH from pH 7, passing through a maximum at pH 0, and then decreasing.<sup>76</sup> This characteristic pH dependence of the RuO<sub>2</sub>-loaded *α*-Ge<sub>3</sub>N<sub>4</sub> photocatalyst deviates significantly from the general character of transition-metal oxide-based photocatalysts. For example, NiO<sub>x</sub>-loaded SrTiO<sub>3</sub><sup>9</sup> and NiO-loaded NaTaO<sub>3</sub><sup>20</sup> photocatalysts favor neutral or alkaline solutions for overall water splitting.

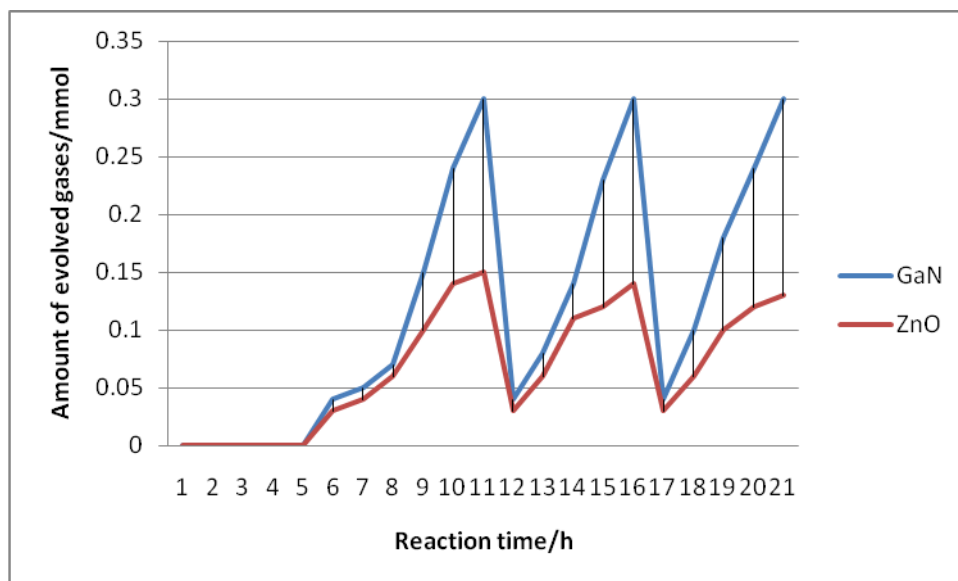
TABLE 3: UV-visible diffuse reflectance spectra for various (Ga<sub>1-x</sub>Zn<sub>x</sub>)(N<sub>1-x</sub>O<sub>x</sub>) solid solutions

wavelength		300	350	400	450	500	600
x=0.05	kubelka	6	6.5	6.7	1	0.8	0
	Munk/au						
x=0.12	kubelka	6	6.5	6.8	2	0.9	0
	Munk/au						
x=0.23	kubelka	6	6.5	6.8	2	0.9	0
	Munk/au						
x=0.42	kubelka	7	7.5	7.9	5.5	2	0.8
	Munk/au						



**Fig.3 (A) Powder XRD patterns and (B) UV-visible diffuse reflectance spectra for various (Ga<sub>1-x</sub>Zn<sub>x</sub>)(N<sub>1-x</sub>O<sub>x</sub>) solid solutions.**

**GaN-ZnO Solid Solution.** To devise a new (oxy)nitride with d<sup>10</sup> electronic configuration that can decompose water under visible light, the solid solution of GaN and ZnO, (Ga<sub>1-x</sub>Zn<sub>x</sub>)-(N<sub>1-x</sub>O<sub>x</sub>), was examined. As both GaN and ZnO have wurtzite structures with similar lattice parameters,<sup>5,6</sup> a solid solution can be formed between the two. Taking into account the large band gap energies of GaN and ZnO (>3 eV), it had been considered that the band gap of the solid solution should exceed 3 eV. However, for II-VI semiconductors, it has been pointed out that p-d repulsion (e.g., O2p-Zn3d) shifts the valence band maximum upward without affecting the conduction band minimum.<sup>79</sup> Similarly, it was hypothesized that p-d repulsion in the GaN-ZnO solid solution (i.e., N2p-Zn3d repulsion) may cause the top of the valence band formed by N2p atomic orbitals to lift up to a higher potential energy, resulting in a narrower band gap for GaN. The (Ga<sub>1-x</sub>Zn<sub>x</sub>)(N<sub>1-x</sub>O<sub>x</sub>) solid solution is typically synthesized by nitriding a mixture of Ga<sub>2</sub>O<sub>3</sub> and ZnO.<sup>7,8</sup> Elemental analyses by inductively coupled plasma optical emission spectroscopy (ICP-OES) have revealed that the ratios of Ga to N and Zn to O in the as-prepared material are close to unity and that the N and O concentrations increase with the Ga and Zn concentrations, respectively.<sup>80</sup> The atomic composition of (Ga<sub>1-x</sub>Zn<sub>x</sub>)-(N<sub>1-x</sub>O<sub>x</sub>) is controllable by changing the nitridation conditions.<sup>81</sup> Figure 3 shows XRD patterns of samples with various compositions. Figure 4 shows a typical time course of overall water splitting on (Ga<sub>1-x</sub>Zn<sub>x</sub>)(N<sub>1-x</sub>O<sub>x</sub>) (x = 0.12) loaded with 5 wt % RuO<sub>2</sub> under visible irradiation ( $\lambda > 400$  nm). No reaction took place without irradiation, whereas both H<sub>2</sub> and O<sub>2</sub> evolved steadily and stoichiometrically upon irradiation in the visible region. Although it is known that O<sub>2</sub> evolution occurs on a ZnO electrode as a result of degradation when employed as a photoanode for water oxidation



**Fig 4. Typical time course of overall water splitting on 5 wt % RuO<sub>2</sub>-loaded (Ga<sub>1-x</sub>Zn<sub>x</sub>)(N<sub>1-x</sub>O<sub>x</sub>) (x = 0.12) under visible light ( $\lambda > 400$  nm). Reaction conditions: 0.3 g of catalyst and 390 mL of distilled water; high-pressure mercury lamp light source (450 W); Pyrex inner irradiation-type reaction vessel with aqueous NaNO<sub>2</sub> filter.**

#### IV. RESULTS AND CONCLUSIONS

A range of non-oxide materials for photocatalytic water splitting and we found that (Oxy)nitrides and oxysulfides are function as stable photocatalysts for water reduction and oxidation under visible irradiation, and the (Ga<sub>1-x</sub>Zn<sub>x</sub>)(N<sub>1-x</sub>O<sub>x</sub>) and (Zn<sub>1+x</sub>Ge)-(N<sub>2</sub>O<sub>x</sub>) solid solutions have been shown to achieve water splitting under visible light without noticeable degradation. As all of the successful photocatalysts developed for overall water splitting in the past 30 years are comprised solely of metal oxides and are largely ineffective under visible light, the discovery of non-oxide photocatalysts achieving the same function is expected to reinvigorate research on photocatalysts for solar energy conversion.

We suggested that a tentative goal for research on hydrogen production via solar-driven overall water splitting using a particulate photocatalyst is to develop a stable material that can achieve quantum efficiency of 30% at 600 nm. If such a photocatalytic system can be successfully constructed, the solar-to-hydrogen energy conversion efficiency is estimated to be ca. 5%, which is still lower than that achieved by PEC cells. Nevertheless, such a goal is considered to be a good starting point for practical application, given the simple and scalable nature of this approach. The state of the art in this field is, at most, quantum efficiency of a few percent at wavelengths as long as 500 nm. Therefore, more efficient photocatalytic materials with a band gap as narrow as 2 eV (corresponding to 600 nm) will need to be developed. At the same time, the reaction kinetics in photocatalysis should be investigated as a means of refining the materials to maximize efficiency and optimize preparation.

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