Communication

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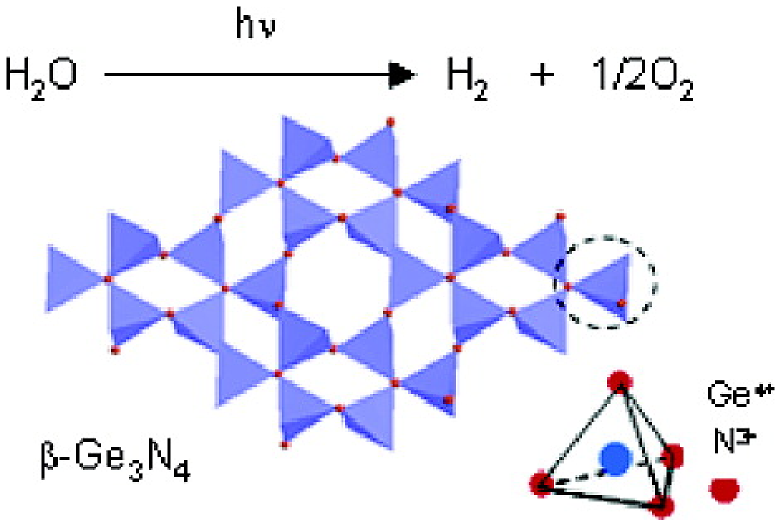
J. Am. Chem. Soc., **2005**, 127 (12), 4150-4151• DOI: 10.1021/ja042973v • Publication Date (Web): 08 March 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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COMMUNICATIONS

RuO_2-Loaded β-Ge_3N_4 as a Non-Oxide Photocatalyst for Overall Water Splitting

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Photocatalytic reactions have been studied extensively in recent years from the viewpoint of environmental accountability and energy conversion. For environmental purposes, TiO_2 with anatase and rutile crystal structures has been dominantly used because of its superior material and economic properties. In recent research, modified TiO_2, such as N-doped TiO_2, has been examined in order to extend the absorption edge into the visible light region.[1] In application to energy conversion, where research was initially triggered by the potential of TiO_2-based photoelectrochemical reactions for the decomposition of water into H_2 and O_2,[2] a range of materials have been examined as powder photocatalysts. These materials include transition metal oxides containing metal ions of Ti^{4+}, Zr^{4+}, Nb^{5+}, or Ta^{5+} with d^0 electronic configuration[3−8] and typical metal oxides having metal ions of Ga^{3+}, In^{3+}, Ge^{4+}, Sn^{4+}, or Sb^{5+} with d^{10} electronic configuration.[9−11] Thus, the group of successful photocatalysts for overall water splitting is comprised solely of metal oxide-based systems. Although some non-oxide materials, such as CdS and CdSe, have been examined, particularly for visible light-driven catalysts, successful photocatalytic systems have yet to be achieved, primarily due to inherent instability of the materials. Carefully designed photoelectrochemical devices, such as monolithic $GaInP_2$/GaAs tandem cells, have also been reported to decompose water without an external bias[12] through a process involving macroscopically separated sites for H_2 and O_2 evolution. However, in view of the emphasis placed on large-scale hydrogen production, powder photocatalyst systems would be much simpler and have greater applications.[13]

Our group recently reported oxynitrides including early transition metal cations with d^0 electronic configuration, such as Ta_3N_5,[14] TaON[15], and $LaTiO_2N$,[16] as potential candidates for overall water splitting under visible light. However, overall water splitting over those materials has yet to be achieved, probably due to the presence of significant amounts of defects in the bulk and surfaces of the materials.

In this paper, β-Ge_3N_4, a nitride of a typical metal with d^{10} electronic configuration, is reported to photocatalyze water into hydrogen and oxygen when combined with RuO_2 nanoparticles.

A single phase of β-Ge_3N_4 was prepared from commercially available GeO_2 powder (Kanto Chemical Co., 99.99%) by nitridation under atmospheric NH_3 flow (100 mL/min) at 1153 K for 10 h. The crystal structure of the product was identified by X-ray diffraction analysis. β-Ge_3N_4 was dispersed with RuO_2 according to our previous method.[9−11]

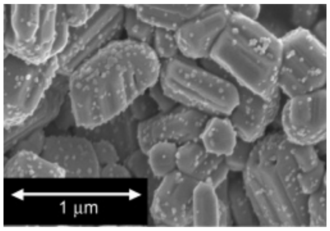

Figure 1. SEM image of RuO_2-loaded β-Ge_3N_4.

β-Ge_3N_4 alone exhibits little photocatalytic activity for water decomposition. However, when loaded with RuO_2, the material became photocatalytically active. The photocatalytic activity increased remarkably with increasing RuO_2 content to a maximum at about 1 wt %, with the activity dropping gradually at higher RuO_2 contents. Figure 1 shows a high-resolution scanning electron microscopy (SEM) image of the 1 wt % RuO_2-loaded β-Ge_3N_4. The image reveals RuO_2 particles with an average diameter of 20−50 nm distributed uniformly on the submicrometer particles of β-Ge_3N_4. The RuO_2 nanoparticles on the β-Ge_3N_4 surface function as H_2 production sites, as discussed in previous work.[10]

The photocatalytic performance of the RuO_2-loaded β-Ge_3N_4 was found to be strongly dependent on the pH of the aqueous solution. The activity increased as the pH decreases from pH 7.0, passing through a maximum at pH 0, and then decreasing. N_2 evolution, indicative of degradation of the nitride photocatalyst, was observed in the initial stage of reaction at pH 7.0, but was almost entirely depressed at pH 0. The total amount of N_2 produced (0.03 mmol) during 24 h of reaction was 0.3% of the amount of H_2 produced (11.2 mmol) (see below). This characteristic pH dependence of the RuO_2-loaded β-Ge_3N_4 photocatalyst deviates significantly from the general character of transition metal oxide-based photocatalysts. For example, NiO/$SrTiO_3$[17] and NiO/$NaTaO_3$[18] photocatalysts favor neutral or alkaline solutions for overall water splitting.

The photocatalytic activity of RuO_2-loaded β-Ge_3N_4 decreased considerably with each reaction run of 2 h, particularly in the initial period, but with prolonged light irradiation relatively stable photocatalytic performance was achieved, as shown in Figure 2. The H_2/O_2 production ratio throughout these reactions was the stoichiometric ratio of 2, within experimental error. The total amount of H_2 evolved over 24 h was 11.2 mmol, greater than the amount of catalyst (0.5 g, 1.8 mmol of β-Ge_3N_4). These results clearly demonstrate that RuO_2-loaded β-Ge_3N_4 is a photocatalyst suitable for overall water splitting. It is estimated from the comparison with the reported value of $NaTaO_3$[18] that the quantum efficiency of water splitting on Ge_3N_4 at around 300 nm is ca. 9%.

The X-ray diffraction patterns of the photocatalysts before and after the 24 h reaction were essentially the same. Furthermore, the X-ray photoelectron spectra of the Ge3d, N1s, Ru3p, and O1s levels

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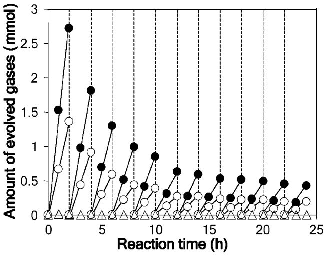

Figure 2. Time course of overall water splitting on RuO_2-loaded β-Ge_3N_4. The system (0.5 g of catalysts in 390 cm^3 aqueous solution adjusted to pH 0 by H_2SO_4) was evacuated every 2 h, and the reaction was continued to observe the change in activity. The reaction was performed in a quartz reaction vessel with internal irradiation from a high-pressure mercury lamp (450 W): ● H_2, ○ O_2, △ N_2.

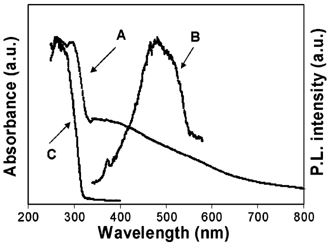

Figure 3. (A) Diffuse reflectance absorption spectrum, (B) photoluminescence spectrum under 300 nm excitation, and (C) excitation spectrum monitored at 480 nm at 77 K for β-Ge_3N_4.

did not change noticeably during the reaction except for an increase in the shoulder peak of O1s at ca. 529 eV. The used photocatalyst for 24 h was simply treated at 673 K for 5 h in air, and it was found that the activity recovered to 60−80% of the initial activity of Figure 2 (reaction time 0−2 h). This result suggests that one of the reasons for the decay of the photocatalytic activity is the loosened interface connection between RuO_2 nanoparticles and Ge_3N_4, leading to inefficient electron transfer.

Figure 3 shows the ultraviolet−visible (UV−vis) diffuse reflectance spectrum and emission and excitation spectra for β-Ge_3N_4. Two absorption bands are apparent in the diffuse reflectance spectrum, a strong absorption in the ultraviolet region below 340 nm, and a broad absorption extending into the visible region. The excitation of β-Ge_3N_4 with 300 nm photons at 77 K induced a photoluminescence peak at 480 nm. The edge of the excitation spectrum at about 320 nm is almost coincident with the edge of the emission spectrum. The band gap of β-Ge_3N_4 is estimated to be 3.8−3.9 eV. The absorption at longer wavelengths of up to 700−800 nm is regarded to be due to impurities and defect sites. Such impurities or defects are attributed to the reduced Ge species (Ge^0, Ge^{2+}) because the present nitridation condition is a rather reductive atmosphere. No significant evolution of H_2 or O_2 was observed under the irradiation of longer wavelengths.

The electronic structure of β-Ge_3N_4 was investigated by plane wave density functional theory (DFT) calculations. Figure 4 shows the energy band dispersion and density of states (DOS). The DOS indicates that the top of the valence bands consist of N2p orbitals, whereas the bottom of the conduction bands is composed of hybridized Ge4s4p orbitals. The band gap of β-Ge_3N_4 is estimated to be 2.1 eV (the band gap calculated by DFT was smaller than that obtained experimentally, which is frequently pointed out as a common feature of DFT calculations). The band structure indicates that charge transfer upon photoexcitation occurs from the N2p orbitals to the hybridized Ge4s4p orbitals. Oxidation of water to form O_2 over existing metal-oxide photocatalysts occurs as a result of contributions from photoexcited holes in the valence bands consisting of O2p orbitals. For the present catalyst, however, the N2p orbitals in the valence band are also able to generate photoexcited holes, which can contribute to the photocatalytic oxidation of water. Two other calculations with the plane wave DFT[19] and LMTO-ASA[20] methods were reported, and wider band gaps were obtained. In the latter, the projected density states were also calculated, which are close to our results.

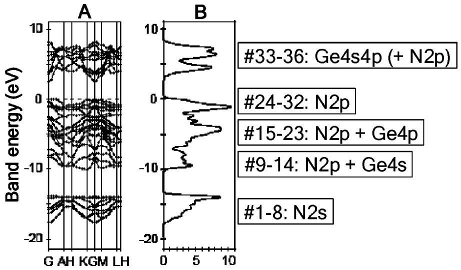

Figure 4. DFT calculations for β-Ge_3N_4: (A) energy band dispersion, and (B) density of states.

In summary, β-Ge_3N_4 with dispersed RuO_2 was found to act as a photocatalyst for the decomposition of H_2O into H_2 and O_2, representing the first successful example of a non-oxide photocatalyst for overall water splitting. Although further research on other metal nitrides and oxynitrides with d^{10} configurations is required and the mechanisms of photocatalysis need to be investigated based on detailed electronic and geometric structures, the finding that d^{10} metal nitrides are active for water decomposition presents important new possibilities for photocatalysis under visible light, as there are a wide variety of metal nitrides and oxynitrides that absorb light in that region. The present result is therefore very encouraging and is expected to lead to the development of a new group of photocatalysts for overall water splitting.

Acknowledgment. This work was supported by the Solution Oriented Research for Science and Technology (SORST) program of the Japan Science and Technology (JST) Corporation, and funded in part by a Grant-in-Aid for Scientific Research in Priority Areas (15033229) from The Ministry of Education, Culture, Sports, Science and Technology of Japan.

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JA042973V