Zinc and Titanium Spinel Oxynitride ($Zn_xTiO_yN_z$) as a d^0–d^{10} Complex Photocatalyst with Visible Light Activity

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The spinel-type oxynitride of zinc and titanium ($Zn_xTiO_yN_z$) reduces H^+ to H_2 and oxidizes H_2O to O_2 in the presence of a sacrificial electron donor and acceptor under visible light irradiation ($\lambda > 420$ nm). $Zn_xTiO_yN_z$ is a d^0–d^{10} complex oxynitride photocatalyst that has the potential to be active for water splitting under visible light.

Over the past three decades, photocatalytic water decomposition has remained an attractive challenge as a means of energy conservation through the efficient use of solar energy. The present authors have reported that some oxynitrides containing metal cations with d^0 or d^{10} electronic configurations are potentially effective materials for photocatalytic water splitting.[1–4] Particularly, $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$[3] and $(Zn_{1+x}Ge)(N_2O_x)$[4] achieve stoichiometric water decomposition to H_2 and O_2 under irradiation at visible wavelengths up to 500 nm. On the other hand, there are few reports on the photocatalytic activity of d^0–d^{10} complex type oxynitrides, although such materials have the potential to be active under visible light as photocatalysts for water splitting. Recently, Grasset et al. prepared colored "ZnTiON" powders and films and mentioned briefly the photodegradation of an aqueous methylene blue solution on the films under visible irradiation.[5,6] In the present study, the photocatalytic activity of zinc (d^{10}) and titanium (d^0) oxynitride ($Zn_xTiO_yN_z$) powder for water decomposition under visible irradiation is investigated.

$Zn_xTiO_yN_z$ was obtained by ammonolysis of an oxide precursor prepared by the polymerized complex method. In a typical synthesis, 0.0412 mol of $Ti[OCH(CH_3)_2]_4$ was hydrolyzed with 111 mL of water, followed by the addition of 0.618 mol citric acid, 0.0824 mol $Zn(NO_3)_2 6H_2O$, and 2.47 mol ethylene glycol. With heating at 453 K under continuous stirring, the suspension became transparent in 30 min, eventually yielding a highly viscous gel. The gel was carbonized at 673 K and then calcined in air to remove carbon. The obtained oxide precursor was finally nitrided at 973–1123 K for 0.5–10 h under 100 $mL \cdot min^{-1}$ NH_3 flow.

Photocatalytic reactions were carried out in a Pyrex reaction vessel connected to a closed gas circulation and evacuation system. $Zn_xTiO_yN_z$ obtained by nitridation at 1023 K for 4 h was used as the test photocatalyst sample. Photoreduction of H^+ to H_2 was performed in an aqueous 10 vol % methanol solution (200 mL) containing 0.20 g of the oxynitride loaded with 1.0 wt % Pt. The Pt was loaded by impregnation from an H_2PtCl_6 aqueous solution followed by reduction under an H_2 atmosphere at 473 K. Photooxidation of H_2O to O_2 was performed in an aqueous solution of 0.01 M $AgNO_3$ (200 mL) containing 0.20 g of the oxynitride and 0.20 g La_2O_3. La_2O_3 was added to prevent the pH from decreasing during the reaction. The light source for irradiation was a 300-W Xe lamp equipped with cutoff filters ($\lambda > 420$ nm).

The X-ray diffraction (XRD) patterns of the $Zn_xTiO_yN_z$ powder were found to be almost identical to literature data for inverse spinel type Zn_2TiO_4 except for a slight shift of diffraction peaks to higher 2θ angle with the increase in duration of nitridation. It was confirmed by energy-dispersive X-ray spectroscopy (EDX) that the Zn/Ti ratio of $Zn_xTiO_yN_z$ became smaller with increasing nitridation time and temperature. Composition of $Zn_xTiO_yN_z$ obtained by nitridation at 1023 K for 4 h was roughly estimated to be $Zn_{1.64}TiO_{3.26}N_{0.35}$ by EDX and nitrogen oxygen analysis. The absorption edges of $Zn_xTiO_yN_z$ shifted to longer wavelengths with increasing nitridation time and temperature, although excessive nitridation caused partial reduction of Ti^{4+}, as confirmed by ultraviolet–visible diffuse reflectance spectra (DRS) and X-ray photoelectron spectroscopy (XPS).

Figure 1 shows the time course of H_2 evolution under visible irradiation ($\lambda > 420$ nm). H_2 evolved steadily at a rate of 0.08 $\mu mol \cdot h^{-1}$ under irradiation, and the evolution of O_2 and N_2 was not observed at any time during the reaction. These results indicate that $Zn_xTiO_yN_z$ is essentially stable during the H_2 evolution reaction, providing steady photocatalytic reduction of water in the presence of methanol as an electron donor.

Figure 2 shows the time course of O_2 evolution under visible irradiation ($\lambda > 420$ nm). The initial rate of O_2 evolution was estimated to be 112 $\mu mol \cdot h^{-1}$, and the reaction was initially accompanied by the production of a small amount of N_2 (8 μmol). The nitrogen is thought to derive from the competing oxidation of N^{3-} in $Zn_xTiO_yN_z$ to N_2, that is, the photoexcited holes oxidize both $Zn_xTiO_yN_z$ and water. The evolution of O_2 ceased

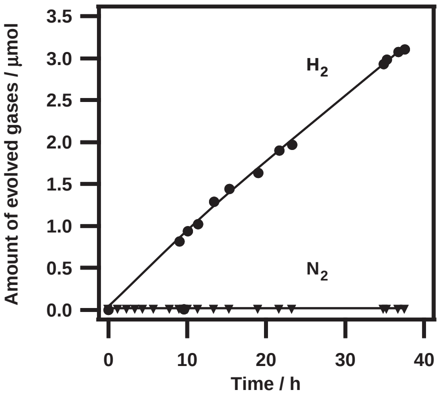

Figure 1. Time course of H_2 evolution under visible irradiation ($\lambda > 420$ nm). Pt-loaded $Zn_xTiO_yN_z$, 0.20 g; 10 vol % methanol solution, 200 mL.

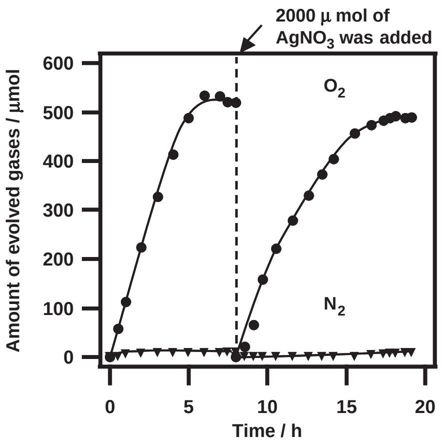

Figure 2. Time course of O_2 evolution under visible irradiation ($\lambda > 420$ nm). $Zn_xTiO_yN_z$, 0.20 g; La_2O_3, 0.20 g; 0.01 M $AgNO_3$ solution, 200 mL.

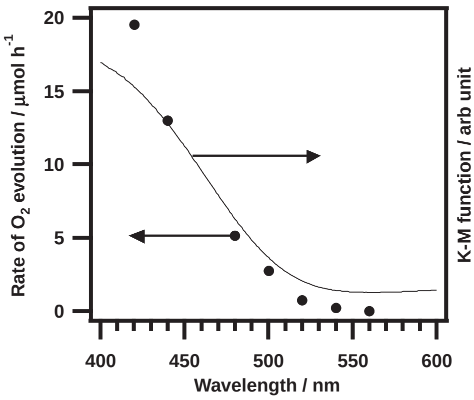

Figure 3. Dependence of initial O_2 evolution rate on cutoff wavelength of incident light. UV–vis DRS trace of the $Zn_xTiO_yN_z$ sample is also shown. $Zn_xTiO_yN_z$, 0.20 g; La_2O_3, 0.20 g; 0.01 M $AgNO_3$ solution, 200 mL.

after several hours of reaction because of consumption of Ag^+ introduced as an electron acceptor. The amount of O_2 evolved (ca. 500 μmol) corresponds to the amount of O_2 that could be evolved in association with the reduction of Ag^+ in the solution (2000 μmol), indicating that the oxidation of water to O_2 and the reduction of Ag^+ to metallic Ag proceeded stoichiometrically. Subsequent addition of 2000 μmol $AgNO_3$ to the exhausted solution resulted in further photocatalytic evolution of O_2 at ca. 80 μmol·h^{-1} with negligible N_2 production. The amount of O_2 produced in the second reaction also reached 500 μmol. XRD analysis indicated no significant changes in the powder upon reaction except for the appearance of metallic Ag. These results suggest that $Zn_xTiO_yN_z$ is a stable and highly active photocatalyst for the oxidation of water to O_2 under visible light. The slower rate of O_2 evolution in the second reaction run is probably due to the deposition of metallic Ag on the surface of the $Zn_xTiO_yN_z$ particles.

Figure 3 shows the relationship between the photocatalytic activity for water oxidation and the cutoff wavelength of incident light for the $Zn_xTiO_yN_z$ sample. The DRS trace is also shown. Absorption edge wavelength of the $Zn_xTiO_yN_z$ was estimated to be approximately 540–550 nm from the DRS trace. Photocatalytic O_2 evolution from the $AgNO_3$ solution was observed at wavelengths as long as 540 nm, although the activity was markedly lower than that at 420 nm. No O_2 evolution was observed under irradiation at wavelengths longer than 560 nm. These results are justified by the absorption edge wavelength of the $Zn_xTiO_yN_z$. In this system, photoexcited electrons reduce Ag^+ to metallic Ag, while photoexcited holes oxidize H_2O to O_2 under irradiation at wavelength as long as 540 nm. Light absorption by reduced titanium species did not appear to contribute to photocatalysis. Irradiation at wavelengths longer than 560 nm does not induce the photogeneration of electrons and holes, and thus the photocatalytic reaction does not proceed. Consequently, it is concluded that the photooxidation of water proceeds via the band-gap transition of $Zn_xTiO_yN_z$.

Based on the results of the photocatalytic reaction in the presence of sacrificial reagents, it is expected that $Zn_xTiO_yN_z$ has an appropriate band structure for water decomposition. However, the photocatalytic activity for H_2 evolution from aqueous methanol solution is relatively low, whereas the evolution of O_2 in the presence of Ag^+ ion proceeds efficiently over $Zn_xTiO_yN_z$. Such slow rates of H_2 production are commonly observed for oxynitride photocatalysts. In general, an oxynitride synthesized at high temperature contains relatively high densities of N vacancies in the crystal, producing n-type semiconductor behavior that acts as a potential barrier hindering electron transfer between the oxynitride surface and the solution.[7] To achieve efficient photocatalytic water splitting over $Zn_xTiO_yN_z$, it is necessary to improve the photocatalytic activity for H_2 evolution, which is currently under investigation. Successful modification of $Zn_xTiO_yN_z$ would open a new frontier of materials chemistry for photocatalytic water splitting, because $Zn_xTiO_yN_z$ is a novel type of functional material, a d^0–d^{10} complex oxynitride.

In summary, a spinel oxynitride containing zinc and titanium ($Zn_xTiO_yN_z$) displayed photocatalytic activity for reduction and oxidation of water in the presence of a sacrificial electron donor and acceptor under irradiation at visible wavelengths (420–540 nm).

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