$TiN_xO_yF_z$ as a Stable Photocatalyst for Water Oxidation in Visible Light (<570 nm)

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$TiN_xO_yF_z$ prepared from $(NH_4)_2TiF_6$ and SiO_2 under NH_3 flow at 773 K has a bandgap-absorption edge at about 570 nm and functions as a stable photocatalyst for water oxidation.

An important topic in the advancement of heterogeneous photocatalysis is the development of materials that are both stable and nontoxic yet provide sufficient photoresponse in the visible light region. Although TiO_2 is at present the most widely used photocatalyst for various applications, it is activated only in the ultraviolet region (<400 nm).[1]

The present authors recently reported that some (oxy)nitrides such as Ta_3N_5 ($\lambda \leq 600$ nm),[2] TaON ($\lambda \leq 500$ nm)[3] and $LaTiO_2N$ ($\lambda \leq 600$ nm)[4] function as stable visible light-driven photocatalysts for the reduction of H^+ to H_2 and oxidation of H_2O to O_2 in the presence of appropriate sacrificial reagents. The common feature of these (oxy)nitrides is that the bottoms of the conduction bands consist of empty d orbitals of Ta^{5+} and Ti^{4+} cations, while the tops of the valence bands consist of N2p orbitals, with a small contribution from O2p orbitals in the case of oxynitrides.

In this paper, $TiN_xO_yF_z$ is reported as a novel stable photocatalyst for water oxidation under visible light irradiation. C. Wüstefeld et al.[5] reported the synthesis of TiNF with a very similar crystal structure to TiO_2 anatase from $(NH_4)_2TiF_6$ under NH_3 flow at 773 K, producing a green material that was very stable in both acidic and basic media. Density function theory (DFT) calculations by the present authors for such TiNF structure suggest a semiconducting property with a valence band consisting of N2p orbitals and a conduction band formed by empty Ti3d orbitals. TiNF therefore appears to be promising as a visible light-responsive photocatalyst.

Following the procedure detailed in the literature,[5] the authors synthesized TiNF, obtaining an olive-green product that was revealed by X-ray diffraction (XRD) analysis to have an exact anatase structure. Elemental analysis of the product, however, revealed that the material contained a large amount of oxygen, with a composition of $TiN_{0.13}O_{1.78}F_{0.05}$. The source of oxygen contamination appeared to be the quartz tube reactor used for preparation. When using a Ni tube inserted into the reactor to prevent corrosion of the quartz, no product was obtained because the sublimation temperature of $(NH_4)_2TiF_6$, about 650 K, was much lower than the preparation temperature of 773 K. After careful examination, it was concluded that to obtain a solid product with anatase structure, it is necessary to add an oxygen source such as SiO_2 to the precursor. In the present experiments, an oxygen source was intentionally added to $(NH_4)_2TiF_6$ then subjected to NH_3 flow in a quartz reactor sealed with a Ni tube.

Various $TiN_xO_yF_z$ samples were prepared, using a variety of oxide powders as oxygen sources, including MgO, Al_2O_3, and GeO_2. A sample prepared with SiO_2 exhibited the highest photocatalytic activity for water oxidation. In the following synthesis, $TiN_xO_yF_z$ samples were prepared from mixtures of $(NH_4)_2TiF_6$ and SiO_2 powder (particle size; ca. 10 nm) at various ratio ($SiO_2/(NH_4)_2TiF_6 = 0.5$, 1 and 2) and examined in detail. The product consisted of well-crystallized particles of 1–5 μm in size, with no noticeable difference between the XRD patterns of the $TiN_xO_yF_z$ samples and TiO_2anatase. A small amount of $TiOF_2$ was also detected as an impurity phase at $SiO_2/(NH_4)_2TiF_6$ ratios of 0.5 and 1. No Si was detected by energy dispersive X-ray (EDX) analysis for small amounts of added SiO_2 ($SiO_2/(NH_4)_2TiF_6 = 0.5$ or 1), suggesting that the Si species volatilized as fluorides associated with decomposition of the precursor. The compositions of the various $TiN_xO_yF_z$ samples are summarized in Table 1. It should be noted that O^{2-} is the dominant anion for all samples, and the atomic ratio N/F is not unity, indicating the existence of considerable numbers of defect sites. This $TiN_xO_yF_z$ materials is denoted here as TiNOF.

Table 1. Compositions of TiNOF prepared from mixtures of $(NH_4)_2TiF_6$ precursor and SiO_2 at various molar ratios

$SiO_2/(NH_4)_2TiF_6$ ratio	Ti	N	O	F
0.5	1	0.07	1.71	0.37
1	1	0.05	1.64	0.58
2	1	0.01	1.95	0.07

Recently, N-doped TiO_2, $TiO_{2-x}N_x$, was reported as a visible light-responsive photocatalyst.[6] The amount of N in the N-doped material is more than ten-fold lower than in the present TiNOF, and the physicochemical and photocatalytic properties are very different, as shown below.

Figure 1 shows the UV-vis diffuse reflectance spectra of TiNOF ($TiN_{0.07}O_{1.71}F_{0.37}$), $TiO_{2-x}N_x$ ($x = 0.006$) and TiO_2 anatase. $TiO_{2-x}N_x$ was obtained by nitriding TiO_2 anatase under a flow of NH_3 at 773 K for 10 h. The absorption edge of TiNOF occurs at ca. 570 nm, and the bandgap energy is estimated to be about 2.2 eV. There is a featureless absorption above 600 nm, attributable to a small amount of Ti^{3+} species produced under the present preparation conditions. The absorption of $TiO_{2-x}N_x$ in the visible light region is much weaker than that of TiNOF, and the absorption edge of TiNOF is sharp while that of $TiO_{2-x}N_x$ is indistinct. One of the reasons for these differences is the dissimilar

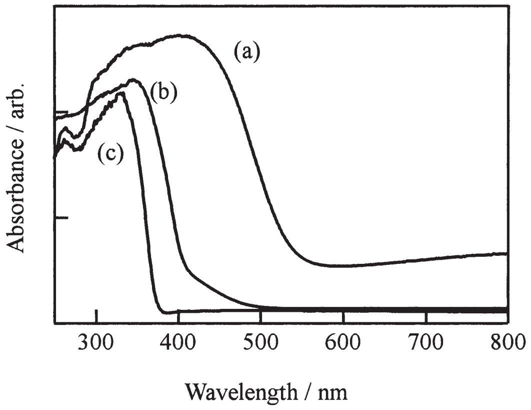

Figure 1. UV-vis DR spectra of Ti-based compounds: (a) TiNOF, (b) $TiO_{2-x}N_x$, (c) anatase-TiO_2. TiNOF was prepared from a 1:0.5 (molar) mixture of $(NH_4)_2TiF_6$ precursor and SiO_2.

amounts of nitrogen in the two samples. Another possibility is the difference between nitrogen sites; XPS gives a strong N1s peak at 396 eV for TiNOF, and weak peaks at 400 eV and 396 eV for $TiO_{2-x}N_x$.

Figure 2 shows the progress of O_2 evolution on TiNOF ($TiN_{0.07}O_{1.71}F_{0.37}$) and $TiO_{2-x}N_x$ under the irradiation by Xe lamp (300 W) through a cut-off filter ($\lambda > 420$ nm) in an aqueous $AgNO_3$ (0.01 M) solution at pH 8.5. It was confirmed that TiO_2 anatase did not show any photocatalytic activities under the present illumination condition. No reaction took place in the dark. Upon irradiation, O_2 evolution occurred on TiNOF, the rate of which decreased slightly with reaction time, probably due to a decrease in Ag^+ concentration and the aggregation of metallic Ag particles onto the catalyst surface. The quantum efficiency of this reaction was estimated to be approximately 1% (420 nm $< \lambda <$ 570 nm). In the initial stages of the reaction, a small amount of N_2 evolution due to the oxidation of N^{3-} in TiNOF to N_2 by the photogeneration of holes was detected. Similar N_2 evolution was observed for the cases of (oxy)nitrides, attributed to the oxidation of surface nitrogen species. The total amount of evolved N_2 was 1.8 μmol, which was much lower than the amount of evolved O_2, and N_2 evolution did not continue after the initial stage.

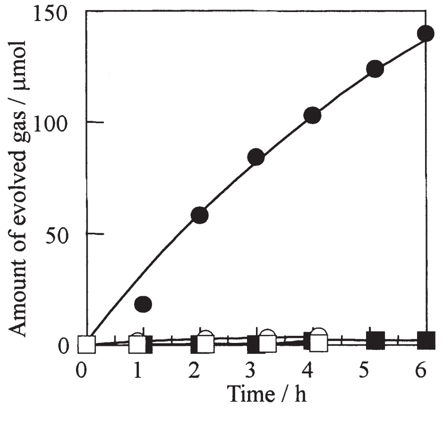

Figure 2. Progress of O_2 and N_2 evolution on TiNOF (●, O_2; ■, N_2) and TiN_xO_{2-x} (○, O_2; □, N_2): 0.1 g of catalyst; 200 ml of 0.01 M $AgNO_3$ solutions; 300 W Xe lamp irradiation ($\lambda > 420$ nm). TiNOF was prepared from 1:0.5 (molar) mixture of $(NH_4)_2TiF_6$ precursor and SiO_2.

These results indicate that TiNOF functions as a stable visible light-driven photocatalyst with good water oxidation potential. In comparison with (oxy) nitrides, it is noticeable that TiNOF evolves O_2 in an aqueous acidic solution with negligible N_2 evolution, although the rate of O_2 evolution was lower (5 μmol h^{-1}) than under basic conditions. The O_2 evolution rate on TiNOF decreased with increasing $SiO_2/(NH_4)_2TiF_6$ ratio in the precursor, thought to be due to the decrease in nitrogen content.

Under visible light irradiation, platinized TiNOF also evolved H_2 from an aqueous methanol solution, although the rate of H_2 evolution (typically 0.2 μmol h^{-1}) was very low compared to O_2 evolution.

O_2 evolution on $TiO_{2-x}N_x$ under the same reaction conditions is negligible, as shown in Figure 2. H_2 evolution on platinized $TiO_{2-x}N_x$ was also negligible in an aqueous methanol solution.

In summary, TiNOF with an anatase crystal structure was prepared by nitriding a $(NH_4)_2TiF_6$ precursor with added SiO_2 powder as an oxygen source. The nitrogen, oxygen and fluorine contents in the product were not controllable under the present preparation conditions, however, good absorption in the visible region ($\lambda < 570$ nm) was obtained to drive water oxidation to O_2 in the presence of Ag^+ cations without noticeable catalyst degradation. TiNOF is therefore a promising visible light-driven photocatalyst. Further improvement of the preparation method for TiNOF is currently being pursued.

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References and Notes

1 P. Pichat, in "Handbook of Heterogeneous Catalysis," ed. by G. Etrl, H. Knözinger, and T. Weitkamp, Wiley-VCH, Weinheim (1997), Vol. 4, p 2111; A. Mills and S. L. Hunte, *J. Photochem. Photobiol.*, **108**, 1 (1997); L. Palmisano and A. Sclafani, in "Heterogeneous Photocatalysis," ed. by M. Schiavello, John Wiley & Sons, Inc., West Sussex (1997), p 109.

2 G. Hitoki, A. Ishikawa, T. Takata, J. N. Kondo, M. Hara, and K. Domen, *Chem. Lett.*, **2002**, 736.

3 G. Hitoki, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, and K. Domen, *Chem. Commun.*, **2002**, 1698.

4 A. Kasahara, K. Nukumizu, G. Hitoki, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, and K. Domen, *J. Phys. Chem. A*, **106**, 6750 (2002).

5 C. Wüstefeld, T. Vogt, U. Löchner, J. Strähle, and H. Fuess, *Angew. Chem., Int. Ed. Engl.*, **27**, 929 (1988).

6 R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, *Science*, **293**, 269 (2001).