Nitrogen/fluorine codoped rutile titanium(IV) oxide as a visible-light-driven photocatalyst for water oxidation

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Abstract: Nitrogen/fluorine codoped rutile TiO2 (TiN6O6F6) was synthesized and its photocatalytic activity for oxygen evolution from AgNO3 aqueous solution was examined. Synthesized TiN6O6F6 showed higher activity than the non-doped TiO2 and only nitrogen doped TiO2 did under visible light (λ > 420 nm). The higher activity of TiN6O6F6 was primarily attributed to the enhanced visible light absorption due to enhanced introduction of nitrogen by fluorine codoping.

Keywords: Nitrogen/fluorine codoping, Photocatalyst, Water oxidation.

1. Introduction

Significant efforts have been made to develop a photocatalyst that functions under visible light. Nitrogen/fluorine codoping into anatase TiO2 allowed introduction of more nitrogen compared to only nitrogen-doped one, resulting in enhanced photocatalytic activity under visible light irradiation. On the other hand, it is well known that crystal structure affects the functionality of the given material. This work focuses on the nitrogen/fluorine codoping of rutile TiO2 (R-TiO2), which is another representative polymorph of TiO2. It was revealed that the nitrogen/fluorine codoped rutile TiO2 showed enhanced visible light absorption and higher photocatalytic activity, relative to only-nitrogen doped TiO2.

2. Experimental

Nitrogen/fluorine codoped rutile TiO2 (TiN6O6F6) was synthesized by nitriding mixture of R-TiO2 and (NH4)2TiF6. The TiO2 and (NH4)2TiF6 were mixed in an agate mortar and a pestle with various molar ratio using appropriate amount of methanol. The mixture was heated at 773 K for 1 h under a NH3 flow. For convenience, synthesized material is denoted as TiN6O6F6-C, where C stands for the nominal concentration of (NH4)2TiF6 in the mixture in the unit of mol%. TiN6O6F6-0 (873 K) was synthesized by nitriding R-TiO2 in the same manner at 873 K, without adding (NH4)2TiF6.

The synthesized materials were characterized by X-ray diffraction (XRD), diffuse reflectance spectra (DRS), elemental analysis, and X-ray absorption fine structure (XAFS). To gain the information about dynamics of photogenerated carriers, time-resolved absorption spectra (TAS) measurement was also conducted. Photocatalytic oxygen evolution from AgNO3 solution was measured by dispersing 50 mg of photocatalyst and 200 mg of La2O3 buffer, in 140 mL of 10 mM AgNO3 aqueous solution and irradiating visible light. 300 W xenon lamp fitted with CM1 mirror and L42 cutoff filters (λ > 420 nm) was used as light source. Analysis and quantification of evolved gases were conducted using a gas chromatograph.

3. Results and discussion

The XRD patterns of synthesized materials revealed that they consisted mainly of rutile TiO2 (Figure 1). Furthermore, diffraction peaks corresponding to rutile TiO2 show shoulders at the lower angles side for the materials synthesized with higher concentration of (NH4)2TiF6. This suggests that the anions are
This peak shift has been observed in nitrogen/fluorine codoped anatase TiO₂.² Although impurity phases emerge by the excess addition of (NH₄)₂TiF₆, samples prepared with C ≤ 20 did not show such distinct peaks, so that they are considered to be essentially single phase rutile. Elemental analysis also revealed the presence of nitrogen and fluorine in the obtained samples. Additionally, N K-edge XAFS measurement revealed that doped nitrogen are incorporated in oxygen site of the TiO₂ lattice.

Figure 2 shows the DRS of the synthesized samples. Samples synthesized using (NH₄)₂TiF₆ (C ≥ 10) showed more pronounced absorption in visible light region compared to TiN,O,F₀ and TiN,O,F₁₀ (873 K). Furthermore, the visible light absorption was more pronounced with increasing C value. It has been reported that the fluorine codoping with nitrogen into anatase TiO₂ enhances the nitrogen incorporation, which causes more visible light absorption.² Therefore, the pronounced visible light absorption in the TiN,O,F₂ is attributed to increased nitrogen content, which was also confirmed by elemental analysis.

Photocatalytic activity of TiN,O,F₂ for water oxidation was tested using AgNO₃ as a sacrificial electron acceptor (Table 1). The activity of TiN,O,F₁₀ (C ≥ 10) was higher than samples synthesized without fluorine source (TiN,O,F₀ and TiN,O,F₁₀ (873K)). The primary reason for the higher activity of TiN,O,F₁₀ (C ≥ 10) is thought to be the increase in visible light absorption. However, the decrease in the activity for C values higher than 15 suggests that there is another factor that affects the photocatalytic activity.

TiN,O,F₂ with various C values showed difference in carrier dynamics in TAS measurements. The C = 50 sample showed signals corresponding to deeply trapped electrons (≈5000 cm⁻³) and no free electrons (< 2000 cm⁻³). On the other hand, the C = 15 sample had less deeply trapped electrons, but more free electrons. Free electrons generally show higher reactivity compared to the trapped electrons.³,⁴ Thus, the decrease in the activity for C > 15 is most likely attributed to the less free electrons available for reaction and/or the presence of higher concentration of trap states.

4. Conclusions
Nitrogen/fluorine codoped rutile TiO₂ was successfully synthesized. Fluorine codoping enhanced nitrogen incorporation into rutile TiO₂ lattice. As a result, TiN,O,F₂ showed new absorption in visible light region. This new absorption band can be used for photocatalytic water oxidation. The highest activity of TiN,O,F₂ was about 5 times that of only-nitrogen doped rutile TiO₂.

References