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 TiO_2 ($TiN_xO_yF_z$) was synthesized and its photocatalytic activity for oxygen evolution from $AgNO_3$ aqueous solution was examined. Synthesized $TiN_xO_yF_z$ showed higher activity than the non-doped TiO_2 and only nitrogen doped TiO_2 did under visible light ($\lambda > 420$ nm). The higher activity of $TiN_xO_yF_z$ 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 TiO_2 allowed introduction of more nitrogen compared to only nitrogen-doped one, resulting in enhanced photocatalytic activity under visible light irradiation.[1,2] 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 TiO_2 (R-TiO_2), which is another representative polymorph of TiO_2. It was revealed that the nitrogen/fluorine codoped rutile TiO_2 showed enhanced visible light absorption and higher photocatalytic activity, relative to only-nitrogen doped TiO_2.

2. Experimental

Nitrogen/fluorine codoped rutile TiO_2 ($TiN_xO_yF_z$) was synthesized by nitriding mixture of R-TiO_2 and $(NH_4)_2TiF_6$. The TiO_2 and $(NH_4)_2TiF_6$ 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 NH_3 flow. For convenience, synthesized material is denoted as $TiN_xO_yF_z$_*C*, where *C* stands for the nominal concentration of $(NH_4)_2TiF_6$ in the mixture in the unit of mol%. $TiN_xO_yF_z$_0 (873 K) was synthesized by nitriding R-TiO_2 in the same manner at 873 K, without adding $(NH_4)_2TiF_6$.

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 $AgNO_3$ solution was measured by dispersing 50 mg of photocatalyst and 200 mg of La_2O_3, buffer, in 140 mL of 10 mM $AgNO_3$ aqueous solution and irradiating visible light. 300 W xenon lamp fitted with CM1 mirror and L42 cutoff filters ($\lambda > 420$ 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 TiO_2 (Figure 1). Furthermore, diffraction peaks corresponding to rutile TiO_2 show shoulders at the lower angles side for the materials synthesized with higher concentration of $(NH_4)_2TiF_6$. This suggests that the anions are incorporated into the rutile TiO_2 lattice, causing the change in lattice constants. This peak shift has been observed in nitrogen/fluorine codoped anatase TiO_2.[2] Although impurity phases emerge by the excess addition of $(NH_4)_2TiF_6$, samples prepared with $C \leq 20$ 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 TiO_2 lattice.

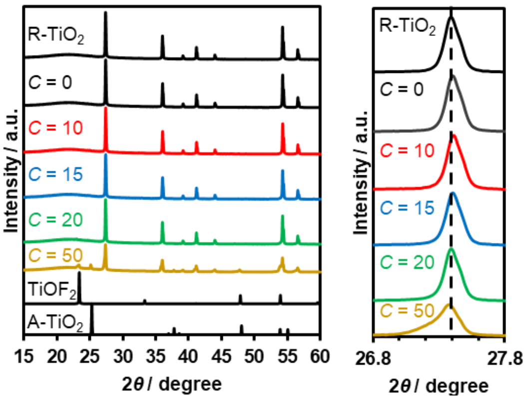

Figure 1. XRD patterns of $TiN_xO_yF_z\_C$.

Figure 2 shows the DRS of the synthesized samples. Samples synthesized using $(NH_4)_2TiF_6$ ($C \geq 10$) showed more pronounced absorption in visible light region compared to $TiN_xO_yF_z\_0$ and $TiN_xO_yF_z\_0$ (873 K). Furthermore, the visible light absorption was more pronounced with increasing C value. It has been reported that the fluorine codoping with nitogen into anatase TiO_2 enhances the nitrogen incorporation, which causes more visible light absorption.[2] Therefore, the pronounced visible light absorption in the $TiN_xO_yF_z$ is attributed to increased nitrogen content, which was also confirmed by elemental analysis.

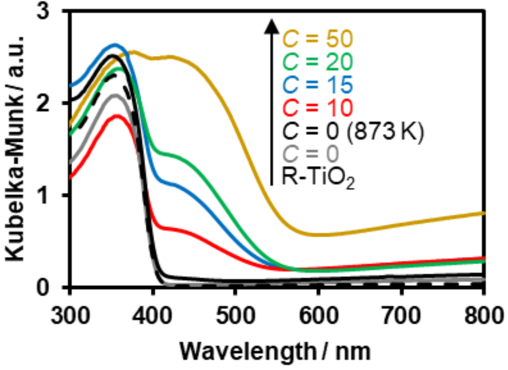

Figure 2. DRS of $TiN_xO_yF_z\_C$.

Photocatalytic activity of $TiN_xO_yF_z$ for water oxidation was tested using $AgNO_3$ as a sacrificial electron acceptor (Table 1). The activity of $TiN_xO_yF_z\_C$ ($C \geq 10$) was higher than samples synthesized without fluorine source ($TiN_xO_yF_z\_0$ and $TiN_xO_yF_z\_0$ (873K)). The primary reason for the higher activity of $TiN_xO_yF_z\_C$ ($C \geq 10$) 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.

Table 1. Photocatalytic activity of $TiN_xO_yF_z\_C$.

Entry	Sample	O_2 evolution rate / µmol h^{-1}
1	$R\text{-}TiO_2$	0.3
2	$TiN_xO_yF_z\_0$	0.5
3	$TiN_xO_yF_z\_0$ (873 K)	2.2
4	$TiN_xO_yF_z\_10$	4.9
5	$TiN_xO_yF_z\_15$	11.4 ± 1.3
6	$TiN_xO_yF_z\_20$	9.8
7	$TiN_xO_yF_z\_50$	4.8

Reaction conditions: Catalyst, 50 mg, La_2O_3, 200 mg, 10 mM $AgNO_3$ 140 mL, Light source: 300 W Xe lamp fitted with CM1 mirror and L42 cutoff filter ($\lambda > 420$ nm).

$TiN_xO_yF_z$ 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^{-1}) and no free electrons (< 2000 cm^{-1}). 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 TiO_2 was successfully synthesized. Fluorine codoping enhanced nitrogen incorporation into rutile TiO_2 lattice. As a result, $TiN_xO_yF_z$ showed new absorption in visible light region. This new absorption band can be used for photocatalytic water oxidation. The highest activity of $TiN_xO_yF_z$ was about 5 times that of only-nitrogen doped rutile TiO_2.

References

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