

# Preparation and characterizations of Fe- or Ni-substituted titania nanosheets as photocatalysts

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## Abstract

Fe- or Ni-substituted titania nanosheets have been synthesized by chemically exfoliating precursor layered titanates into colloidal single sheets. Obtained nanosheets were self-assembled via consecutive adsorption with polycations to produce multilayer ultrathin films, which exhibit photocatalytic properties. In the case of Fe system, UV absorption band was widened towards the visible light region in comparison with that of titania nanosheets of  $\text{Ti}_{0.9}\text{O}_2$ . © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Exfoliated nanosheets; Self-assembled ultrathin films; Layered titanates; Photocatalysis

## 1. Introduction

Titanium dioxide is well known not only because it acts as efficient photocatalysts to mineralize various types of harmful compounds [1–6], but also exhibits photo-induced superhydrophilic property [6]. However, as  $\text{TiO}_2$  absorbs only the UV light, there has been intensive research activities to develop titanium oxide photocatalysts which can operate effectively on visible light illumination.

It has been recognized in many industrial fields that fabrication of thin  $\text{TiO}_2$  films is very significant from the viewpoint of practical use. Although there are various kinds of method to produce thin films, one of the most attractive methods is a layer-by-layer chemical adsorption approach [7]. Using this technique, it is easy to prepare inorganic/organic nanocomposite films on various types of supports under mild conditions.

Recently we have reported that a layered protonic titanate,  $\text{H}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4\cdot\text{H}_2\text{O}$  ( $\square$ , vacancy), can be exfoliated into colloidal single sheets having thickness of 0.75 nm by being shaken with an aqueous solution containing bulky organic compounds [8–10]. The resulting titania nanosheet crystallites and polycations are layer-by-layer deposited onto a substrate to produce an ultrathin film which exhibited considerable spectral blue shift compared to bulk  $\text{TiO}_2$  and highly efficient UV absorption [11,12].

Delamination of isotopic layered titanates in which Ti sites are partially substituted with various transition metals is of great interest for preparation of new nano-sized semiconductors which can act as photocatalysts under visible light.

In the present paper, we report on Fe- or Ni-substituted layered titanate that can be exfoliated into single layer sheets. In addition, we describe the fabrication of thin films with these exfoliated materials and their photocatalytic properties.

## 2. Experimental

### 2.1. Preparation of Fe- or Ni-substituted titania nanosheets

A starting layered titanate,  $\text{K}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4$  and  $\text{K}_{0.8}\text{Ni}_{0.4}\text{Ti}_{1.6}\text{O}_4$  [13] was prepared by heating a mixture of  $\text{K}_2\text{CO}_3$ ,  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  or  $\text{NiO}$  (>99.9% purity) at 1373 K for 24 h. In order to compensate for the volatilization of potassium, an excess amount (~5%) of  $\text{K}_2\text{CO}_3$  was added in advance before calcination.

The titanates with Fe or Ni were converted into their protonic forms by being stirred in a HCl solution ( $1\text{ mol dm}^{-3}$ ) at ambient temperature for 24 h. After five cycles of acid exchange ( $24\text{ h} \times 5$ ), the samples were filtered, washed with a large amount of water to remove excess acid, and finally air-dried.

The resulting acid-exchanged form (0.4 g),  $\text{H}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4\cdot\text{H}_2\text{O}$  and  $\text{H}_{0.8}\text{Ni}_{0.4}\text{Ti}_{1.6}\text{O}_4\cdot\text{H}_2\text{O}$ , was shaken vigorously with a tetrabutylammonium hydroxide,  $(\text{C}_4\text{H}_9)_4\text{NOH}$  (TBAOH) solution ( $100\text{ cm}^3$ ) at ambient temperature for

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more than 10 days. The amount of TBAOH corresponds to 0.2–20-fold excess to the ion exchange capacity for  $\text{H}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4 \cdot \text{H}_2\text{O}$  and  $\text{H}_{0.8}\text{Ni}_{0.4}\text{Ti}_{1.6}\text{O}_4 \cdot \text{H}_2\text{O}$ .

## 2.2. Fabrication of multilayer ultrathin films of Fe- or Ni-substituted titania nanosheet

Experimental procedures to construct the multilayer films are as follows: A substrate such as quartz glass or Si wafer was primed with positively charged poly(ethylenimine) (PEI). (1) Dipping of the precoated substrate into the colloidal suspension of negatively charged Fe- or Ni-substituted titania nanosheets ( $0.08 \text{ g dm}^{-3}$ ,  $\text{pH} = \text{ca. } 9$ ) for 20 min; (2) washing with water; (3) immersion in an aqueous solution of poly(diallyldimethylammonium chloride) (PDDA) ( $20 \text{ g dm}^{-3}$  with  $0.5 \text{ mol dm}^{-3}$  NaCl,  $\text{pH} = \text{ca. } 9$ ) for 20 min; (4) washing with water. These steps (1)–(4) led to the self-assembly production of a one bilayer (Fe- or Ni-substituted titania nanosheets/PDDA).

## 2.3. Characterizations

X-ray diffraction (XRD) data were collected by a Rigaku Rint-2000S diffractometer ( $\text{Cu K}\alpha$ ). A relative humidity in the sample chamber can be controlled in the range 5–95%. The colloidal aggregates recovered by centrifugation were allowed to the XRD measurements at the humidity of 95%. UV–Vis absorption spectra were obtained by a Hitachi U-4000 spectrophotometer.

## 3. Results and discussion

### 3.1. Preparation and characterizations of Fe- or Ni-substituted titania nanosheets

Fig. 1 shows XRD patterns in the exfoliation process on contact with aqueous solutions of TBAOH. The XRD pattern for the protonic titanate of  $\text{H}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4 \cdot \text{H}_2\text{O}$  is shown in (a) as a comparison, indicates a lepidocrocite-like structure with the interlayer distance of 0.91 nm.

A stable suspension was obtained by treating the resulting solid with an aqueous TBAOH solution. XRD data for colloids of Fe-substituted titanates recovered by centrifugation clearly shows that the degree of swelling can be controlled by the molar ratio of tetrabutylammonium (TBA) ions over exchangeable protons in titanates ( $\text{TBA}^+/\text{H}^+$ ). In the case of  $\text{TBA}^+/\text{H}^+ = 20$  (b), sharp diffraction series attributable to a basal spacing of 4.5 nm were observed. This is largely expanded from original value of 0.91 nm for  $\text{H}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4 \cdot \text{H}_2\text{O}$  and can be explained by osmotic swelling or colloidal hydration. A large volume of the TBA solution is included into the gallery to compensate the negative charge of the host layer. By decreasing TBA concentrations,  $\text{TBA}^+/\text{H}^+ < 10$  (c), the interlayer expansion

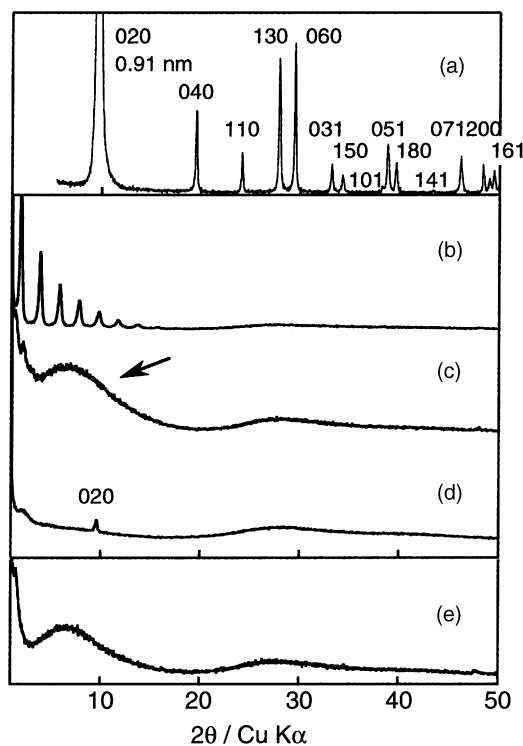


Fig. 1. XRD patterns for a protonic layered titanate: (a)  $\text{H}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4 \cdot \text{H}_2\text{O}$ , and a colloidal aggregate centrifuged from suspensions: (b)  $\text{H}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4 \cdot \text{H}_2\text{O}$ ,  $\text{TBA}^+/\text{H}^+ = 20$ ; (c)  $\text{H}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4 \cdot \text{H}_2\text{O}$ ,  $\text{TBA}^+/\text{H}^+ = 5$ ; (d)  $\text{H}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4 \cdot \text{H}_2\text{O}$ ,  $\text{TBA}^+/\text{H}^+ = 0.2$  and (e)  $\text{H}_{0.8}\text{Ni}_{0.4}\text{Ti}_{1.6}\text{O}_4 \cdot \text{H}_2\text{O}$ ,  $\text{TBA}^+/\text{H}^+ = 5$ .

proceeded further and finally a broad diffraction pattern was resulted. This broad diffraction envelope especially below  $2\theta = 15^\circ$  (shown by arrows) is quite similar to that observed for completely exfoliated  $\text{H}_{0.7}\text{Ti}_{1.825}\text{O}_{0.175}\text{O}_4 \cdot \text{H}_2\text{O}$  [8,9]. Therefore, the obtained pattern is due to the scattering from a disordered aggregate of exfoliated  $\text{H}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4 \cdot \text{H}_2\text{O}$ , suggesting that the layered structure was exfoliated into single layers, or Fe-substituted titania nanosheets. At  $\text{TBA}^+/\text{H}^+ < 1$ , e.g.  $\text{TBA}^+/\text{H}^+ = 0.2$  (d), the unreacted protonic titanate was observed. Thus we have concluded that the optimum conditions to produce the single layer nanosheets are  $1 < \text{TBA}^+/\text{H}^+ < 5$ .

Similar evidence for delamination was also obtained for the Ni-substituted system as shown in Fig. 1(e), although it was needed to remove an unexfoliated residue by mild centrifugation.

Fig. 2 shows the optical absorption spectra of the colloidal suspensions. The linear relationship or Lambert–Beer behavior indicates that the nanosheets are present in the suspension as individual colloidal particles. Note that the incorporation of Fe into nanosheets widens the UV absorption bands towards a visible light region as compared to the case for the pure titania nanosheets [10].

In the case of Ni substitution (b), the observed spectra look similar to that of the titania nanosheets at these con-

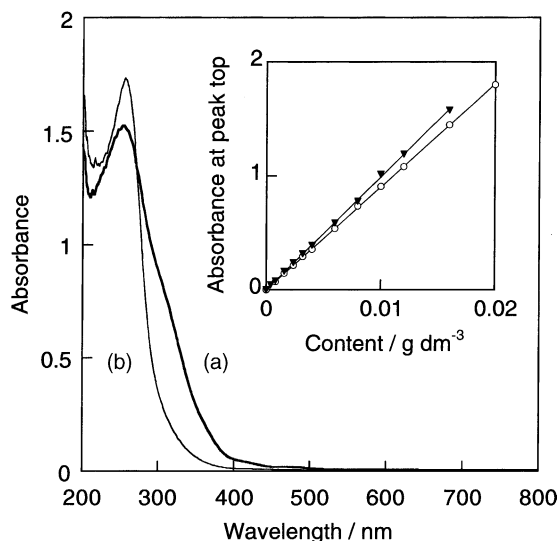


Fig. 2. Optical absorption spectra of the colloidal suspension of (a)  $\text{H}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4 \cdot \text{H}_2\text{O}$  and (b)  $\text{H}_{0.8}\text{Ni}_{0.4}\text{Ti}_{1.6}\text{O}_4 \cdot \text{H}_2\text{O}$  ( $0.16 \text{ g dm}^{-3}$ ). The inset shows the absorbance at peak top as a function of the colloid content: (C)  $\text{H}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4 \cdot \text{H}_2\text{O}$  and (V)  $\text{H}_{0.8}\text{Ni}_{0.4}\text{Ti}_{1.6}\text{O}_4 \cdot \text{H}_2\text{O}$ .

centrations although original colloidal solutions ( $4 \text{ g cm}^{-3}$ ) have yellow color.

XRD study and UV–Vis measurements have led to a conclusion that the Fe- or Ni-substituted titania nanosheets are obtained and they exhibit optical properties distinct from titania nanosheets.

### 3.2. Preparation and characterizations of multilayer ultrathin films of Fe- or Ni-substituted titania nanosheets

Fig. 3 shows the UV–Vis absorption spectra when the depositing procedure is repeated. The observed peak is char-

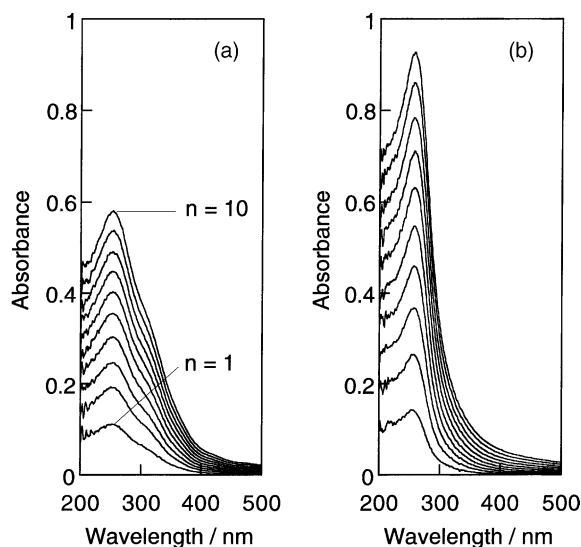


Fig. 3. UV–Vis absorption spectra of multilayer films of (a) (Fe-substituted titania nanosheets/PDDA) $_n$  and (b) (Ni-substituted titania nanosheets/PDDA) $_n$ .

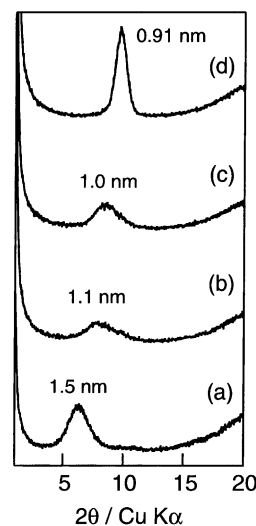


Fig. 4. XRD patterns for multilayer films of (Fe-substituted titania nanosheets/PDDA) $_{10}$ : (a) as grown sample, UV irradiated for 3 h (b), 5 h (c) and 30 h (d).

acteristic of colloidal nanosheets (Fig. 3), and its regular enhancement evidently indicates the layer-by-layer growth of a multilayer film.

In addition, the film shows an XRD peak with  $d = 1.5 \text{ nm}$ , reflecting a nanostructure of titania nanosheets and polycations (Fig. 4(a)). The value,  $d = 1.5 \text{ nm}$ , is similar to one reported previously for the other nanosheet of  $\text{Ti}_{0.9}\text{O}_2$  [11,12].

The multilayer films constituted of Ni-substituted titania nanosheets was also evidenced by UV–Vis spectra shown in (b). These results indicate that the multilayer ultrathin titania films of titania nanosheets with transition metals were successfully prepared.

### 3.3. Photocatalytic properties of multilayer ultrathin films

We have examined the photocatalytic reactivity of these ultrathin films. UV irradiation of the films led to the diminution of the multilayer repeat distance (1.5 nm) (see Fig. 4). Finally, the basal spacing have reached a constant value of 0.91 nm. This result indicates that polycations included in the films was decomposed and removed under UV irradiation. These polycations do not absorb UV–Vis light, suggesting that the Fe-substituted titania nanosheets act as effective photocatalysts to decompose the polymers. Similar results were also found for the case of Ni system. Detailed study for the photocatalytic properties of the resulting films is now under way.

## References

- [1] M.A. Fox, M.T. Dulay, Chem. Rev. 93 (1993) 341.
- [2] P.V. Kamat, Chem. Rev. 93 (1993) 267.
- [3] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.

- [4] A. Mills, S.L. Hunte, J. Photochem. Photobiol. A 108 (1997) 1.
- [5] M. Anpo, M. Che, Adv. Catal. 44 (1999) 119.
- [6] A. Fujishima, T.N. Rao, D.A. Tryk, J. Photochem. Photobiol. C 1 (2000) 1.
- [7] G. Decher, Science 277 (1997) 1232.
- [8] T. Sasaki, M. Watanabe, H. Hashizume, H. Yamada, H. Nakazawa, J. Am. Chem. Soc. 118 (1996) 8329.
- [9] T. Sasaki, M. Watanabe, J. Am. Chem. Soc. 120 (1998) 4682.
- [10] T. Sasaki, M. Watanabe, J. Phys. Chem. B 101 (1997) 10159.
- [11] T. Sasaki, Y. Ebina, M. Watanabe, G. Decher, Chem. Commun. (2000) 2163.
- [12] T. Sasaki, Y. Ebina, T. Tanaka, M. Harada, M. Watanabe, G. Decher, Chem. Mater. 13 (2001) 4661.
- [13] D. Groult, C. Mercey, B. Raveau, J. Solid State Chem. 32 (1980) 289.