Synthesis and Properties of Tubular Titanate Two-Dimensionally Deposited Carbon Nanosheet Composite

Wen-Qin Peng[1], Mami Aizawa[1], Zheng-Ming Wang[1] and Takahiro Hirotsu[2]
[1]National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan
[2]National Institute of Advanced Industrial Science and Technology, Takamatsu, Kagawa, Japan

Abstract

Carbon nanosheets were used as template for two-dimensional deposition of tubular titanate, and subsequent calcination at high temperature led to the transformation of titanate nanotubes into titania nanorods. Microscopic observation confirmed that both nanotubes and naorods deposit along the surface of carbon nanosheets, forming a stacking structure. The composites with the novel structure exhibit good adsorbing ability and high photoactivity toward organic molecules due to the synergy effect of adsorption and catalysis.

Introduction

Titanium oxide (TiO_2) have been widely studied as a photocatalytic material because of great potential in environmental purification and pollution abatement.[1-3] A wide variety of organic pollutants can be degraded into CO_2 and H_2O on TiO_2 under UV illumination at ambient temperature and pressure. Low cost, non-toxicity, and chemical stability further prompt its practical application. In recent years, much effort has been devoted to the synthesis of nanosized TiO_2 with larger specific surface area and high pore volume. [4-6]

Adsorption is an important step in the photocatalytic process and effective degradation can be achieved by pre-concentration of target pollutants on the surface of TiO_2 or its vicinity. Porous carbon is widely used as adsorbent because of high permeability to gas and liquid. High photocatalytic activity can be achieved by composing TiO_2 with carbon matrix due to the enhancement of adsorbing affinity toward organic species. Recently, some research has focused on C-TiO_2 composites.[7-9] It was reported that carbon-nanoscaled TiO_2 composites had synergy effect and showed higher photocatalytic activity than pure TiO_2.[7] Compared to the usual TiO_2 nanoparticles, One-dimensional (1D) TiO_2 can achieve higher photocatalytic activity. [5] However, till now, no research has been carried out to produce the composite of 1D TiO_2 and carbon, which is expected to combine excellent adsorptivity of carbon and high photocatalytic activity of 1D TiO_2 .

In this paper, we propose the formation of a novel structure which is composed of titanate nanotubes deposited on the surface of carbon nanosheets by a template method. Graphite oxide, which has excellent intercalation properties, was used as template and carbon source.

Experimental

First, titanium tetraisoproxide (Ti(*i*-OC_3H_7)$_4$, TTIP) was interacted with graphite oxide to allow intercalation of Ti species between GO layers, resulting in the formation of a Ti species-pillared GO materials (GOTi). Then, Ti-intercalated GO was mixed with 10 M NaOH solution and treated in a Teflon-lined container at 423 K for 24 h to obtain carbon nanosheet-titanate nanotube composite (C-TNT). Finally, carbon nanosheet-titania nanorod composite (C-TNR) were obtained after calcining the nanotube composite under inert atmosphere at 823 K. XRD, RAMAN, FTIR, FE-SEM, HRTEM, EDX and N_2 adsorption at 77 K were used to characterize structure, morphology and composition of the samples. Their adsorption and photodecomposing activities toward methyl orange (MO) were examined at 303 K.

Results and Discussion

The morphology and size were characterized by FE-SEM and TEM. As shown in Fig. 1 (a), two-dimensional planar structure can be clearly observed in the intercalated sample (GOTi). Though no nanoparticles were observed on carbon platelets, the element analysis confirms the presence of Ti and O components beside C in GOTi.[10] This indicates that Ti species were successfully intercalated in between GO layers. After hydrothermal treatment, tubular morphology was produced (Fig. 1 (b)). These nanotubes deposit two-dimensionally

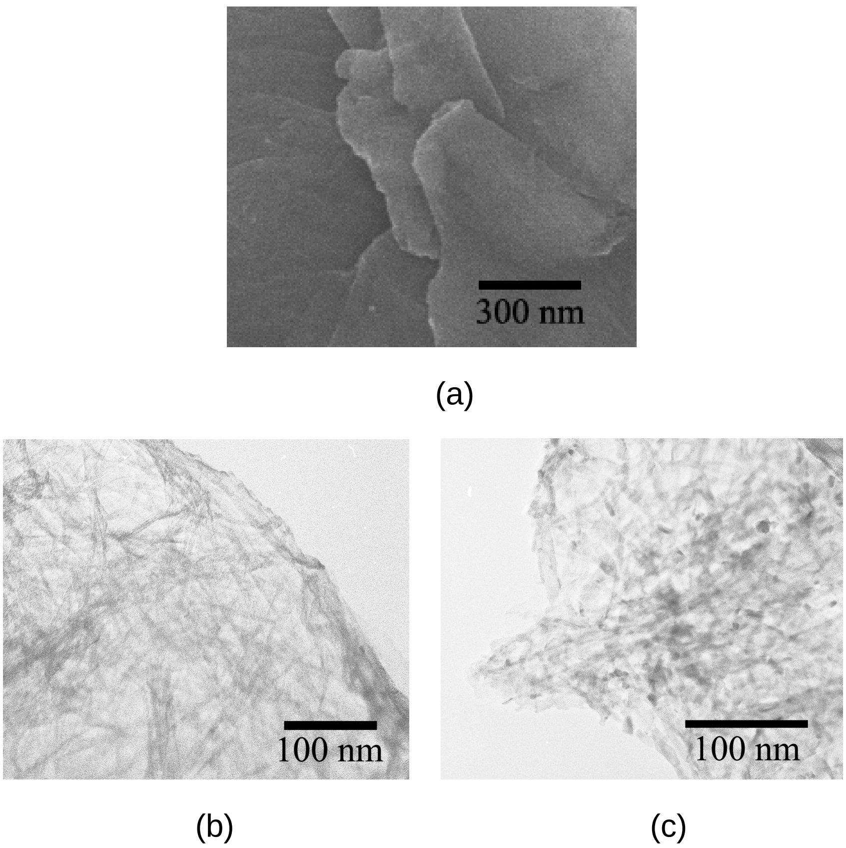

Fig. 1 (a) FE-SEM image of GOTi, (b) TEM image of C-TNT, and (c) TEM image of C-TNR.

along the surface of carbon nanosheets, forming a stacking composing structure. Further high-resolution TEM observation shows that these tubular materials belongs to hydrogen titanate.

After calcined at high temperature under vacuum, hollow tubes was turned into solid rods. As shown in Fig. 1 (c), these nanorods randomly lie on the surface of carbon nanosheets, with the stacking structure remaining. High-resolution TEM observation reveals that nanorods are single-crystalline anatase titania, obtained by thermal pyrolysis of titanate nanotubes. The anatase structure is proved by Raman spectrum (Fig. 2) from the characteristic peaks of anatase between 140-700 cm^{-1}.[11] In addition, two strong peaks are also found in the high wavelength range, which can be attributed to D and G bands of carbon.

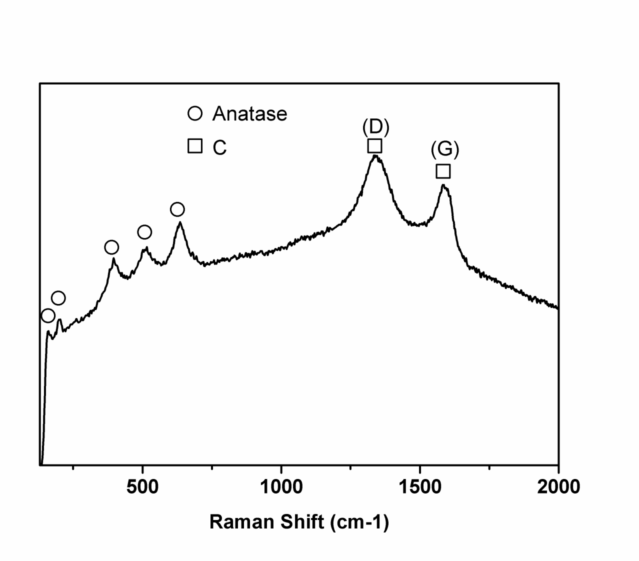

Fig. 2 Raman spectrum of C-TNR.

The adsorbing and catalytic activity of the composites were tested in terms of the degradation of methyl orange in comparison of commercial high-performance anatase ST-01. Before light illumination, the samples were agitated under dark state for 24 h to ensure adsorption equilibrium of MO on the surface of the samples. As presented in the inset

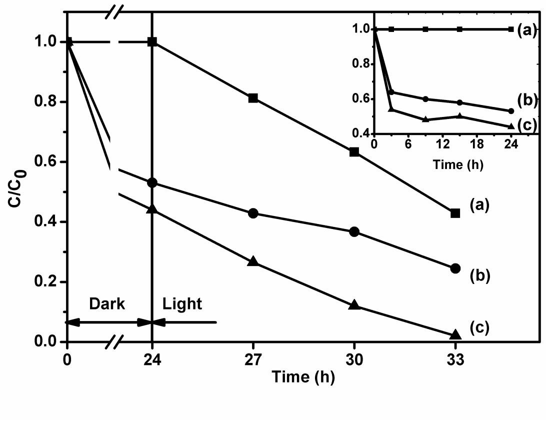

Fig. 3 Adsorption (dark range) and photodegradation (light range) toward methyl orange on (a) ST-01, (b) C-TNT, and (c) C-TNR.

of Fig. 3, under dark state, both the nanotube composite and the nanorod composites exhibit good MO adsorptivity while ST-01 has no adsorption. After dark state, the photocatalytic activity was measured under UV illumination. It can be seen that the photodegradation of MO follows pseu-zero-order equation for all the samples. The calculated degradation rate constants are 3.2, 3.8, and 5.9 x 10^{-3}/h for ST-01, C-TNT, and C-TNR, respectively. The results show that the composites have excellent adsorptivity and photocatalytic activity due to the synergy effect of adsorption and photocatalysis.

Conclusion

In summary, carbon nanosheets have been used as template for the two-dimensional deposition of titanate nanotubes and titania nanorods. The nanotube- and nanorod-based composites exhibit both excellent adsorptivity and photodecomposing ability toward organic pollutants and are promising materials for photocatalytic application.

References

1. Li D, Haneda H, Hishita S, and Ohashi N. (2005), "Visible-light-driven N-F-codoped TiO_2 photocatalysts. 2. Optical characterization, photocatalysis, and potential application to air purification," *Chem. Mater.* , 17 (10), pp. 2596-2602.
2. Goeringer S, Chenthamarakshan CR, Rajeshwar K (2001), "Synergistic photocatalysis mediated by TiO_2: mutual rate enhancement in the photoreduction of Cr(VI) and Cu(II) in aqueous media ," *Electrochem. Commun.*, 3 (6), pp. 290-292.
3. Pichat P, Disdier J, Hoang-Van C,Mas D, Goutailler G, Gaysse C (2000), "Purification/deodorization of indoor air and gaseous effluents by TiO_2 photocatalysis ," *Catal. Today*, 63 (2-4), pp. 363-369.
4. Zhu JF, Chen F, Zhang JL, Chen HJ, Anpo M (2006), "Fe^{3+}-TiO_2 photocatalysts prepared by combining sol-gel method with hydrothermal treatment and their characterization," *J. Photoch. Photobio. A*, 180 (1-2), pp. 196-204.
5. Yu JG, Yu HG, Cheng B, Trapalis C. (2006), "Effects of calcination temperature on the microstructures and photocatalytic activity of titanate nanotubes ,"*J. Mol. Catal. A: Chem.*, 249(1-2), pp. 135-142.
6. Liu YJ, Aizawa M, Peng WQ, Wang ZM, Hatori H, Uekawa N, Kanoh H (2004), "Room-temperature formation of alkoxide-derived anatase nanoparticles by peroxotitanic acid approach ," *Chem. Lett.*, 36 (9), pp. 1094-1095.
7. Liu SX, Chen XY, Chen X (2007), "A TiO_2/AC composite photocatalyst with high activity and easy separation prepared by a hydrothermal method," *J. Hazard. Mater.*, 143 (1-2), pp. 257–263.
8. Lin L, Lin W, Zhu YX, Zhao BY, Xie YC, He Y, Zhu YF (2005), "Uniform carbon-covered titania and its photocatalytic property," *J. Mol. Catal. A*, 236 (1-2), pp. 46-53.

9. Inagaki M, Kojin F, Tryba B, Toyoda M (2005), “Carbon-coated anatase: the role of the carbon layer for photocatalytic performance,” *Carbon*, 43(8), pp. 1652-1659.

10. Peng WQ, Wang ZM, Yoshizawa N, Hatori H, Hirotsu T (2008), “Lamellar carbon nanosheets function as templates for two-dimensional deposition of tubular titanate,” *Chem. Commun.*, pp. 4348–4350.

11. Balachandran U, Eror NG (1982), “Raman-spectra of titanium-dioxide,” *J. Solid State Chem.*, 42 (3), pp. 276-282.