

Doped Titania(B) Nanobelts with Anatase Nanocrystals for Improved Photocatalytic Activity

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Keywords: Titania(B), Nanobelt, Photocatalytic Activity

Abstract. Titania(B) nanobelt and anatase titania nanobelt could be prepared by calcining hydrogen titanate nanobelt at 450 °C and 550 °C respectively. When the hydrogen titanate was previously treated with HNO₃ for some time before calcination at 450 °C, titania(B) and anatase mixed phase titania could be obtained. The ratio of anatase phase in the product could be changed by control the time of HNO₃ treating. TEM images show that the mixed phase product was anatase nanocrystals doted on titania(B) nanobelts. The mixed phase product shows higher photocatalytic activity on the decomposition of Methylene Blue (MB) than the pure titania(B) nanobelt and anatase nanobelt.

Introduction

Titanium dioxide (TiO₂), an important wide-bandgap semiconductor, has shown diverse applications in photocatalysis, dye-sensitized solar cells and white pigments^[1-3]. TiO₂ as a photocatalyst has been extensively studied because of its environmental friendly and chemical stability. There are mainly four phases titania in nature, anatase, rutile, brookite and TiO₂(B)^[4-5]. Among them, anatase has been considered as the most photoactive single phase. Furthermore, mixed phase titania may exhibit higher photocatalytic activity than either of the single phase. For example, the well-known Degussa P25 have shown great photocatalytic performance due to its mixed phase nature of about 20% rutile and 80% anatase. The principal reason for the high activity of P25 is considered to be the difference conduction band of the two phase which facilitate charge transfer from one phase to another and reduce the recombination of photogenerated electrons and hole^[6-8]. Recently, a mixed phase core@shell nanostructure of anatase covered TiO₂(B) have been discovered to have superior photocatalytic activity. Herein, we show a high photocatalytic titania nanostructure of mixed phase with the TiO₂(B) nanobelts doted with anatase nanocrystals.

Experimental Section

Synthesis of Samples. 16 g Ti(SO₄)₂ was dissolved into 80 ml H₂O, then it was added to 200 ml 15 M NaOH solution. After stirring for 30 min, the mixture was transferred to Teflon-lined autoclave and hydrothermal reaction at 180 °C for 48 h. After hydrothermal processing, the obtained white product was washed with 0.1 M HCl and deionized water to pH about 7.0, then the product was dried at 80 °C for 12 h. For single phase titania preparation, the dried product was calcined at 450 °C, 500 °C for 2 h to get TiO₂(B) and anatase phase titania respectively. The samples were denoted as BT and AT respectively. The mixed phases were prepared by a two-step treatment. First, the product was hydrothermally treated with 0.05 M HNO₃ at 110 °C for different time. Typically, 0.3 g of the product was added to 30 ml HNO₃ solution and hydrothermal at 110 °C for 20 h, 40 h respectively. Second, they were then calcined at 450 °C for 2h. The mixed phase products were labeled as ABT20 and ABT40 respectively. The numbers in the label indicate the time duration of hydrothermal.

Sample Characterization. The powder-phase composition was identified by X-ray diffraction (XRD; Model D/MAX-RB, Rigaku Co., Tokyo, Japan), using Cu K α radiation. The morphologies of the resulting products were examined with transmission electron microscope (TEM, JEOL-2100F) and field-emission scanning electron microscope (SEM, JSM-6700F).

Photocatalytic Activity Test. Photocatalytic experiments were carried out by adding 1.0 g titania powder into a 450 mL Pyrex photoreactor containing 400 mL of 5.35×10^{-5} mol/L (20 ppm) methylene blue aqueous solution. Before irradiation, the suspensions were magnetically stirred in the dark for 30 min to ensure equilibrium of the solution. Oxygen was bubbled into the aqueous suspension at a flow rate of 100 mL/min. At given time intervals, 4 mL aliquots were sampled, diluted with 16 mL water, and centrifugated to remove the particles. The concentrations of resultant solution were determined by measuring their absorbance at 660 nm by the Perkin-Elmer Lambda 950 UV-vis spectrometer.

Results and Discussion

XRD Patterns. The XRD patterns of the prepared samples are shown in Figure 1. It shows that titania(B) (JCPDS 74-1940) and anatase phase (JCPDS 21-1272) are get by calcinations at 450 °C and 500 °C respectively. When acid hydrothermal were applied for a time duration before calcinations, both anatase and TiO₂(B) phase were observed in the product as shown in samples ABT20, ABT40. The ABT20 and ABT40 are acid hydrothermal for 20 and 40 h respectively. By comparing the peak intensity at 33.4° and 37.8°, it can be conclude that the anatase content increase with increasing acid hydrothermal reaction time.

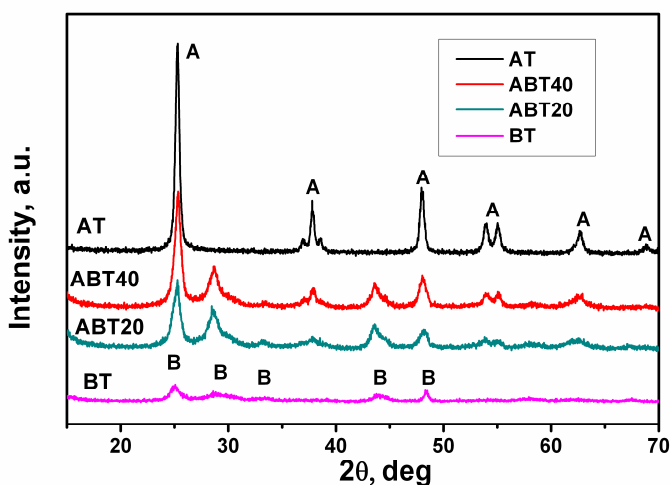


Fig. 1. XRD Patterns of the prepared samples.

Morphology. TEM and SEM was used to study the structural of the prepared samples. The images of the products were shown in figure 2. Fig 2a shows that after calcinations at 450 °C for 2h the samples was nanobelt structure. According to it's XRD pattern, it can be concluded that the samples calcinations at 450 °C for 2h is TiO₂(B) nanobelt. The SEM image in fig. 2b further confirmed the nanobelt structure. When acid hydrothermal is applied firstly, the produced products are nanobelts doted with nanocrystals as shown in fig 2c and 2d. XRD pattern shows that the nanobelts doted nanocrystals product is of anatase and TiO₂(B) mixed phase. As we know calcinations at 450 °C lead to TiO₂(B) nanobelts, so it can be inferred that the doted nanocrystals is of anatase phase. The mixed phase structure is TiO₂(B) nanobelts doted with anatase nanocrystals.

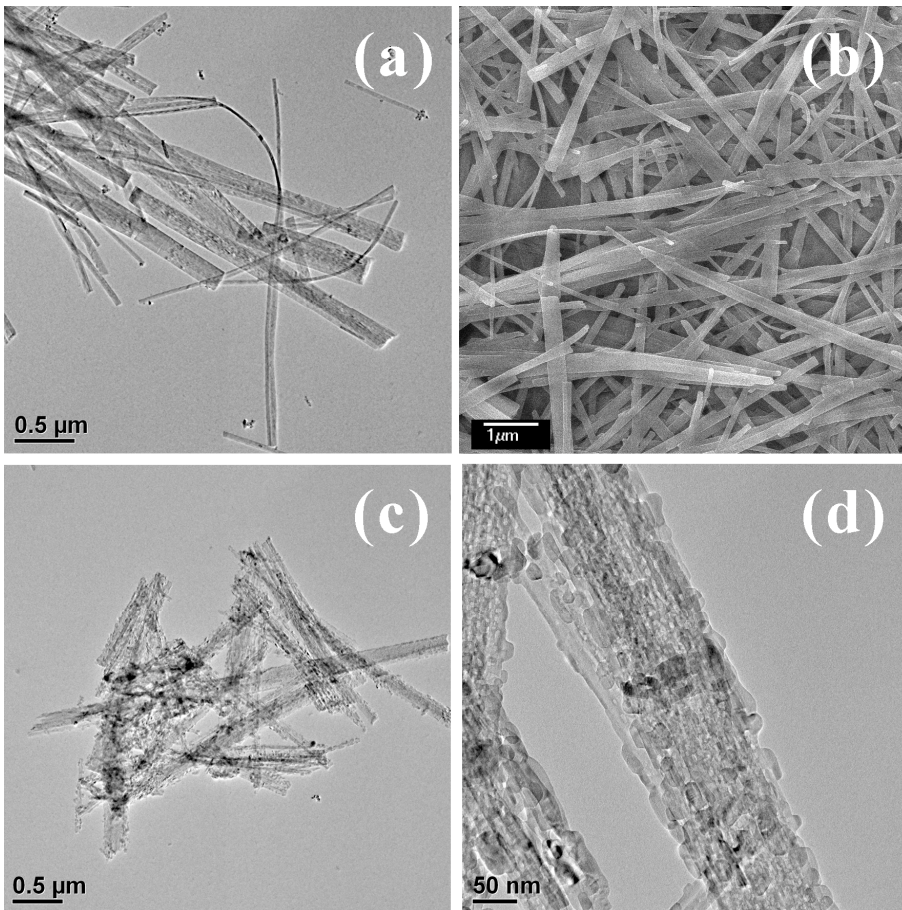


Fig. 2. TEM and SEM images of as-synthesized products. (a) TEM of BT, (b) SEM of BT, (c) TEM of ABT40, (d) higher magnification TEM of sample ABT40.

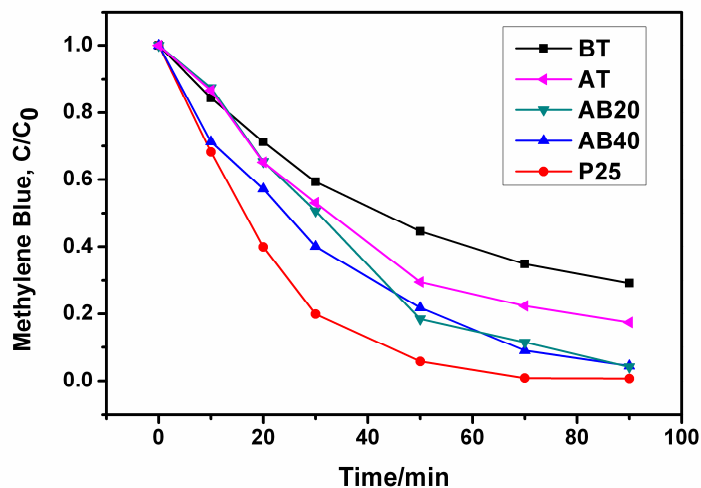


Fig. 3 Photocatalytic activity of the prepared samples and P25.

Photocatalytic Activity. The photocatalytic activity of the prepared pure anatase, $\text{TiO}_2(\text{B})$ phase and mixed phase products, and P25 powder were evaluated by degradation of methylene blue. The experimental results are shown in Figure 3. After 90 min of reaction, the methylene blue is almost decomposed with ABT20 and ABT40 and P25 as catalysts, while with BT and AT, there are nearly 30% and 20% methylene blue left. It shows that the anatase and $\text{TiO}_2(\text{B})$ mixed phase have photocatalytic performance higher than the pure anatase and $\text{TiO}_2(\text{B})$ phase, and comparable to the well-known high performance catalysts P25. The high photocatalytic activity of mixed phase may be

attributed to the heterostructure exists in the anatase and $\text{TiO}_2(\text{B})$. The bandgaps of $\text{TiO}_2(\text{B})$ and anatase have been shown about 3.05 and 3.20 eV, respectively. This means there will be a difference between their band edge which can promote charge transfer from anatase to the $\text{TiO}_2(\text{B})$ phase, similar to the situation of P25, leading to a higher photocatalytic activity.

Summary

Mixed phase titania with structure of anatase titania doped on $\text{TiO}_2(\text{B})$ nanobelt were prepared by a two step treatment of hydrogen titanate nanobelt: hydrothermal reaction and heating process. The anatase phase content ratio could be increased with increasing acid treating time. The photocatalytic activity to methylene blue decomposition reaction of the mixed phase product is higher than their single phase counterpart and comparable to the well-known Degussa P25.

Acknowledgement

The work was supported by the Shanghai Rising-Star Program (No. 08QA14073), the Shanghai Talents Program Foundation, the National Natural Science Foundation of China (No. 50672112; No. 50602049); the Knowledge Innovation Program of the Chinese Academy of Sciences (No. SCX200709); the Science Foundation for Youth Scholar of State Key Laboratory of High Performance Ceramics and Superfine Microstructures (SKL200903).

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Eco-Materials Processing and Design XII

doi:10.4028/www.scientific.net/MSF.695

Doped Titania(B) Nanobelts with Anatase Nanocrystals for Improved Photocatalytic Activity

doi:10.4028/www.scientific.net/MSF.695.485