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Photocatalytic Performance of Multi-Morphological Nb-doped TiO_2 Nanofibers

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Abstract

A series of niobium-doped titanium dioxide (Nb-TiO_2) was prepared by combining hydrothermal method and subsequent heat treatment. The primary objective is to develop high-performance photocatalyst that are easy to produce in industrial quantities. Niobium-ion doping has triggered the morphological diversity of Nb-TiO_2. it demonstrates the sub-microscale fiber catalysts (doping level lower than 1.00 mol%) and the nanoscale rod catalysts (doping level above 5.00 mol%). For the catalyzed photodegradation of methyl orange under visible light irradiation, 0.50mol% Nb-TiO_2 shows the highest activity among the synthesized Nb-TiO_2. Its photocatalytic activity is even higher than the commercial TiO_2-P25. The well-studied Nb-TiO_2, might be a reasonable alternative for photocatalytic applications in the decomposition of organic dyes.

1. Introduction

Anatase TiO_2 is one of the most important materials, because it exhibits the high performance in the applications of solar cells, photocatalysis, and transparent conducting oxide films.[1,2] However, anatase TiO_2 still has a great disadvantage due to its large band gap since it only utilizes ultraviolet range of the solar radiation.[3,4] Ultraviolet light only occupies five percent of the sunlight energy. The overall efficiency is low in the photocatalytic application. How to take advantage of visible band to increase the absorption becomes an important question for scientific researchers. Many efforts have been carried out to enhance light absorbing ability over the visible spectrum by doping metals onto TiO_2 in bulk or on surface.[5,6] The photocatalytic activity of metal doped TiO_2 photocatalysts substantially depends on the character and the concentration of the dopant ions, the method of preparation, and its thermal and reductive treatment.[7] Niobium-doped titanium dioxide (Nb-TiO_2) is introduced in here for its great potential application in wastewater treatment. The synthesized Nb-TiO_2 is nanofiber type which is separated easily from aqueous solution after being used.[8,9] Many studies reported that niobium ion doped into TiO_2 can enhance photocatalytic activity because of the extended light absorption range and the suppression of electron-hole pair recombination.[10,11]

In this study, we searched for the optimal Nb doping concentrations to obtain the highest performance Nb-TiO_2 photocatalyst. A series of fiber and/or rod shaped Nb-TiO_2 were developed by varying Nb doping concentrations. Moreover, the Nb doping effects on TiO_2 catalysts for photodecolorization of organic dye under various UV spectrum and visible spectrum irradiation were discussed in detail. The developed Nb-TiO_2 is able to compete the commercial photocatalyst for applications in the decomposition of organic dyes and photocatalytic hydrogen generation in the near future.

2. Experimental Method

A various Nb-TiO_2 were prepared by suspending 1.00 g TiO_2 anatase powder (Acros Organics, 98%) and various amount of niobium chloride ($NbCl_5$, Acros Organics, 99.999%) in 25mL of 10.0M NaOH aqueous solution, followed by a treatment in a teflonlined autoclave at 150°C for 24 hr. Then, it is washed with 0.10M HCl to exchange Na^+-ions for protons. The product was washed several times with deionized water, filtered and dried in the air at 70°C. Finally, the products doped with various Nb concentrations were calcined at various temperatures with a heating rate of 5°C/min for different calcination time.

Transmission electron microscopy (TEM, JEOL, JEM-ARM200FTH, Japan) was used to observe the microstructures of various Nb-TiO_2. For the photodegradation experiment, six pieces of lamps were placed in a hexagonal arrangement around the reactor. The synthesized Nb-TiO_2 were tested in the degradation of methyl orange, which is a commonly used model reaction in photocatalysis. In a typical experiment, 20.0 mg of catalyst was sonicated for 10 min in 150 mL of 1.0 mg/L methyl orange (Acros Organics, pure) aqueous solution. The suspension was irradiated under vigorous stirring at ambient conditions. The light source includes UV-B lamps (Sankyo Denki G8T5E UV-B lamps, and the power was 8.0W) and visible lamps (Goodly F8T5/D visible lamp, and the power was 8.0W). The absorption spectrum of the retained methyl orange and its derivatives in the supernatant was recorded by absorption spectrophotometer (JASCO Analytical Instruments, V-630, Japan) in the 300-900 nm wavelength range. The concentrations of the methyl orange were calculated from the absorbance at λ=464 nm and extrapolated by a previously plotted calibration curve.

3. Results and Discussion

TEM images of pristine TiO_2 and various Nb-TiO_2 are shown in **Fig. 1**. It is noted that Nb doping results in the morphological diversity for Nb-TiO_2. The as-made pristine TiO_2

material has a length of up to a few micrometers and a diameter of ~100-200 nm (**Fig. 1(a)**). The morphologies of the 0.25mol% Nb-TiO_2 and 0.50mol% Nb-TiO_2 are similar to that of the pristine TiO_2, as shown in **Fig.1 (b,c)**. However, some small rod-shaped materials become obvious when the doping concentration reaches 1.00mol% (**Fig. 1(d)**). The diameter of Nb-TiO_2 materials decreases to ~50 nm when the doping concentration is over 5.00mol%, as shown in **Fig. 1(e,f)**. It suggests that the Nb-TiO_2 broke into small pieces and scattered into rod-shaped materials. For Nb doping concentration is over 5.00mol%, substantial Nb ions incorporate into the TiO_2 lattice. The morphological scale of synthesized Nb-TiO_2 catalysts decreases as the elevated of Nb doping concentration.

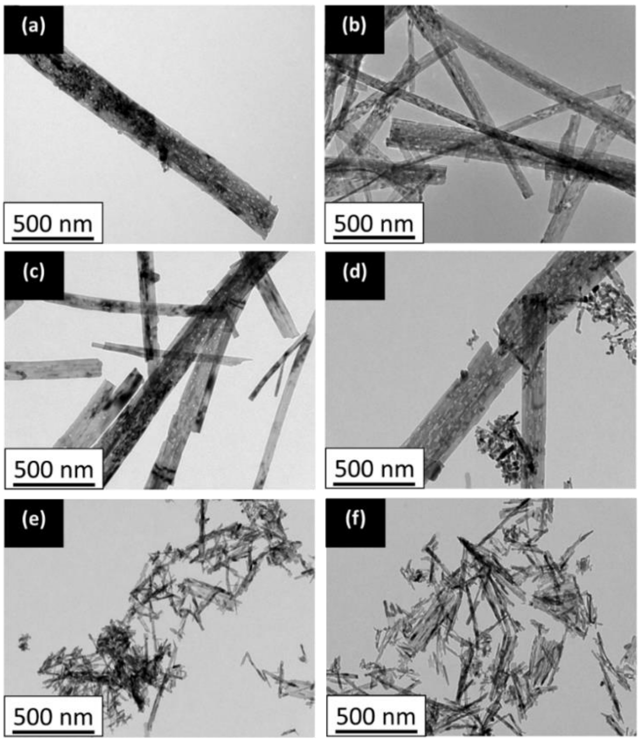

Fig. 1. TEM images of **(a)** pristine TiO_2, **(b)** 0.25mol%, **(c)** 0.50mol%, **(d)** 1.00mol%, **(e)** 5.00mol%, and **(f)** 10.00mol% Nb-TiO_2.

For the photodegradation activity of these Nb-TiO_2 materials under UV irradiation, 0.50mol% Nb-TiO_2 materials shows the highest photodegradation reaction rate constant (**Fig. 2(a)**). Moreover, the Nb-TiO_2 materials were also tested under visible light irradiation. As shown in **Fig. 2(c)**, 0.50mol% Nb-TiO_2 material shows the highest activity among the Nb-TiO_2 materials studied. The photodegradation reaction rate constants are shown using bar charts in **Fig. 2(b,d)**. The 0.50 mole% Nb-TiO_2 material show the highest activity on the photodegradation of methyl orange under UV light and visible light irradiation due to the optimal condition for the photon absorption, chemical composition, crystal structure, and active surface area.

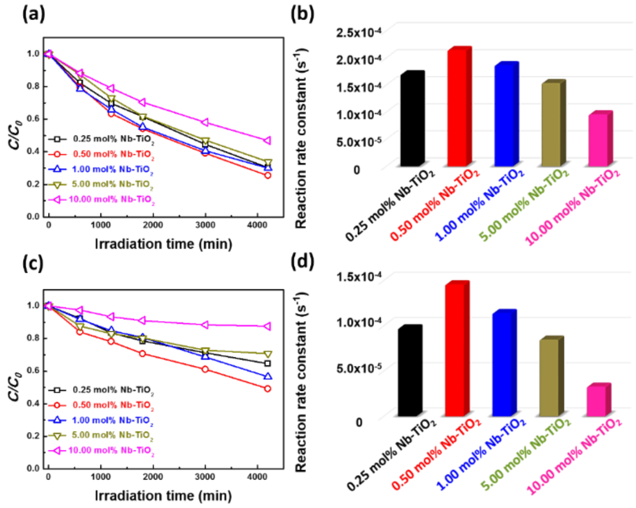

Fig. 2. (a,c) The plots of C/C_o and **(b,d)** column charts of pristine TiO_2 and Nb-TiO_2 with various doping concentrations over the photodegradation of methyl orange under the following light source irradiations: **(a,b)** UV light and **(c,d)** visible light.

4. Conclusions

In summary, the synthesized Nb-TiO_2 with several niobium levels shows significant morphologies, including sub-microscale fiber (<1.00mol% Nb doping) and nanoscale rod (>5.00mol% Nb doping). The study focuses on the Nb doping on TiO_2 for organic dye decolorization. The Nb-TiO_2 with 0.50mole% Nb doping concentration exhibits the highest activity for catalyzed photodegradation of methyl orange under UV light or visible light irradiation. The obtained Nb-TiO_2 may be a reasonable alternative of the commercial photocatalyst for photocatalytic applications in the decomposition of organic dyes.

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References

[1] A. Fujishima and K. Honda., Nature, **238** (1972), 37-38.
[2] M. Fujihira *et al.*, Nature, **293**(1981), 206-208
[3] D.A. H. Hanaor and C. C. Sorrell., J. Mater. Sci., **46**(2011), 855-874.
[4] M. C. Wu *et al.*, J. Nanosci. Nanotechnol., **12**(2012), 1421-1424.
[5] O. Zuas and H. Budiman., Nano-Micro Lett, **5**(2013), 26-33.
[6] H. Park *et al.*, J. Photochem. Photobiol. C: Photochem. Rev., **15**(2013), 1-20.
[7] M. C. Wu et al., ACS Nano, 5(2011), 5025-5030.
[8] Z. Xu *et al.*.J. Mater. Sci. Technol., **28**(2012),865-870.
[9] F. S. Shieu *et al.,* J. Electrochem. Soc., **155**(2008), 173-179 .
[10] X. Zhang *et al.,*Solid State Sci., **14**(2012), 139-144.
[11] H. Znad *et al.,* Int. J. of Photoenergy, **2012**(2012), 1-9.