Synthesis of Ag-TiO$_2$ Nanotubes in Ambient Atmosphere and Kinetics of Photocatalytic Reaction*

LI Jingling[1,2], CHEN Wenzhe[1,2], BI Jingjing[1], GUO dajing[1],

YANG Bingcan[1], ZHOU Zhiwu[1]

(1. *Fujian University of Technology*, *Fuzhou* 350108, *China*;
2. *College of Materials Science and Engineering*, *Fuzhou University*, *Fuzhou* 350108, *China*)

Abstract: Ag-TiO$_2$ composite nanotubes were synthesized for the first time by using the hydrothermal crystallization with TiO$_2$, NaOH and AgNO$_3$ at 700 ℃ in ambient atmosphere. The synthesized nanotubes were then characterized using TEM and XRD techniques. The experimental conditions for the nanotube synthesis and the photocatalytic degradation mechanism of methyl orange (MO) with nanotubes as a photocatalyst were also examined. The results show that there is a distinct effect on nanotube's photocatalytic characteristics under different synthesizing conditions such as melting and hydrothermal crystallization temperature and time. The photocatalytic degradation rate (η) reached about 99 % when the reaction was kept for 4 h and the initial concentration of MO solution (C_o) was 4 mg/L. The relationship between the rate constant (k) of the degradation and C_o conformed to an order of 0. 996 6 reaction.

Key words: Ag-TiO$_2$ nanotubes; synthesis; photocatalysis; degradation; kinetics

EEACC: 0520

常压下 Ag-TiO$_2$ 纳米管制备及光催化反应动力学研究*

李静玲[1,2],陈文哲[1,2],毕晶晶[1],郭大敬[1],杨炳灿[1],周志武[1]

(1. 福建工程学院,福州 350108;2. 福州大学材料科学与工程学院,福州 350108)

摘　要:首次在常压下,以试剂 TiO$_2$、NaOH 和 AgNO$_3$ 为原料,碱熔温度为700 ℃,水热法制备了 Ag-TiO$_2$ 复合纳米管光催化剂。TEM 和 XRD 用于纳米管组织与形貌表征。研究了纳米管制备以及用于模拟污染物甲基橙(MO)光催化降解的实验条件。结果表明,原料是否碱熔,水热温度高低和时间长短,对光催化剂性能影响明显;当 MO 溶液初始浓度 C_o 为4 mg/L、光催化降解反应持续4 h,光催化降解率达到99 %。降解反应的速率常数 k 与 C_o 呈0. 996 6级的动力学关系。

关键词:Ag-TiO$_2$ 纳米管;制备;光催化;降解;动力学

中图分类号:TB383;O614　　　**文献标识码**:A　　　**文章编号**:1004 - 1699(2010)05 - 0617 - 04

TiO$_2$ is an sort of important material for its inorganic function of chemical, photochemical stability and for its low cost. It finds applications in the storage of solar energy, photovoltaic conversion and photocatalytic degradation of air and water pollutants[1-3]. Studies have shown that TiO$_2$ nanotubes have a greater surface area than their nanoparticles or nanofilm and thus have a higher absorption capacity[4]. TiO$_2$ nanotubes, having tube-like structure, often show a remarkable effect of quantum size because of its nano-scale hollow channels[5]. To a certain extent, the photocatalytic reaction rate of TiO$_2$ nano-materials depends on the amount of the light quanta namely the carriers, pairs of photo-electrons and holes. The smaller the proportion of the neutralized pairs of photo-electrons and holes, the higher the photocatalytic activity. The metal ions, particularly noble metal ions, i. e. Ag$^+$ and Au$^+$ ions added into the TiO$_2$ crystal lattice will result in the lattice defects or change the crystallinity[6-8]. The carriers's life would be prolonged if the neutralization between photo-electrons and holes was reduced. The activity and quantity of photo-electrons would also effect upon its applica-

tions to a great extent in above areas.

There are two common ways used for TiO$_2$ nanotubes synthesis, i. e., hydrothermal method and anodizing method[9-10]. We focus on the hydrothermal method, that is a simple, low cost way to fabricate nanotube and is widely adopted in this field. However due to its pressurization, it is not preferred in industrial production. In order to find an improved modest synthesis way, low-cost and simple operation has a top priority. This research brings into focuses on the hydrothermal way in ambient pressure for use in the fabricating Ag-TiO$_2$ nanotubes.

1 Experimental Procedure Synthesis of Ag-TiO$_2$ Nanotubes

Raw materials TiO$_2$, AgNO$_3$ and NaOH in a certain proportion were mixed in a silver crucible, and melted in the furnace at 700 ℃ for 30 min. The crucible with the melted material was removed out of the furnace to cool down at room temperature and then the melted material was poured out into a teflon beaker. An appropriate amount of distilled water was added into the teflon beaker to solve the NaOH conserved in the melted material and to make an NaOH solution of concentration ⩾ 10 mol/L in which a part of melted material dispersed and, then Ag-TiO$_2$ nanoparticles formed and deposited in the process. The beaker which contains the deposition of Ag-TiO$_2$ nano particles was put in an oven at 110 ℃ for 48 h. After being cooled to room temperature, the deposition in which Ag-TiO$_2$ nanotubes involved, was washed with tap water, distilled water and 2 % HNO$_3$ solution separately. In order to dry the Ag-TiO$_2$ nanotubes separated from above deposition, Ag-TiO$_2$ nanotubes was placed in a glass beaker, heated at an increasing rate of 5 ℃/min from room temperature to 500 ℃ in a furnace and maintained to 500 ℃ for 2 h. The Ag-TiO$_2$ nanotubes were cooled down at room temperature and grinded, to be used as the photocatalyst.

1.1 Photocatalytic Degradation of MO

Adequate amount of MO solution (1 mg/L, pH ~ 3) was placed into the beaker, adding in appropriate amount of the photocatalyst, and stirred with magnetic rod, and then the photocatalytic reaction was conducted with ultraviolet irradiation. A part of the solution was immediately removed to the centrifuge tubes for centrifugation. The supernatant solution was taken out from the tube for absorbance determination and concentration calculation. The rate of photocatalytic degradation (η) was calculated by the following equation.

$$\eta = \frac{C_o - C}{C_o} \times 100 \%\qquad(1)$$

Where C_o and C is the initial and degradation reaction concentration of MO solution(mg/L).

1.2 Instruments

The experimental instruments involved as follows: UV Spectrmphotometer(Beijing Rayleigh Analytical Instruments Inc.), 8 W ultraviolet light(Tianjin Amethyst light Ltd.), XRD (Philips Company D/Max-Mc) and TEM(Hitachi Model JEM-2010).

2 Results and Discussion

2.1 Characterization

The characterization of Ag-TiO$_2$ composite nanotubes were done by XRD (shown in Fig. 1). Compared with peaks of the TiO$_2$ raw material the peak values of anatase and rutile from TiO$_2$ nanotubes dropped dramatically. The characteristic peaks of TiO$_2$ tubular structure and the noble metal Ag, were shown in Fig. 1(a) and Fig. 1(b). Preliminary studies indicated that Ag$^+$ was involved in the TiO$_2$ nanotube crystalline structure to form composite Ag-TiO$_2$ nanotubes. Ag$^+$ was used as inhibitor to reduce the carriers' neutralization. The photocatalytic degradation reactions for organic compound were essentially free radical reactions[11].

TiO$_2$ excited by ultraviolet light will produce photo-electrons and holes. But at the same time there was a possibility for the neutralization of two kinds of carriers. Using noble metal elements as inhibitor to reduce their neutralization was the key to improving the photocatalytic capacity. When oxygen was available, the photo-electrons could be removed timely in response to the noble metal ions, significantly to reduce the chance of their neutralization. However the amount of the noble metal ions affected the photocatalysis. If there were too many noble metal ions, they would bind together to hinder the carrier's transmission, and would not be conducive to the free radical reaction. The study showed that an addition of 0. 1 g to 0. 3 g of Ag$^+$ was preferable as inhibitor.

As shown in TEM images(Figure 2), the tubular diameter of Ag-TiO$_2$ nanotubes is about 5 nm, the wall

thickness is about 0.2 nm and the length is about 500 nm. As Ag and TiO_2 nanoparticles adhered to the surfaces of TiO_2 nanotubes, of which ends are open.

The composition of the nanotubes contains Ti, Ag, Na, and other elements, in which Ag was involved in synthesis of nanotubes (as shown in Figure 3).
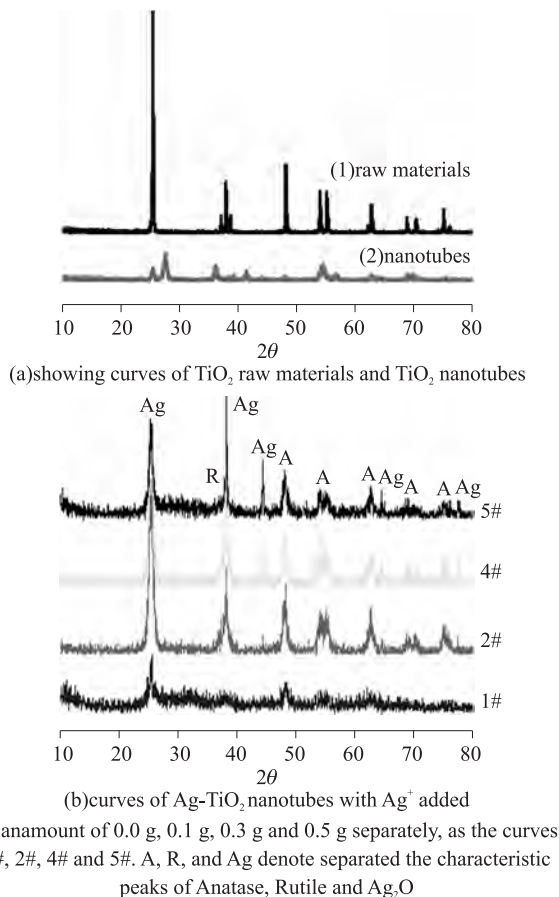

(a)showing curves of TiO_2 raw materials and TiO_2 nanotubes

(b)curves of Ag-TiO_2 nanotubes with Ag^+ added an anamount of 0.0 g, 0.1 g, 0.3 g and 0.5 g separately, as the curves 1#, 2#, 4# and 5#. A, R, and Ag denote separated the characteristic peaks of Anatase, Rutile and Ag_2O
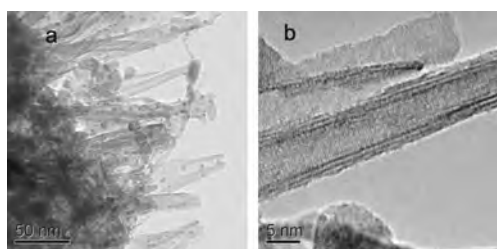
Fig. 1   XRD patterns of nanotubes

Fig. 2   TEM images of composite Ag-TiO_2 nanotubes
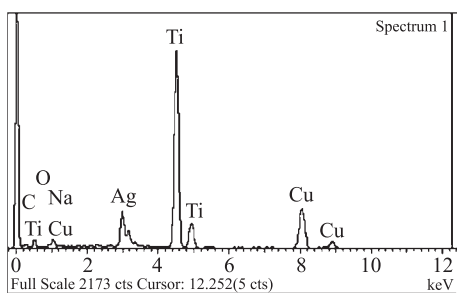

Fig. 3   The composition of Ag-TiO_2 nanotubes

2.2   Synthesis of Composite Ag-TiO₂ Nanotubes

Ag－TiO_2 Nanotubes were obtained by the special synthesis (melted at 700 ℃ in advance) in this paper. The tubular length was extended as compared to the usual ways (as shown in Fig. 4). Without melting, TiO_2 nanoparticles still existed in nanotube material although it was placed at 25 ℃ for 30 d, and TiO_2 nanotubes with the length 100～200 nm were shorter than that melted at 700 ℃, the latter longer than 500 nm. The studies also showed that the hydrothermal temperature ⩾ 110 ℃ and the hydrothermal time longer than 48 h were in favor of the synthesis (in Fig. 4)
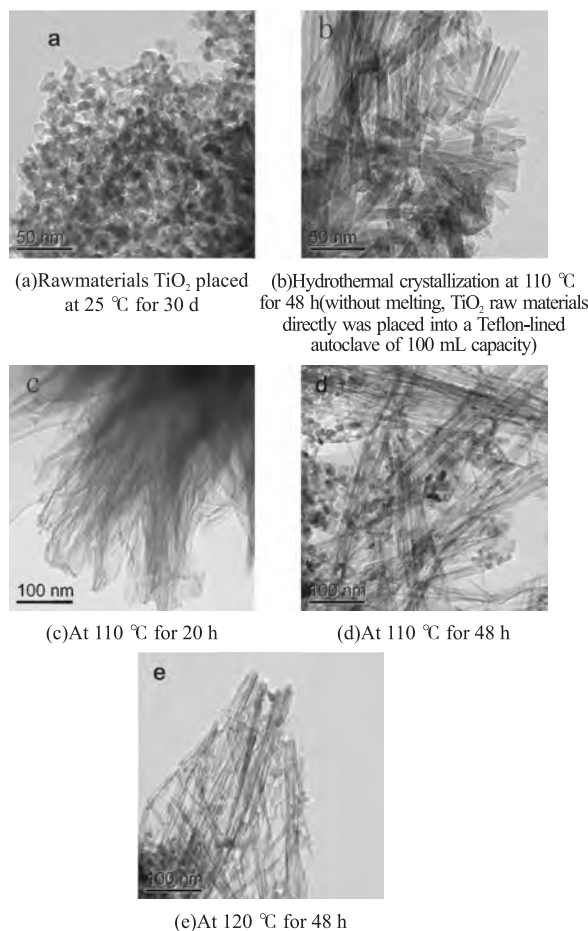

(a)Rawmaterials TiO_2 placed at 25 ℃ for 30 d

(b)Hydrothermal crystallization at 110 ℃ for 48 h(without melting, TiO_2 raw materials directly was placed into a Teflon-lined autoclave of 100 mL capacity)

(c)At 110 ℃ for 20 h

(d)At 110 ℃ for 48 h

(e)At 120 ℃ for 48 h

Fig. 4   TEM images of TiO_2 nano-materials fabricated with different ways (TiO_2 nanoparticles melted at 700 ℃)

2.3   Photocatalytic Degradation Kinetics of MO

The photocatalytic degradation rate (η) reached about 99 % when the reaction was kept for 4 h with concentration C_o of 4 mg/L of MO solution(as shown in Fig. 5).

The experimental results were deal with Langmuir Hinshelwood kinetic formula[12-14].

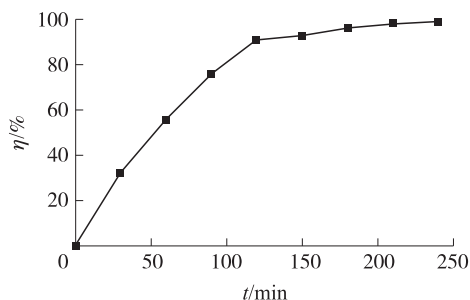$$v = -\frac{dC}{dt} = \frac{kK_AC_A}{1 + kK_AC_A} \approx kK_AC_A \qquad (2)$$

Fig. 5 Effect of the degradation time on MO

Where k is the rate constant of the photocatalytic degradation on MO, and K_A is the adsorptive constant, and C_A is the concentration of MO in solution at any time.

When the concentration of MO in solution is so low

$$1 + k \, K_A \, C_A \approx 1$$

$$\ln(C_o/C_t) = kt \qquad (3)$$

The formula (3) was transferred as followed,

$$k = aC_o^n \qquad (4)$$

$$\ln k = \ln a + n \ln C_o \qquad (5)$$

where, a is the correlation coefficient, n is a power factor of C_o. The results were shown as in Fig. 6. When C_o is 1, 2, 4, 6 and 8 mg/L, the rate of the degradation reaction and the concentration of MO in solution show as the following lines.
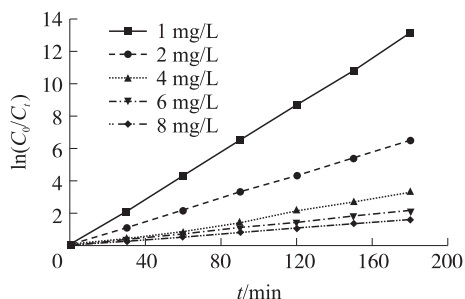

Fig. 6 The degradation rate with C_o of MO in solution

Followed the above formulas and Fig. 3 to Fig. 6, n was calculated: $n = -0.996\ 6$. That is to say, k was comformed to C_o in n of $-0.996\ 6$ in the kinetics relationship (as Formula (6)).

$$\ln k = -2.635 - 0.996\ 6 \ln C_o \qquad (6)$$

3 Conclusion

Composite Ag-TiO$_2$ nanotubes were first time fabricated using the hydrothermal crystallization in ambient atmosphere. Hydrothermal temperature $\geqslant 110\ ℃$, and hydrothermal time longer than 48 h were favorable for the formation of nanotubes. The rate (η) of photocatalytic degradation on MO reached 99 % when the reaction was kept for longer than 4 h and the C_o was 4 mg/L. The rate

constant k of the degradation in kinetics relationship was conformed to C_o inn magnitude 0.996 6.

References:

[1] Wang Z S, Huang C H, Huang Y Y, et al. A Highly Efficient Solar Cell Made from a Dye-Modified ZnO-Covered TiO$_2$ Nanoporous [J]. Electrode. Chem. Mater. 2001, 13: 678 – 682.

[2] Craig A. Grimes, Keat G. Ong, Oomman K. Varghese, et al. A Sentinel Sensor Network for Hydrogen Sensing [J]. Sensors, 2003, 3: 69 – 82.

[3] Gopal K. Mor. A Room-Temperature TiO$_2$-Nanotube Hydrogen Sersor Able to Self-Clean Photoactively from Environmental Contamination[J]. J. Mater. Res., 2004, 19(2): 629 – 634.

[4] Yu H G, Yu J G, Cheng B, et al. Synthesis, Characterization and Photocatalytic Activity of Mesoporous Titania Nanorod/Titanate Nanotube Composites. Journal of Hazardous Materials, 2007, 147: 581 – 587.

[5] Sergiu P. Albu, Andrei Ghicov, Jan M. Macak, et al. Self-Organized, Free-Standing TiO$_2$ Nanotube Membrane for Flow-through Photocatalytic Applications[J]. Nano Letters, 2007, 7(5): 1286 – 1289.

[6] Paramasivam I, Macak J M, Schmuki P. Photocatalytic Activity Of TiO$_2$ Nanotube Layers Loaded With Ag and Au Nanoparticles [J]. Electrochemistry Communications, 2008, 10: 71 – 75.

[7] Paramasivam I, Macak J M, Ghicov A, et al. Enhanced Photochromism of Ag Loaded Self-Organized TiO$_2$ Nanotube Layers[J]. Chemical Physics Letters, 2007, 445: 233 – 237.

[8] Christina Hippe, Michael Wark, Enno Lork, et al. Platinum-Filled Oxidic Nanotubes[J]. Microporous and Mesoporous Materials, 1999, 31: 235 – 239.

[9] Nian J N, Teng H S. Hydrothermal Synthesis of Single-Crystalline Anatase TiO$_2$ Nanorods with Nanotubes as the Precursor[J]. J. Phys. Chem. B, 2006, 110: 4193 – 4198.

[10] Patrick Hoyer. Formation of a Titanium Dioxide Nanotube Array [J]. Langmuir, 1996, 12: 1411 – 1413.

[11] Shao Y, Xue G, Yu Y F, et al. TiO$_2$ Nanotube Light Catalyst [J]. Applied Chemistry, 2003, 20(5): 433 – 436.

[12] Zhao H, Xu S H, Zhong J B, et al. Kinetic Study on the Photo-Catalytic Degradation of Pyridine in TiO$_2$ Suspension Systems[J]. Catalysis Today, 2004, 93 – 95 (1): 857 – 861.

[13] Rosana M A, Wilson F J. Photocatalytic Destruction of VOCs in the Gas- Phase Using Titanium Dioxide[J]. Appl. Catal B: Environ, 1997, 14(1 – 2): 55 – 68.

[14] Kamat P V. Photochemistry on Nonreactive and Reactive (Semiconductor) Surfaces[J]. Chem. Rev, 1993(93): 267 – 300.

李静玲(1963 -), 女, 副教授, 主要研究方向为纳米功能材料的制备及应用, 先后主持或参加省部级项目近十项, 近年来发表论文十余篇, 中国微米纳米协会会员, ljl118@163.com.