Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Fabrication of porous titanium dioxide fibers and their photocatalytic activity for hydrogen evolution

Huilin Hou [a,b], Lin Wang [b], Fengmei Gao [b], Guodong Wei [b], Jinju Zheng [b], Bin Tang [a,*], Weiyou Yang [b,*]

[a] Research Institute of Surface Engineering, Taiyuan University of Technology, Taiyuan City 030024, PR China
[b] Institute of Materials, Ningbo University of Technology, Ningbo City 315016, PR China

ARTICLE INFO

Article history:
Received 6 November 2013
Received in revised form
19 February 2014
Accepted 24 February 2014
Available online 18 March 2014

Keywords:
Porous TiO_2 fiber
Electrospinning
Photocatalysis
Hydrogen evolution

ABSTRACT

TiO_2 semiconductor is one of the important photocatalysts for solar light conversion. The challenge is how to improve their efficiency. Creation of porous structures on/in the fibers could favor them a higher surface area as compared to the conventional solid counterparts, which thus could make the achievement for the desired high efficiency. In present work, we report the fabrication of porous TiO_2 fibers with high purity via electrospinning of butyl titanate (TBOT) and polyvinylpyrrolidone (PVP) combined with the subsequent calcination in air. It is found that the TBOT content in the spinning solution plays a profound effect on the growth of the fibers, enabling the synthesis of porous TiO_2 fibers with tunable structures and high purity. The photocatalytic activity for hydrogen evolution of the as-fabricated TiO_2 nanostrcutres has been investigated, suggesting that porous TiO_2 nanomaterials with a high purity and well-defined one-dimensional fiber shape could be an excellent candidate to be utilized as the photocatalyst for hydrogen evolution.

Introduction

Recently, the utilization of solar energy for splitting water to hydrogen has been considered as a promising solution to energy and environmental problems [1–4]. Since the pioneering work of Fujishima and Honda in 1972 [5], various semiconductor photocatalysts, such as TiO_2 [6,7], ZnO [8], WO_3 [9], CdS [10], MoO_3 [11], Bi_2O_3 [12] and such on, have been investigated to catalyze the evolution of hydrogen from aqueous solutions. Among these semiconductors, TiO_2 is one of the most remarkable photocatalysts owing to its unique and excellent properties such as superior photocatalytic performance, easy availability, long-term stability and non-toxicity [13,14]. For its practical applications, one of the crucially important keys is how to enhance the photocatalytic activities. In the past decades, many efforts have been devoted to improve the photocatalytic ability of TiO_2 material [15–18]. Typically, porous structure has been considered as an effective way to enhance the light adsorption capacity due to the increased surface area and multiple interparticle scattering, leading to the enhancement of photocatalytic reactions [19–21]. Up to date, some strategies have been adopted to prepare porous TiO_2, such as sol–gel process [22],

* *Corresponding authors*. Tel.: +86 574 87080966; fax: +86 574 87081221.
E-mail addresses: tangbin@tyut.edu.cn (B. Tang), weiyouyang@tsinghua.org.cn (W. Yang).

http://dx.doi.org/10.1016/j.ijhydene.2014.02.151
0360-3199/

hydrothermal process [23], ultrasonic process [24], template assisted method [25], and et al.

Electrospinning is a versatile, low cost and simple strategy for generating fibers in various materials system with controllable diameters, compositions and morphologies [26–30]. By virtue of the merits of this technique and assisted by subsequent air calcined process, TiO_2 porous fibers have been successfully fabricated to meet the requirements of light weight, high surface area, as well as suitable pore structure to be utilized as the photocatalysts [31–33]. These works demonstrated that, as compared to other nano counterparts (*i.e.*, nanoparticles), the porous TiO_2 fibers could not only facilitate the interparticle charge transfer, but also inhibit the charge recombination, which might meet the challenge for the desired high efficiency.

In current work, we report the fabrication of porous TiO_2 fibers via electrospinning of polymeric precursors containing TBOT and PVP, followed by calcination in air. The as-fabricated porous TiO_2 fibers exhibit high crystallinity and high purity. Meanwhile, the fiber formations can be tailored by controlling the concentrations of TBOT in the precursor solutions. The photocatalytic activities of the as-fabricated TiO_2 nanostructures were explored in terms of hydrogen production.

Experimental procedure

Preparation and characterization of TiO_2 fibers

The raw material of TBOT (Aladdin, Shanghai, China) and PVP ($M_W \approx 30000$, Aladdin, Shanghai, China) was commercially available and directly used without further purification. Absolute ethyl alcohols and acetic acid were used as the solvents to make the TBOT and PVP mixed homogenously. In a typical experimental procedure, PVP, TBOT and solvents were firstly mixed with stirring vigorously for 8 h. The resultant solution was transformed into a plastic syringe with a stainless steel nozzle (used as the anode, diameter: 0.22 mm). The tip of the stainless steel nozzle was placed in the front of a metal cathode (used as the collector) with a fixed distance of 20 cm between the nozzle and the collector. An electrical potential of 15 kV was applied for electrospinning TBOT/PVP polymer precursor fibers. The as-spun polymer fibers were then located in a quartz crucible and placed at the center of a conventional tube furnace. Subsequently, the samples were heated up to the desired temperature of 500 °C with a heating rate of 1 °C min^{-1} and maintained there for 2 h, followed by furnace-cool to ambient temperature. For comparison, five solutions were prepared with TBOT compositions decreased from 30 to 10 wt% with keeping PVP amount as a constant of 20 wt%, which were detailed shown in Table .1. The obtained products were referred to Sample A–E, respectively.

The as-fabricated products were characterized with X-ray powder diffraction (XRD, D8 Advance, Bruker, Germany) with Cu Kα radiation ($\lambda = 1.5406$ Å), field emission scanning electron microscopy (SEM, S-4800, Hitachi, Japan), and high-resolution transmission electron microscopy (HRTEM, JEM-2010, JEOL, Japan) equipped with energy dispersive X-ray spectroscopy (EDS).

Table 1 – Solutions used for electrospinning polymer precursor fibers.

Sample	PVP (g)	TBOT (g)	Alcohol (g)	Acetic acid (g)	PVP:TBOT
A	2.0	3.0	3.5	1.5	2:3
B	2.0	2.5	4.25	1.25	4:5
C	2.0	2.0	5.0	1.0	1:1
D	2.0	1.5	5.75	0.75	4:3
E	2.0	1.0	6.5	0.5	2:1

Photocatalytic reaction of the as-prepared TiO_2 fibers

The photocatalytic activity of the resultant products was evaluated for hydrogen evolution. The photocatalytic reaction is performed in an inner-irradiation quartz annular reactor with a 300 W Xenon lamp (CEL, HUL300), a vacuum pump, a gas collection, a recirculation pump and a water-cooled condenser. The as-synthesized samples (0.05 g) were suspended in deionized water and methanol mixed solutions (40 mL, 3:1) by an ultrasonic oscillator, respectively. Then the mixture was transferred into the reactor and deaerated by the vacuum pump. The Xenon lamp was utilized as a light source, and cooling water was circulated through a cylindrical Pyrex jacket located around the light source to maintain the reaction temperature. The reactor was sealed with ambient air during irradiation, and the hydrogen evolution were monitored by an online gas chromatography (GC, 7900) equipped with a Porapak-Q column, high-purity nitrogen carrier and a thermal conductivity detector (TCD).

Results and discussion

Characterization of as-prepared TiO_2 nanostructures

SEM was firstly employed to characterize the morphology and structure of the electrospinning precursor fibers and the corresponding calcinated products. Fig. 1(a) and Fig. S1(a–b) (Supplementary information) show the typical SEM images of electrospun polymer precursor fibers of Sample B with 25 wt% TBOT under lower magnifications. It suggests that all the resultant precursor fibers are averagely sized in ~530 nm (the inset in Fig. 1(a), which are statistically calculated form 30 fibers in random under SEM)) in diameter and up to several hundred millimeters in length, respectively. The obtained precursor fibers are uniformly sized along the axial direction with circular solid cross-sections (Fig. S1, Supplementary information). Fig. 1(b–c) and Fig. S2(a) (Supplementary information) display the typical SEM images under different magnifications of the corresponding calcinated fibers, which were calcinated at 500 °C for 2 h in air. It seems that all the precursor fibers have been completely converted into porous fibers with a rough surface, disclosing that the obtained nanostructures exhibit a high purity and well-defined fiber shape. Their average diameters are reduced to be of ~425 nm (the inset in Fig. 1(b)) from ~530 nm (the inset in Fig. 1(a)) of the as-spun polymeric precursor fibers, which could be caused by the elimination of impurities, carbon loss by conversion to CO and/or CO_2 and the formation of crystalline TiO_2 after the