

Regular Article

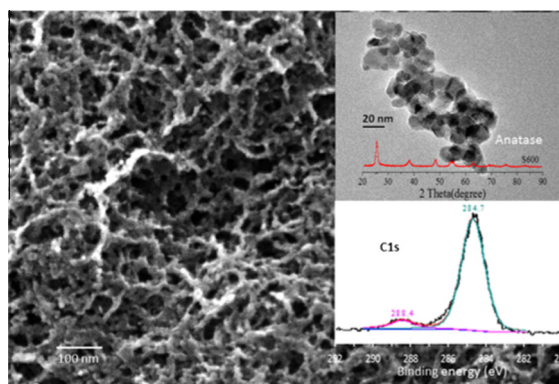
C-doped mesoporous anatase TiO₂ comprising 10 nm crystallites

Chong Xie^{a,1}, Shenghui Yang^{a,1}, Beibei Li^a, Hongkong Wang^a, Jian-Wen Shi^{a,*}, Guodong Li^b, Chunming Niu^{a,*}

^a Center of Nanomaterials for Renewable Energy, State Key Lab of Electrical Insulation and Power Equipment, School of Electrical Engineering, Xi'an Jiaotong University, Xi'an 710049, China

^b State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 31 October 2015

Revised 27 January 2016

Accepted 30 January 2016

Available online 9 May 2016

Keywords:

TiO₂
MWCNT
Photocatalysis
Carbon doping
Mesoporous

ABSTRACT

We report a C-doped mesoporous anatase TiO₂ with high surface area synthesized using multi-walled carbon nanotube (MWCNT) mat as a “rigid” template and carbon doping source. The characterization by SEM, HRTEM, X-ray diffraction and nitrogen adsorption revealed that TiO₂ samples have a porous structure which are figuratively a inverse copy of MWCNT network and pore walls are formed by inter-connected TiO₂ nanoparticles with average diameter of ~10 nm. We found that annealing temperatures from 400 to 1000 °C before MWCNT template removal had very limited effect on particle size (~10 nm), surface area (112–129 m²/g) and total pore volume (0.74–0.85 m³/g) of the samples through a significantly delayed phase transition from anatase to rutile started at 800 °C, resulting in only ~9.1% conversion at 1000 °C. The pore size distribution is in mesopore range from 6 to 60 nm peaked at ~24 nm. XPS analysis showed a relatively strong C1s peak at 288.4 eV, indicating C doping at Ti sites, which is responsible for red shift of adsorption edge of UV–vis spectra and photocatalytic activity in visible-light region.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

TiO₂ is one of the most important catalytic materials. It has been widely used as active catalyst component and catalyst support for the preparation of heterogeneous catalysts [1,2], and more significantly it is highly photocatalytic active [3–5] and has been

* Corresponding authors.

E-mail addresses: shijwnw@163.com (J.-W. Shi), cniu@mail.xjtu.edu.cn (C. Niu).

¹ These authors contributed equally.

continuously attracting worldwide attention ever since its photocatalytic activity was discovered by Fujishima in 1972 [3]. Despite over several decades of study and searching for alternatives, TiO₂ remains a bench mark against which any new photocatalytic material is measured. In addition to its superior photocatalytic activity, several other properties, including chemical stability, nontoxicity and low cost have also contribute to TiO₂ popularity, especially for environmental applications.

TiO₂ exists naturally in three crystal polymorphs of rutile, anatase and brookite. The rutile is thermodynamically most stable, anatase and brookite irreversibly convert to rutile upon heating at temperatures between 600 and 800 °C. It has been proved that anatase is most photocatalytic active phase [6–8]. Fundamental issues which still limit photocatalytic performance of TiO₂ and hinder its practical applications, remain to be its limited optical response in UV region below 387 nm [9–11] due to its wide band gap of ~3.2 eV, and its fast charge-carrier recombination rate. Therefore there is a continued interesting in searching for means to modify TiO₂, so that its photocatalytic response could be extended into visible light region and its charge carrier recombination rate could be reduced.

Several methods have been used to low the band gap energy of TiO₂, including defects generation by H₂ reduction [12–14], doping by transition metal [15,16] and nonmetallic ions (S, N, C, etc.) [9,10,17–19]. It has been proven that nonmetallic ion doping is most effective. Asahi et al. [9] reported that doping TiO₂ with N atoms shifts its optical absorption and photodegradation activity of methylene blue and gaseous acetaldehyde into the visible light region of <500 nm. Khan et al. [10] prepared TiO₂ by control combustion in a natural gas flame, resulting in some substitution of lattice O by C atoms and a band gap energy reduction from 3.0 eV to 2.32 eV. The material showed significantly improved water splitting photocatalytic activity.

In addition to doping, it has been demonstrated that modification of TiO₂ with low band gap semiconducting nanoparticles, such as CdS (~2.4 eV) induces visible light photo response with lower recombination probability due to charge carrier exchange between CdS and TiO₂ [20–23]. Deposition of noble metal nanoparticles on TiO₂ surface [24–26] has been shown to greatly enhance photocatalytic activity of TiO₂ through a mechanism in which metal nanoparticles play a role of “quarterback”-accepting photoelectron from TiO₂ then transferring to reactants with a net effect of extension of charge carrier life time. Structural and morphological aspects of TiO₂ are also important to its photocatalytic activity. It has been demonstrated that photocatalytic activity of TiO₂ is crystallographic facet dependent [19,27–29]. The (0 0 1) surface is more active than (1 0 1) surface due to its higher surface energy, which facilitates charge carrier transport to reactants, resulting in reduction of charge carrier recombination rate. Several physical properties of TiO₂, including specific surface area, pore size and pore size distribution are morphology dependent. Specific surface area and porosity are directly related to concentration of active surface sites and how fast reactants can diffuse to, and products can diffuse away from these sites. Therefore control of the morphology of TiO₂ is one of the important tasks for the preparation high photoactive TiO₂ catalyst. A number of reports have been focused [29–37] on study of the effect of TiO₂ morphology on its photocatalytic activity. TiO₂ with various morphologies, such as nanoparticles [15], nanorods [31,32], nanotubes [33,37], nanosheets [29,30,34] and nanowires [35,36] have been investigated.

In general, it is highly desirable to have TiO₂ with following properties for photocatalytic applications, including high crystallinity, high surface area, mesoporous with narrow pore size distribution, high content of anatase phase and photo responsive in visible light region. In this work, we explore use of prefabricated

MWCNT mat as a “rigid” pore template and carbon doping source for synthesis of C-doped mesoporous TiO₂. The crystallization and phase evolution of TiO₂ inside the MWCNT network from 400 to 1000 °C were studied by SEM, HRTEM and X-ray diffraction, nature of doped C atoms in TiO₂ was probed by XPS, specific surface area and pore size distribution were measured by N₂ adsorption, and finally, the visible light photocatalytic activities of the samples were demonstrated by degradation of methyl orange (MO) under visible light irradiation.

2. Experimental method

2.1. Materials synthesis

MWCNTs were prepared by chemical vapor deposition (CVD) using Co/Fe–Al₂O₃ as the catalyst, ethylene as the carbon source [38]. As-prepared MWCNTs were soaked in a mixture solution of H₂SO₄ and (NH₄)₂S₂O₈ with a mole ratio of 1:1 for 7 days, then collected by filtration and washed with excess water to neutral. The process removes amorphous carbon from the surface of MWCNTs and introduces functional groups, such as –OH and –COOH to the defective sites.

MWCNT dense mats were prepared by a vacuum filtration method [39]. Typically, 0.125 g of functional MWCNTs was dispersed in 100 ml deionized water assisted by high speed mechanical shearing (20,000 rpm), then MWCNTs were collected on the top of a PVDF membrane by vacuum filtration, washed and dried at 100 °C for 1 h to obtain a freestanding mat. The dried MWCNT mats were stored under vacuum for subsequent use.

C-doped mesoporous TiO₂ was prepared using freestanding MWCNT mat as the pore template and carbon doping source. Typically, a dried MWCNT mat was placed into a 50 mL saline bottle, the bottle was pumped to 10^{–2} Torr with an Edwards RV12 pump, then 28 mL solution mixture of butyl titanate (AR, Sinopharm Chemical Reagent Co. LTD) and ethanol with a volume ratio of 1:6 was quickly injected into the saline bottle with a syringe through a rubber septa. After soaking in the solution for 2 h, the MWCNT mat saturated with butyl titanate ethanol solution was transferred into a stainless steel autoclave lined with PTFE and heated at 180 °C for 24 h. After it was cooled down to room temperature, the film was taken out from the vessel and rinsed with ethanol for several times to remove the materials on external surface of the mat and then dried at 60 °C under argon atmosphere, resulting in an intermediate product denoted as TiO₂/MWCNT. Then, TiO₂/MWCNT samples were heated under flowing Ar at high temperature from 400 to 1000 °C to crystallize TiO₂. After high temperature treatment, MWCNT template was removed by heating at 600 °C under flowing mixture gases of Ar and O₂ (8:1) for one hour to yield C-doped mesoporous TiO₂.

2.2. Characterization

SEM images were obtained using a FEI Quanta 250 microscope (FEI, US). TEM study was carried out with a JEM-2100 HT (JEOL, Japan) microscope. X-ray diffraction (XRD) patterns were recorded on a D2 Phaser X-ray diffractometer (Bruker, Germany) at room temperature using CuK α radiation. The nitrogen adsorption isotherms of the samples were measured using an Autosorb-iQ analyzer (Quantachrome, US). Before the measurements, all samples were degassed at a temperature of 100 °C for 6 h. Specific surface area was calculated by BET method using linear portion of adsorption branch of the isotherms. Pore size and pore volume analysis were carried out with BJH method using desorption branch of the isotherms. X-ray photoelectron spectroscopy (XPS) analysis were carried out with a AXIS Ultra OLD X-ray Photoelectron Spec-

Download English Version:

<https://daneshyari.com/en/article/6994009>

Download Persian Version:

<https://daneshyari.com/article/6994009>

[Daneshyari.com](https://daneshyari.com)