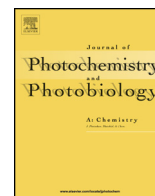




Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

N-doping Ta₂O₅ nanoflowers with strong adsorption and visible light photocatalytic activity for efficient removal of methylene blue

Xiaomin Shi^a, Delong Ma^a, Ying Ma^a, Anming Hu^{a,b,*}^a Institute of Laser Engineering, Beijing University of Technology, Beijing 100124, China^b Department of Mechanical, Aerospace, and Biomedical Engineering, University of Tennessee, 509 Doughty Engineering Building, 1512 Middle Drive, Knoxville, TN 37996, USA

ARTICLE INFO

Article history:

Received 2 September 2016

Accepted 14 September 2016

Available online 19 September 2016

Keywords:

N-doping

Ta₂O₅

Strong adsorption

Visible light

Photo-degradation

MB

ABSTRACT

Novel 3D N-doping Ta₂O₅ nanoflowers (NFs) photocatalysts were synthesized at different annealing temperatures ranging from 700 °C to 850 °C. The microstructure, phase composition, and chemical states of those photocatalysts were characterized in details. The adsorption kinetics as well as photocatalytic performance under visible light irradiation were also investigated. Importantly, compared to N-doping Ta₂O₅ NFs samples obtained at other nitriding temperatures, the Ta₂O₅ NFs nitrided at 750 °C displayed high surface adsorption and photocatalytic degradation activity of Methylene Blue (MB) due to the synergistic effect of large surface area, strong surface adsorption, light absorption and photosensitization. The experiment results confirmed that the adsorption of MB to these samples and photocatalytic degradation follow the pseudo-second order chemisorption mechanism and pseudo first order degradation kinetics, respectively. The main reactive species were identified through the scavenging reaction following the order of $h^+ > \cdot OH > \cdot O_2^-$. Additionally, degradation product analysis was conducted using liquid chromatography tandem mass spectrometry (LC-MS) technique combined with the UV-vis absorption spectrum. The results showed that the degradation was initiated by demethylation of the dye molecule. The current work may contribute to additional applications of these 3D N-doping Ta₂O₅ hierarchical nanostructures such as photoelectric chemical (PEC) water splitting, surface adsorption, supercapacitors, solar cells, etc.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

With the rapid development of economy, the environment protection and sustainability is facing unprecedented pressure. In particular, the widespread presence of organic dyes in wastewater has attracted health concerning. Most of the dyes with complex aromatic ring structure are difficult to be biodegraded [1,2]. Conventional wastewater-treatment techniques (such as adsorption, sedimentation, coagulation, etc.) are being gradually eliminated due to either the high cost or the release of harmful by-products [3]. Accordingly, developing nondestructive, green, and sustainable methodologies for water treatment is hence of great significance. In recent years, advanced oxidation processes (AOPs) (photocatalytic degradation, Fenton method, photofenton, ozonolysis, sonolysis, etc.) are increasingly employed as high

efficiency methods to non-selectively decompose various organic dyes [4,5]. Photocatalytic degradation as one of the widely used AOPs involves a photochemical process that catalysts (such as semiconductors) adsorb ultraviolet or visible light energy larger than the band gap of themselves, and produce valence band holes and conduction band electrons which can further react with species adsorbed on the catalyst surface.

TiO₂ has been widely studied as one of semi-conductive photocatalyst owing to its cost-effectiveness, nontoxicity, unique photocatalytic efficiency, and high stability [6,7]. However, it can only be excited by ultraviolet light (only accounting for 3–5% of the whole solar spectrum). To better utilize the sunlight in tackling water contamination issues, numerous efforts have been made to modified TiO₂ such as non-metallic elements doping [8], sensitization [9], semiconductor coupling [10], etc. Among these strategies, nitrogen doping has triggered intensive interests since visible-light-responsive photocatalyst of N-doped TiO₂ was first reported by Asahi and colleagues [11]. As we know, the conduction band and valence band energy levels in semiconductors are mainly composed of empty d orbital of transition metal ions and empty p

* Corresponding author at: Institute of Laser Engineering, Beijing University of Technology, Beijing 100124, China.

E-mail address: anminghu@bjut.edu.cn (A. Hu).

orbital of nonmetallic ions, respectively. Compared to the potential of the oxygen 2p orbital in metal oxides, the more negative potential of the nitrogen 2p orbital can result in different (oxy) nitrides with narrow band gaps. The wide solar spectrum energy can thus be harvested [12].

Similar nitrogen doping strategies have been applied to Ta₂O₅ (E_g ~ 4.0 eV), a good photocatalyst for both contaminant degradation and hydrogen generation from water splitting. The doping can shift the optical response from UV to the visible spectral range. To date, different shaped N-doped Ta₂O₅ photocatalysts (such as Ta₃N₅ nanoparticles [13], TaON ellipsoids [14], Ta₃N₅ nonwoven cloth [15], mesoporous Ta₃N₅ microspheres [16], etc.) have been reported, however, systematic studies of adsorption kinetics, photocatalytic degradation kinetics and dye degradation products analysis for 3D layered N-doping Ta₂O₅ have not yet reported in previous researches. In this work, we synthesized N-doping Ta₂O₅ NFs with hierarchical structures, investigated their adsorption kinetics of MB, and photocatalytic degradation performance under visible light irradiation. By further analyzing the degradation products, we proposed the photocatalytic mechanism based on the identification of the main active species. The results showed that these hierarchical Ta₂O₅ NFs or N-doping Ta₂O₅ NFs possessed a strong chemisorption ability towards MB. Notably, compared to Ta₂O₅ NFs, the photocatalytic degradation activities towards MB by N-doping Ta₂O₅ NFs were significantly enhanced under visible light illumination.

2. Experimental details

2.1. Materials

Unless otherwise noted, all the chemicals used in this study were without further purification and deionized water was used in all the reactions. Hydrofluoric acid (HF, 99.6%, AR, 40 wt%), hydrogen peroxide (H₂O₂, 99.9%, AR, 30 wt%), tantalum powder (99.97% purity), methanol (99.9%, AR), MB (373.9, AR), iso-propyl alcohol (IPA), *p*-Benzoquinone (BQ), and triethanolamine (TEOA) were purchased from Tianjin Fu Chen Chemical Reagents Factory.

2.2. Preparation of photocatalysts

The preparation of N-doping Ta₂O₅ NFs includes two consecutive steps: anodization and nitridation similar to that described by Su et al. [17]. In a typical anodization step, 500 mg tantalum powder, 20 mL of 0.5 M HF aqueous solution and 2 mL H₂O₂

solution were mixed and then transferred into a Teflon-lined autoclave reactor with a volume of 50 mL for the thermal treatment at 240 °C for 12 h. After naturally cooling to room temperature, the as-anodized samples (labeled F-Ta₂O₅ NFs) were obtained by centrifugation, washed with ethanol for three times and dried in oven at 60 °C for 8 h. The counterparts of Ta₂O₅ were obtained by calcining F-Ta₂O₅ samples at 700 °C in air for 5 h. The nitridation step involved the annealing of Ta₂O₅ NFs under NH₃ atmosphere with a flow of 30 mL/min at 700 °C, 750 °C, 800 °C, and 850 °C for 5 h, respectively. The resultant final products were labeled as N-Ta₂O₅-700 °C, N-Ta₂O₅-750 °C, N-Ta₂O₅-800 °C, and N-Ta₂O₅-850 °C. The detailed preparation procedure is depicted in Fig. 1.

2.3. Characterization techniques

The phase structure of samples was identified by using X-ray diffraction (XRD) with Cu K α radiation. The morphology of the resultant products was characterized by a Hitachi S-4800 field-emission scanning electron microscope (SEM). Transmission electron microscopy (TEM) images were obtained by a transmission electron microscope (Tecnai G2 F20) operating at an acceleration voltage of 200 kV. The chemical states were analyzed using X-ray photoelectron spectroscopy (XPS) (Thermo Escalab 250Xi, a monochromatic Al K α X-ray source). Optical properties of samples were investigated by UV–vis diffuse reflectance spectroscopy (UV–vis DRS) using a UV–vis spectrophotometer (UV-5500, Shimadzu). Brunauer-Emmett-Teller (BET) surface area and pore size distribution were determined by an ASAP 2020 physisorption apparatus. The chromatographic experiment with HPLC–UV/Vis system was carried out on a HP 1100 liquid chromatograph (Agilent, USA) and the mass spectrometer was equipped with an electrospray ionization source and operated in a positive polarity.

2.4. Adsorption and photocatalytic activity measurement

Photocatalytic degradation activities of the samples were evaluated by the degradation of MB dye as a model molecule under visible light irradiation using a 500 W Xe lamp (with a UV filter at 450 nm) as the light source. In each experiment, 100 mg of photocatalyst was dispersed in MB aqueous solution (100 mL, 14.2 mg/L). Before illumination, the suspensions were magnetically stirred in the dark for 60 min to reach an adsorption–desorption equilibrium of MB on catalysts. At given time intervals, a 3 mL suspension was sampled and centrifuged to remove the

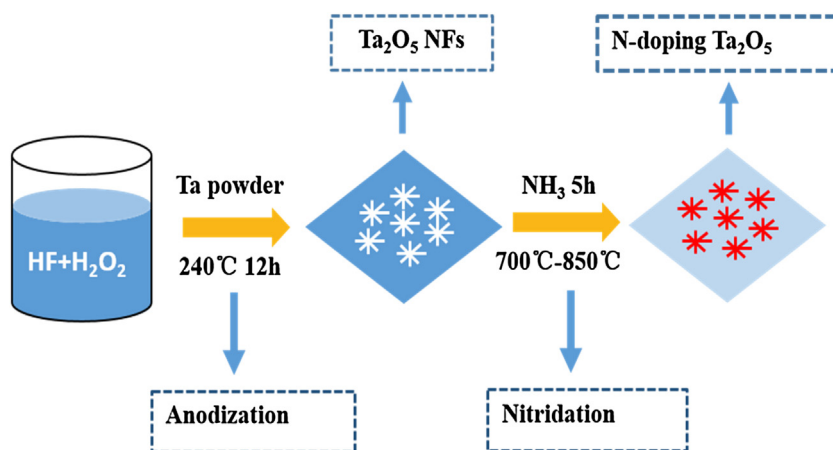


Fig. 1. Schematic processes of N-doping Ta₂O₅ NFs fabricated at different temperatures.

Download English Version:

<https://daneshyari.com/en/article/4754246>

Download Persian Version:

<https://daneshyari.com/article/4754246>

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