Applied Surface Science 357 (2015) 160–166

Contents lists available at ScienceDirect

Applied Surface Science

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

Fabrication of copper decorated tungsten oxide–titanium oxide nanotubes by photochemical deposition technique and their photocatalytic application under visible light

Mohamad Mohsen Momeni

Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran

ARTICLE INFO

Article history:
Received 4 July 2015
Received in revised form 31 August 2015
Accepted 1 September 2015
Available online 3 September 2015

Keywords:
Photocatalyst
Photochemical deposition
Nanotubes
Copper
Visible light

ABSTRACT

Copper decorated WO_3–TiO_2 nanotubes (Cu/WTNs) with a high photocatalytic activity were prepared by anodizing and photochemical deposition. Highly ordered WO_3–TiO_2 nanotubes (WTNs) on pure titanium foils were successfully fabricated by electrochemical anodizing and copper deposited on these nanotubes (Cu/WTNs) by photoreduction method. The resulting samples were characterized by various methods. Only the anatase phase was detected by X-ray diffraction analysis. The presence of copper in the structure of thin films was confirmed by energy dispersive X-ray spectrometry and X-ray diffraction. The extension of optical absorption into the visible region of as-prepared films was indicated by UV/Vis spectroscopy. The degradation of methylene blue was used as a model reaction to evaluate the photocatalytic activity of the obtained samples. Results showed that the photocatalytic activity of Cu/WTNs samples is higher than bare WTNs sample. Kinetic research showed that the reaction rate constant of Cu/WTNs is approximately 2.5 times higher than the apparent reaction rate constant of bare WTNs. These results not only offer an economical method for constructing Cu/WTNs photocatalysts, but also shed new insight on the rational design of a low cost and high-efficiency photocatalyst for environmental remediation.

1. Introduction

Since Zwilling et al. firstly showed that titanium could be converted to highly ordered TiO_2 nanotubes using self-assembly during electrochemical anodizing, there have been lots of efforts to study these nanostructures and discover their potential applications [1–5]. It has been well recognized that TiO_2 nanotubes have different application due to its unique highly ordered array structure, good mechanical and chemical stability, excellent corrosion resistance and high specific surface area [5–7]. Nevertheless, the practical application of TiO_2 nanotubes was limited by several defects. On the one hand, the wide band gap (3.2 eV) of TiO_2 can only be excited by ultraviolet (UV) light, which only accounts for 5% of the solar spectrum. On the other hand, the rapid recombination of photoinduced electrons and holes greatly lowered the quantum efficiency [8]. In order to effectively extend the photoresponse of TiO_2 in to visible light region and improve its visible light absorption and separate the photoinduced charge carriers, a great deal of attempts has been performed [5]. In order to improve the photocatalytic efficiency and extending the spectral response of TiO_2 nanotube to the visible spectrum, many attempts have been made such as doping noble metals such as Pt, Pd, Au and Ag. The doped metal ion enhances the photocatalytic activity by reducing electron-hole pair recombination and/or reducing the band gap. However, these noble metals are very scarce and very expensive [9]. In this context, one potential metal dopant for TiO_2 is copper. Copper, as an important metallic material with excellent electronic conductivity, is abundant in the earth, environmentally benign, and low in price, and hence is a good candidate for loading of TiO_2.

In the present study, we reported an effective synthetic strategy for preparation of WO_3–TiO_2 nanotubes decorated with copper with excellent photocatalytic performance. Highly ordered WO_3–TiO_2 nanotubes (WTNs) were prepared through anodizing, followed by annealing treatment. Subsequently, copper was deposited onto the as-prepared WTNs by photochemical deposition. Compared with nanoparticles, nanotubes arrays not only have three-dimensional tubular structure and large specific surface area, but also can be used repeatedly and conveniently. After then, the resulting samples were characterized by scanning electrons microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX) and UV–Vis light diffuse reflection spectroscopy. In addition, photocatalytic activity of WTNs and

E-mail address: mm.momeni@cc.iut.ac.ir

http://dx.doi.org/10.1016/j.apsusc.2015.09.015
0169-4332/

Table 1
The experimental parameters for the synthesis of different samples.

Samples	Anodizing solution and condition	Photochemical deposition in $Cu(NO_3)_2 \cdot 3H_2O$ solution
WTNs	97 ml DMSO + 2 ml HF + 1 ml H_2O + 0.12 mM $Na_2WO_4 \cdot 2H_2O$ (40 V, 8 h at room temperature)	–
Cu/WTNs-1	97 ml DMSO + 2 ml HF + 1 ml H_2O + 0.12 mM $Na_2WO_4 \cdot 2H_2O$ (40 V, 8 h at room temperature)	UV irradiation for 30 min
Cu/WTNs-2	97 ml DMSO + 2 ml HF + 1 ml H_2O + 0.12 mM $Na_2WO_4 \cdot 2H_2O$ (40 V, 8 h at room temperature)	UV irradiation for 60 min
Cu/WTNs-3	97 ml DMSO + 2 ml HF + 1 ml H_2O + 0.12 mM $Na_2WO_4 \cdot 2H_2O$ (40 V, 8 h at room temperature)	UV irradiation for 90 min

corresponding copper modified films (Cu/WTNs) on the degradation of methylene blue (MB) has been systematically investigated. A great deal of research has been directed toward using coupled WO_3–TiO_2 systems with the purpose of promoting the photonic efficiency of TiO_2. Tungsten has a high charge state with six electrons in the outer orbit and its ionic radius was 0.60 Å and was similar to Ti^{4+} (0.605 Å), thus tungsten atom could substitute easily the titanium atom in TiO_2 lattice [10,11]. WO_3 is a semiconductor with a band gap of 2.8 eV, which is activated by visible light illumination [10–14]. The basic disadvantage of WO_3 as a photocatalyst is its low photonic efficiency [12]. The promoting effect of copper on the WTNs efficiency, has received little attention so far in the literature. To the best of our knowledge, till now, very less research has been done to preparing of copper deposited WTNs by photochemical deposition and anodizing process.

2. Experimental

All the used chemicals were of analytical grade without further purifying before experiment and solutions were prepared with distilled water.

WTNs were synthesized by anodizing of titanium in a mixture electrolyte, which was mixing DMSO and HF, followed by the dissolution 12 mM of sodium tungstate. The anodizing experiments were carried out using a two-electrode system with titanium foil as anode and platinum foil as cathode, respectively. Anodizing was carried out under a constant voltage of 40 V for 8 h at room temperature. After anodizing, the as-formed samples were annealed in the air at 400 °C for 2 h (1 °C/min) to obtain crystalline film. Then copper decorated on these samples were prepared using a photochemical deposition method. In a typical synthesis, 20 mM $Cu(NO_3)_2 \cdot 3H_2O$ aqueous solution was prepared and WTNs samples were soaked in this solution and irradiated by using a 400 W high pressure mercury lamp at ambient temperature for different durations. The obtained modified electrode washed thoroughly with distilled water and used for the next experiments. In the present work, we compare the photocatalytic performance of bare WTNs and Cu/WTNs samples. Table 1 summarizes the experimental conditions for different samples. A schematic of the pretreatment method of titanium and producing process of WTNs and Cu/WTNs films on titanium is shown in Fig. 1.

The surface morphology of all samples were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4160, Japan) and the elemental composition was estimated by energy dispersive X-ray spectroscopy (EDX). The crystalline phases were identified by XRD with Equinox 3000 diffractometer (Inel, France). Diffraction patterns were recorded in the 2θ range from 20 to 80° at room temperature. The optical absorption of the samples was determined using a diffuse reflectance UV-visible (DRUV–Vis) spectrophotometer (JASCO V-570).

Photocatalytic activities of all the samples were evaluated by degradation of the aqueous methylene blue (MB) under visible light irradiation. The photocatalytic reaction was carried in a single-compartment cylindrical quartz reactor. A 200 W xenon lamp was used as a light source with a 420 nm cutoff filter to provide visible light. The luminous intensity of the xenon lamp was 100 mW/cm^2. Several fans were used to cool down the reactor tube. The actual experiments were performed at room temperature. The initial concentration of methylene blue was 2 mg/L. Prior to illumination, the photocatalyst sample was immersed in quartz reactor containing methylene blue and magnetically stirred for 2 h in the dark to ensure the establishment of an adsorption–desorption equilibrium between the photocatalyst and methylene blue. Then the solution was exposed to visible light irradiation under magnetic stirring for 1 h. At each 5 min intervals, 5 ml solution was sampled and the absorbance of methylene blue was measured by a UV–Vis spectrophotometer.

3. Results and discussion

Fig. 2 showed the top-view FE-SEM images of the prepared WTNs films before (a) and after the copper was deposited (b–d). Fig. 2a shows top-view FE-SEM images of WTNs samples which clearly show formation of nanotube arrays that the surface of them was open. One can see that the WTNs possesses highly ordered

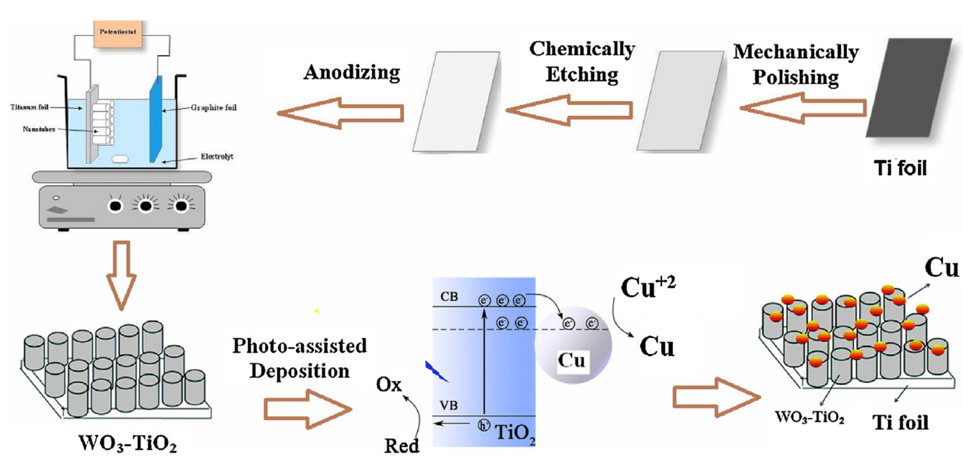

Fig. 1. Schematic presentation of the pretreatment method of titanium sheets and producing process of WTNs and Cu/WTNs films on titanium foils.