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Fabrication, characterization and photocatalytic properties of Au/TiO_2-WO_3 nanotubular composite synthesized by photo-assisted deposition and electrochemical anodizing methods

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ABSTRACT

A photo-assisted deposition (PAD) technique was adopted to construct highly dispersed gold nanoparticles on TiO_2-WO_3 nanotubular composite electrodes prepared by one-step electrochemical anodizing. The morphology, crystallinity, elemental composition and light absorption capability of samples were distinguished based on various characterizations. The degradation of methylene blue (MB) was used as a model reaction to evaluate the photocatalytic activity of the obtained samples. Characterization of the as-prepared TiO_2-WO_3 samples indicated that dopant concentration in anodizing solution significantly influenced the morphology and photocatalytic activity of fabricated films. It was found that the degradation ratio of Au/TiO_2-WO_3 nanotubes was improved as compared with that of bare TiO_2-WO_3 nanotubes. The experimental results showed that the photocatalytic activities of Au/TiO_2-WO_3 were significantly affected by the amount of Au nanoparticles. This work provides an insight into designing and synthesizing new TiO_2-WO_3 nanotubes-based hybrid materials for effective visible light-activated photocatalysis.

1. Introduction

High surface area thin film electrode has wide range of technological applications such as dye-sensitized solar cells, water splitting, water purification, supercapacitor CO_2 reduction, etc. [1–7]. TiO_2 nanotube arrays are superior with its one dimensional oriented architecture, its unique electronic and optical properties, high orientation, tunable mesopore size, large internal surface area, fast electron transport between interfaces and simple electrochemical fabrication technique [8–10]. In comparison with the TiO_2 powders which require filtration after the photocatalysis, TiO_2 nanotube can be easily operated repeatedly in practical applications because the nanotubes grow from the titanium substrate, constructing a photocatalyst with highly physical stability. Furthermore, nanotube shows unique physical and chemical properties because they have much more free spaces in their interior as well as outer space that can be filled with active materials, giving them an essential predominance over powders [11–14]. However, wide band gap of TiO_2 nanotube (3.2 eV) limits the efficiency of photocatalytic reactions (which means that only UV light is efficiently absorbed and thus in view of solar light driven processes, only ~4–7% of the entire solar spectrum can be exploited). In recent years, considerable researches are directed to reduce its band gap by doping or band-gap engineering to develop new photocatalysts capable of utilizing visible light accounting for ~43% of sunlight [15]. So, studies in the field of photocatalysis have therefore focused on the preparation of semiconductor materials capable of utilizing the visible component of solar light, effectively. The aim has been to increase the photonic efficiency of the processes of destruction of water and air contaminants. In order to extend the photocatalytic capability into the visible light range, extensive efforts have been made to narrow the band gaps of TiO_2 by doping the TiO_2 with metal or nonmetal atoms or coupling TiO_2 with some semiconductors, in which one of them is excited by visible light irradiation [16–21]. Another method to promote the photonic efficiency of TiO_2 has been the surface modification with nanoparticles of noble metals [22–24]. Among all methods, the deposition of noble metal nanoparticles has been demonstrated as one of the most promising and viable ways to depress the recombination of photogenerated electron-hole pairs in photocatalytic processes [14,25]. A great deal of research has been directed towards using coupled WO_3-TiO_2 systems with the purpose of promoting the photonic efficiency of TiO_2 in the decomposition of water and air contaminants. Because W^{6+} has an ionic radius similar to that of Ti^{4+}, WO_3 can couple into

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

Samples	Anodizing solution and condition	photo-assisted deposition in 5 mM $HAuCl_4 \cdot 3H_2O$ aqueous solution
A	98 mL glycerol + 2 mL H_2O + 0.13 M NH_4F (60 V, 6 h at room temperature)	–
B	98 mL glycerol + 2 mL H_2O + 0.13 M NH_4F + 0.6 mM $Na_2WO_4 \cdot 2H_2O$ (60 V, 6 h at room temperature)	–
C	98 mL glycerol + 2 mL H_2O + 0.13 M NH_4F + 1.2 mM $Na_2WO_4 \cdot 2H_2O$ (60 V, 6 h at room temperature)	–
D	98 mL glycerol + 2 mL H_2O + 0.13 M NH_4F + 1.8 mM $Na_2WO_4 \cdot 2H_2O$ (60 V, 6 h at room temperature)	–
E	98 mL glycerol + 2 mL H_2O + 0.13 M NH_4F + 0.6 mM $Na_2WO_4 \cdot 2H_2O$ (60 V, 6 h at room temperature)	UV lamp irradiation for 0.5 h
F	98 mL glycerol + 2 mL H_2O + 0.13 M NH_4F + 0.6 mM $Na_2WO_4 \cdot 2H_2O$ (60 V, 6 h at room temperature)	UV lamp irradiation for 1 h

TiO_2 crystals in their co-crystallization process during annealing, resulting in a well doped WO_3-TiO_2 composite. 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 [26–29]. WO_3 is a semiconductor with a band gap of 2.8 eV, which is activated by visible light illumination [27]. The basic disadvantage of WO_3 as a photocatalyst is its low photonic efficiency [24]. The promoting effect of noble metal particles on the TiO_2-WO_3 nanotubular efficiency, has received little attention so far in the literature.

In this work, visible light photocatalytic activity of TiO_2-WO_3 nanotubular composite and Au/TiO_2-WO_3 nanotube was investigated and compared by degradation of Methylene blue (MB). Methylene blue molecular formula is $C_{16}H_{18}N_3SCl$ (molecular weight, 319.85 g/mol). It is a cationic dye, used extensively for dying cotton, wool and silk. The risks of the existence of this dye in waste water have arisen from the burns effect of eye, nausea, vomiting and diarrhea. MB has a maximum absorption in the 660 nm visible area. Methylene blue is chosen as a model contaminant to evaluate the photocatalytic activity of prepared samples due to its stability under visible light irradiation [30]. Chemical structure of methylene blue ($C_{16}H_{18}N_3SCl$) makes it to fall under a group of azin dyes. Au/TiO_2-WO_3 nanotube composite were prepared by the application of a photo-assisted deposition (PAD) and single-step anodizing of titanium in an organic bath containing sodium tungstate. It was found that the presence of gold significantly improved the photocatalytic performance of samples. The morphology and structure were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). Optical properties were investigated by UV–vis diffuse reflectance spectra. Gold nanoparticles modified TiO_2 nanotube were found to possess attractive activities for photocatalytic applications in the literature, and several methods were proposed to load gold nanoparticles on nanotube, including deposition-precipitation, electrodeposition, physical evaporation and so on [13,24]. To the best of our knowledge, till now, very less research has been done to preparing of Au/TiO_2-WO_3 nanotubes by photo-assisted deposition and anodizing process.

2. Experimental

Glycerol, sodium tungstate ($Na_2WO_4 \cdot 2H_2O$), HF, H_2SO_4, and HNO_3 were of analytical grade. Other chemicals were obtained as analytical reagent grade and used without further purification. The solutions were prepared with distilled water. Titanium (Ti) foils (purity >99.99%, 1 mm thickness) were used. Methylene blue (purity, 99%) was used as received.

Pieces of titanium sheets were cut into desired dimensions and were used as working electrodes in the experiment. The working electrodes were sealed with insulation resin leaving only desired

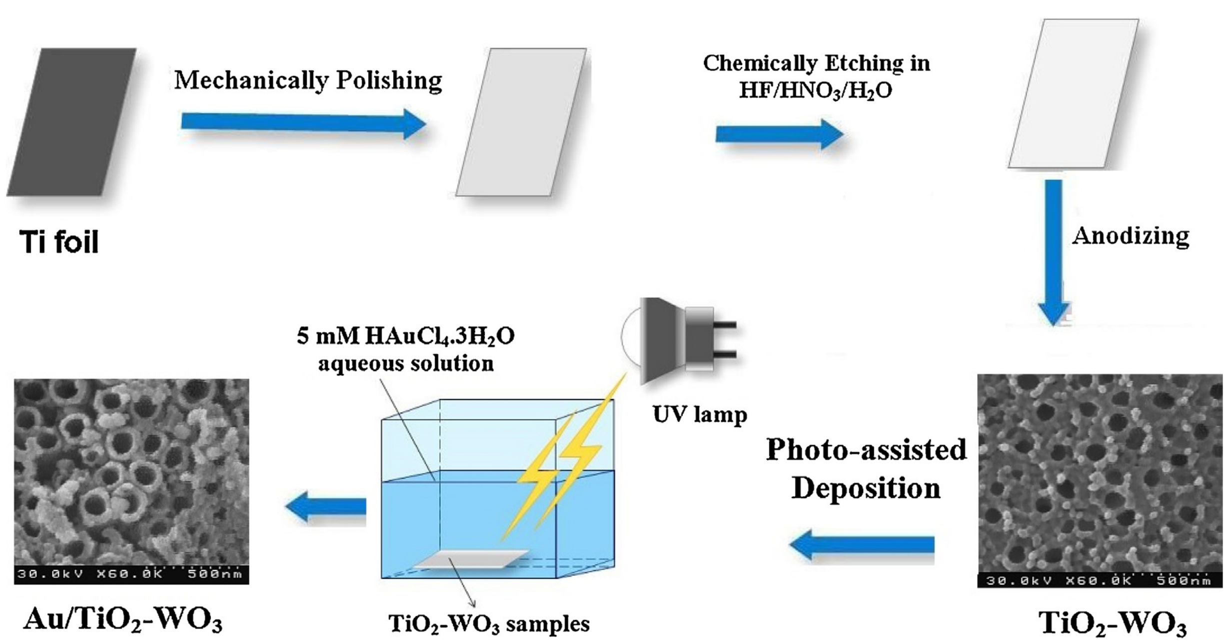

Fig. 1. Schematic presentation of pretreatment method of titanium and producing process of TiO_2-WO_3 and Au/TiO_2-WO_3 samples.