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Novel visible-light-responsive photo-catalysts based on palladium decorated nanotube films fabricated on titanium substrates

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ABSTRACT

A novel visible-light-responsive photo-catalyst was synthesized for the photo-degradation of methylene blue. Highly ordered and uniformly distributed titanium dioxide-tungsten trioxide nanotubes on pure titanium substrates were successfully fabricated by one-step electrochemical anodizing and palladium deposited on these nanotubes by photo-reduction method. The resulting samples were characterized by X-ray diffraction, field emission scanning electron microscope, ultraviolet–visible spectroscopy and energy dispersive X-ray spectrometer methods. The degradation of methylene blue (MB) was used as a model reaction to evaluate the photo-catalytic activity of the obtained samples. After irradiated under visible light for 60 min, degradation ratio of Pd-deposited nanotubes was improved as compared with that of bare titanium dioxide-tungsten trioxide nanotubes. Under the same condition, no obvious photo-degradation of methylene blue was found for bare TiO_2 nanotubes. Kinetic research showed that photo-degradation process followed the first-order reaction; the apparent reaction rate constant of Pd-based nanotubes was approximately 2.19 times higher than that on the unmodified nanotubes. The catalysts prepared in this study exhibit industrially relevant interests due to the low cost and high photo-catalytic activity.

1. Introduction

Photo-catalytic oxidation using a titanium dioxide (TiO_2) based material as the catalyst has attracted substantial attention in recent years, as it is cost-effective, has high catalytic stability and is carried out at room temperature and atmospheric pressure [1–3]. However, with the band gap of ~3.2 eV, TiO_2 is only photo-activated under UV light irradiation, which only accounts for 4% of the solar spectrum. To extend the utilization over the main part (45%) of the visible region in the solar spectrum, several attempts have been made to reduce the band gap of TiO_2 [3]. One strategy is narrowing the band gap of TiO_2 by doping the TiO_2 with metallic or nonmetallic elements, such as Cu, Mn, Fe, Cr, N, C, or coupling TiO_2 with some semiconductors, in which one of them is excited by visible light irradiation [4–7]. Though doping with other elements broadened the spectral response range to the visible region, the recombination of electrons and holes may occur on the lattice defects (vacancies, interstitials and dislocations), which reduce the photo-catalytic activity. Another method to promote the photonic efficiency of TiO_2 has been the surface modification with noble metals [8,9]. The noble metals deposition was reported to produce the Schottky barrier and facilitate electron capture. Therefore, Ag, Au, Ru, Pt and Pd were employed to modify TiO_2 for enhancing UV photo-catalytic efficiency and/or visible light activities [10].

Herein, we reported an effective synthetic strategy for crafting WO_3–TiO_2 nanotubes with palladium with excellent photo-catalytic performance. Highly ordered WO_3–TiO_2 nanotubes were prepared through anodizing, followed by annealing treatment. Subsequently, palladium was deposited onto the as-prepared WO_3–TiO_2 by photo-reduction method. After then, the resulting WO_3–TiO_2 and Pd/WO_3–TiO_2 were characterized by scanning electrons microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX) and UV–vis light diffuse reflection spectroscopy (DRS). In addition, photo-catalytic activity of WO_3–TiO_2 nanotubes and corresponding palladium modified materials were investigated and compared by degradation of methylene blue. It was found that the presence of palladium improved the photo-catalytic performance of samples. 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. 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 [8,9]. WO_3 is a semiconductor with a band gap of 2.8 eV, which is activated by visible light illumination [8]. The basic disadvantage of WO_3 as a photo-catalyst is its low

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

Samples	Anodizing solution and condition	Photo-assisted deposition in $PdCl_2$ aqueous solution
TiO_2	98 ml DMSO+2 ml HF (40 V, 8 h at room temperature)	–
WO_3–TiO_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)	–
Pd/WO_3–TiO_2-1	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 lamp irradiation for 30 min
Pd/WO_3–TiO_2-2	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 lamp irradiation for 60 min

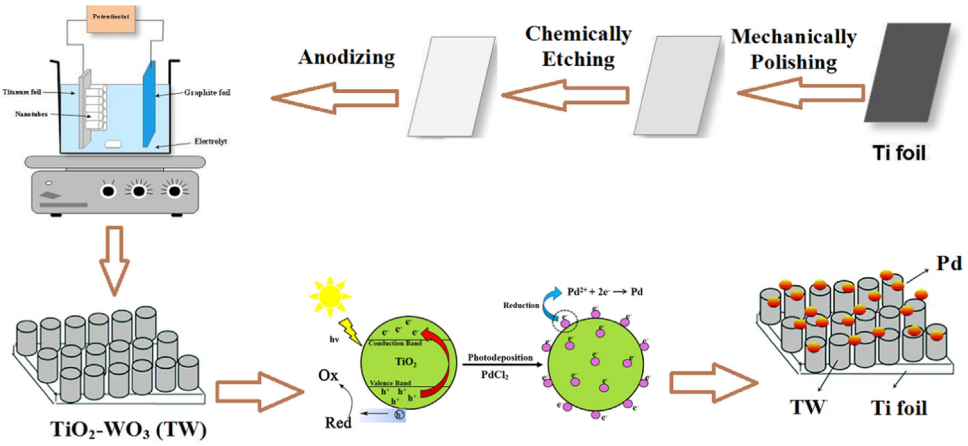

Fig. 1. Schematic presentation of pretreatment method of titanium and producing process of WO_3–TiO_2 and Pd/WO_3–TiO_2.

photonic efficiency [11]. The promoting effect of noble metals particles on the WO_3–TiO_2 nanotubular 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 palladium deposited WO_3–TiO_2 nanotubes by photo-assisted 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.

WO_3–TiO_2 nanotubes 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 (1×1 cm^2) as anode and platinum foil (with geometric area of about 20 cm^2) as cathode, respectively. Anodizing was carried out in mentioned solution under a constant voltage of 40 V for 8 h at room temperature. After anodizing at constant potential, the as-formed samples were annealed in the air at 400 °C for 2 h (1 °C/min) to obtain crystalline film. Then palladium decorated on WO_3–TiO_2 nanotubes was prepared using a photo-assisted deposition (PAD) method. In a typical synthesis, 45 mM $PdCl_2$ aqueous solution was prepared and WO_3–TiO_2 nanotube 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 photo-catalytic performance of bare TiO_2, bare WO_3–TiO_2 and Pd/WO_3–TiO_2 samples. Table 1 summarizes the experimental conditions for different samples. A schematic of the pretreatment method of titanium and producing process of WO_3–TiO_2 and Pd/WO_3–TiO_2 films on titanium is shown in Fig. 1.

The surface morphology of all samples was 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). Elemental mapping was conducted by energy dispersive spectroscopy (EDS). The crystalline phases were identified by XRD (Philips X'Pert). 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 spectrophotometer (JASCO V-570). The values of the band gap energy (E_g) were calculated using following equation:

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^n \quad (1)$$

where E_g is the band gap energy, h is Planck's constant, υ is the frequency of vibration, $h\upsilon$ is the incident photon energy, A is a proportional constant, α is the absorption coefficient per unit length, and n is 0.5 and 2.0 for a direct transition semiconductor and indirect transition semiconductor, respectively [3,6]. The band gap values were determined by extrapolating the linear region of the plot to $h\upsilon = 0$.

Photo-catalytic activities of all the samples were evaluated by degradation of the aqueous methylene blue (MB) under visible light irradiation. The photo-catalytic reaction was carried in a single-compartment cylindrical quartz reactor. A 200 W xenon lamp was used as a light source with a UV cutoff filter to provide visible light. The luminous intensity of the xenon lamp was 100 mW/cm^2. The actual experiments were performed at room temperature. Prior to illumination, the photo-catalyst 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 photo-catalyst and methylene blue. Then the solution was exposed to visible light irradiation under magnetic stirring for 1 h. At certain time intervals, specific amount of the solution was withdrawn and the changes in concentration of MB were observed using a UV–vis spectrophotometer.

3. Results and discussion

Anodizing is an electrolytic process that creates a protective or decorative oxide film over a metallic surface. In anodizing of titanium,