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ARTICLE

Preparation, Characterization and Photocatalytic Activity of Titania Nanotube Arrays Decorated with Tungsten Trioxide

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Abstract: Titania nanotube arrays decorated with WO_3 (WTN) were fabricated by a chemical bath deposition (CBD) technique in combination with a pyrolysis process. The products were uniform and the amount of tungsten can be easily adjusted by the deposition time. The resultant hybrid nanotubes arrays were characterized by SEM, EDX and XRD. Results show that titania nanotubes with an internal diameter of the tubes 90~120 nm, an external diameter 120~160 nm, wall thickness in the range of 30~60 nm and a length of 39 μm are grown on titanium substrate by anodizing. The tungsten trioxide is i decorated on the titania nanotubes, which enhances the photocatalytic activity of the WTN, as indicated by the efficient removal of C.I. Sulphur Red 14. The resultant composite films show better photocatalytic activity than the non-decorated nanotube arrays (TN) under visible light illumination.

Key words: nanotube; film; anodizing; tungsten; titania; photocatalyst

Titania nanotube arrays (TN) have been extensively investigated as photocatalysts for degradation of organic pollutants in water because of their favorable band-edge positions, strong optical absorption, superior chemical stability, photocorrosion resistance, and low cost [1-5]. Nevertheless, the intrinsic band gap of TiO_2 (3.2 eV for anatase and 3.0 eV for rutile) restricts the absorption in the ultraviolet part of the solar spectrum. As UV light is only 4% of the solar spectrum, therefore it is highly desirable to tailor the band gap of TiO_2 in such away so that it can absorb light in the visible region which accounts for about 45% of the solar energy [4]. Therefore, many groups have investigated how to narrow the band gap of TiO_2 to maximize the utilization efficiency of solar energy and increase the yield of the electron-hole pair which is the key factor for the TiO_2 applications. One effective approach is to dope different elements into TiO_2, including metal or nonmetal elements [4-9]. Because W^{6+} has an ionic radius similar to that of Ti^{4+}, WO_3 can couple into TiO_2 crystals in their co-crystallization process during annealing, resulting in a well doped WTN composite. Incorporating WO_3 with TiO_2 not only efficiently inhibits the recombination between the photogenerated holes and electrons but also reduces the band gap of TiO_2 [8]. In the present study, titania nanotube arrays decorated with tungsten trioxide (WTN) were fabricated via an efficient and easily accessible approach. The decoration of tungsten occurred homogenously and tungsten decorated titania nanotubes could be achieved by using chemical bath deposition (CBD) technique. The morphology and structure were characterized by field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). Optical properties were investigated by UV-vis diffuse reflectance spectra. In addition, photocatalytic activity of WTN samples was evaluated through the degradation of C. I. Sulphur Red 14 (CISR) dye. The CISR is highly soluble in water and organic solvent [10]. Its chemical structure is given in Fig.1 and its characteristics are given in Table 1.

1 Experiment

All chemicals were of analytical grade and used as received without further purification or treatment. All solutions were prepared with distilled water. Pieces of titanium metal

Fig.1 Structure of C. I. Sulphur Red 14 (CISR)

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Table 1 Characteristics of C. I. Sulphur Red 14 dye [10]

Variable	Value
Molecular formula	$C_{38}H_{16}N_4O_4S_2$
Molecular structure	Perylene class
Molecular mass/g·mol^{-1}	656.69
λ_{max}/nm	565
Properties and applications	Red. Deep red powder. Used for cotton, hemp, viscose fabric dyeing

sheet (99.99% purity, 1 mm thick) were cut into proper dimensions. Then obtained titanium electrodes were mechanically polished with different emery type abrasive papers (with the following grades: 80#, 240#, 800#, 1200#, and 2400#), rinsed in a bath of distilled water, and then chemically etched by immersing in a mixture of HF and HNO_3 acids for 30 s. The ratio of $HF/HNO_3/H_2O$ in the mixture was 1:4:5 in volume. The last step of pretreatment was rinsing with distilled water. After cleaning, anodic films were grown from titanium by anodizing of titanium foil in a solution of glycerol (90 mL) containing 0.13 mol/L NH_4F and 10 mL distilled water at a constant voltage of 60 V for 6 h at room temperature using a platinum foil as cathode. After anodizing of titanium and preparation of titania nanotube arrays, tungsten were decorated on nanotubes by chemical bath deposition. The titania nanotubes (TN) were soaked in a 0.1 mol/L H_2SO_4 solution for 90 min followed by soaking in a H_2O/ethanol (4:1) solution containing 0.05 mol/L Na_2WO_4 for different time at 70 °C. Then, the samples were rinsed with distilled water and dried in air. Samples were annealed by heating at 400 °C for 2 h, with a heating ramp of 1 °C/min to form tungsten oxide and also to obtain crystalline samples that leading to WTN with varied weight loading percentage of 0.2%, 0.5%, 0.8% and 1.1% referred to as WTN1, WTN2, WTN3 and WTN4, respectively. Table 2 summarizes the experimental conditions for 5 different samples. A schematic of the pretreatment method of titanium and process of producing WTN films on titanium foil is shown in Fig.2.

The surface morphology of all samples was characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4160, Japan). The crystalline phases were identified by XRD (Philips XPert). Diffraction patterns were recorded at room temperature in the 2θ range of 20° to 80°. The optical absorption of the samples was determined using a diffuse reflectance UV-visible (DRUV-Vis) spectrophotometer (JASCO V-570). The values of the band gap energy (E_g) were calculated using following equation:

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

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 and α is the absorption coefficient per unit length[8]. The band gap values were determined by extrapolating the linear region of the plot to $h\upsilon = 0$.

Table 2 Experimental parameters for the synthesis of different samples

Sample	Anodizing solution	Chemical bath#	E_g/eV
TN	90 mL glycerol + 10 mL H_2O + 0.13 mol/L NH_4F (60 V, 6 h at RT)	-	3.20
WTN1	90 mL glycerol + 10 mL H_2O + 0.13 mol/L NH_4F (60 V, 6 h at RT)	Soaking for 1 h at 70 °C	2.70
WTN2	90 mL glycerol + 10 ml H_2O + 0.13 mol/L NH_4F (60 V, 6 h at RT)	Soaking for 2 h at 70 °C	2.60
WTN3	90 mL glycerol + 10 mL H_2O + 0.13 mol/L NH_4F (60 V, 6 h at RT)	Soaking for 3 h at 70 °C	2.30
WTN4	90 mL glycerol + 10 mL H_2O + 0.13 mol/L NH_4F (60 V, 6 h at RT)	Soaking for 4 h at 70 °C	2.15

#: Chemical bath deposition in H_2O/ethanol (4:1) solution containing 0.05 mol/L $Na_2WO_4{\cdot}2H_2O$

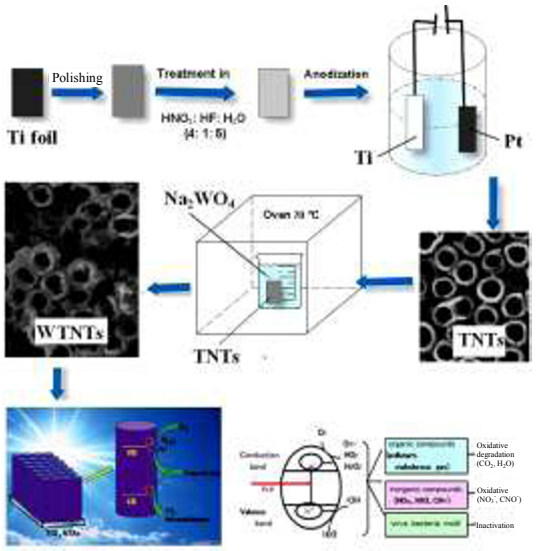

Fig.2 Schematic presentation of the pretreatment method of titanium sheets and producing process of WTN samples

Photocatalytic activity of all the samples was evaluated by degradation of the aqueous C.I. Sulphur Red 14 (CISR) under visible light irradiation. The photocatalytic reaction proceeded 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. 100% of the light was transmitted by the quartz glass as the xenon lamp shone on the samples. A fan was used to cool down the reactor tube. The experiments were performed at room temperature. The initial concentration of CISR was 10 mg/L. The volume of the solution was 50 mL. Prior to illumination, the photocatalyst sample was immersed in quartz reactor containing CISR and magnetically stirred for 2 h in the dark to ensure the