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WO_3/TiO_2 composite coatings: Structural, optical and photocatalytic properties

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ABSTRACT

WO_3/TiO_2 and TiO_2 coatings were prepared on titania substrates using facile and cost-effective plasma electrolytic oxidation process. The coatings were characterized by X-ray diffraction, scanning electron microscopy, Raman, UV–vis diffuse reflectance spectroscopy, and X-ray photoelectron spectroscopy. With increasing duration of PEO process, the monoclinic WO_3 phase became dominant and new monoclinic $WO_{2.96}$ phase appeared. The optical absorption edge in the WO_3/TiO_2 samples, enriched with $WO_3/WO_{2.96}$ phase, was shifted to the visible region. The photocatalytic efficiency of WO_3/TiO_2 and pure TiO_2 samples was evaluated by performing the photodegradation experiments in an aqueous solution of Rhodamine 6G and Mordant Blue 9 under the visible and UV light. The WO_3/TiO_2 catalysts are much more efficient than pure TiO_2 under visible light and slightly better under UV light. The improvement of photocatalytic activity in the visible region is attributed to better light absorption, higher adsorption affinity and increased charge separation efficiency.

1. Introduction

Among semiconductor materials, titanium dioxide (TiO_2) in anatase phase has been shown as excellent and widely used photocatalyst for the degradation of different organic contaminants, because of its physical and chemical stability, high oxidative power, high catalytic activity, long-term photostability, low cost and ease of production. Many organic compounds can be decomposed in an aqueous solution in the presence of TiO_2, illuminated by photons with energies greater than or equal to the band gap energy of titanium dioxide (3.2 eV for anatase TiO_2) [1–6]. The major drawback for TiO_2 commercial use lies in its wide band gap, and relatively high recombination rate of photoinduced electron-hole pairs. The modification of TiO_2 by doping with metals and non-metals [7–12] or by Ti^{3+} self-doping [13,14] have been extensively performed in order to improve its photocatalytic activity under the visible irradiation.

Another very promising approach is the combination of TiO_2 with metal oxides like V_2O_5, ZnS, $InVO_4$, WO_3 [15–19] or graphene [20]. Among the metal oxides, WO_3 has smaller band gap (2.8 eV) than TiO_2 and better absorbs visible light. Moreover, WO_3 has a suitable conduction band potential and acts as a trapping site for photoexcited electrons from TiO_2. The photogenerated holes from the valence band of WO_3 move towards and accumulate in the valence band of TiO_2. In such a way the efficiency of charge separation is increased, enhancing at the same time the photocatalytic acivity of TiO_2 [21]. Additionally, the formation of WO_3 monolayer on TiO_2 increases the acidity of the WO_3/TiO_2 surface enabling the adsorption of greater amount of hydroxyl groups and organic reactants on the surface [21,22]. In recent years, WO_3/TiO_2 composites were synthesized using different methods such as sol-gel, ultrasonic spray pyrolysis, ball milling, hydrothermal, sol-precipitation, and impregnation to improve photocatalytic activity of TiO_2 under the visible light [23–28]. Thin films of TiO_2/WO_3 have also been prepared by dip and spin coating [29,30] or by one-step oxidation method [31]. In most of these reports it was demonstrated that WO_3/TiO_2 composites were found to have much

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higher photocatalytic activity under the visible light than pure TiO_2 [24,26,28,31]. Therefore, the combination of these two materials can lead to increased charge carrier lifetime and improved photocatalytic activity under the visible irradiation. Among different synthesis routs, plasma electrolytic oxidation (PEO) process is very facile, cost-effective and environmentally benign process for producing of well-adhered and crystalline oxide films, but the studies on structural and photocatlytic properties of WO_3/TiO_2 films (coatings), produced by PEO process, are limited [32–34].

In this study WO_3/TiO_2 coatings were synthetized on titanium substrate by using PEO process. Structural and optical properties of the coatings were fully characterized by XRD, SEM, Raman, XPS, and diffuse reflectance spectroscopy. The aim of this work was to tailor the band gap energy of WO_3/TiO_2 coatings towards the visible spectral region, varying the time of PEO process and to explore the photocatalytic properties of the coatings. The photocatalytic efficiency of WO_3/TiO_2 coatings was tested under the visible and UV light irradiation using Rhodamine 6G and Mordant Blue 9 as model pollutants. We demonstrated that this approach provides an efficient route for the formation of cost-effective and improved visible-light-driven photocatalysts.

2. Experimental

2.1. Preparation of WO_3/TiO_2 coatings

WO_3/TiO_2 coatings were prepared on titanium substrate using plasma electrolytic oxidation (PEO) process. PEO process is an anodizing process of lightweight metals (aluminum, magnesium, zirconium, titanium, etc.) or metal alloys above the dielectric breakdown voltage, when thick, highly crystalline oxide coating with high corrosion and wear resistance, and other desirable properties are produced. During the PEO process, numerous small sized and short-lived discharges are generated continuously over the coating's surface, accompanied by gas evolution. Due to increased local temperature, plasma-chemical reactions are induced at the discharge sites modifying the structure, composition, and morphology of such oxide coatings. The oxide coatings formed by PEO process usually contain crystalline and amorphous phases with constituent species originating both from metal and electrolyte. WO_3/TiO_2 coatings were formed on the rectangular titanium samples (99.5% purity, Alfa Aesar) of dimensions 25 mm × 10 mm × 0.25 mm, which were used as working electrodes in the experiment. The working electrodes were sealed with insulation resin leaving only an area of 1.5 cm^2 as an active surface. Before starting the PEO process, titanium samples were degreased in acetone, ethanol, and distilled water, using ultrasonic cleaner and dried in a warm air stream. The anodic oxidation process was conducted in an aqueous solution of 10^{-3} M 12-tungstosilicic acid ($H_4SiW_{12}O_{40}$), at constant current density (150 mA/cm^2). During PEO process, the electrolyte circulated through the chamber–reservoir system. The temperature of the electrolyte was kept fixed at (20 ± 1) °C. Detailed description of PEO process is given in the ref. [33].

After plasma electrolytic oxidation, the samples were rinsed in distilled water to prevent additional deposition of electrolyte components during drying. The WO_3/TiO_2 samples were obtained by varying the time of PEO process from 90 s up to 300 s. The pure TiO_2 sample was obtained after 300 s of PEO process.

2.2. Characterization of WO_3/TiO_2 coatings

The crystal structure of WO_3/TiO_2 samples was analyzed by X-ray diffraction (XRD), using a Rigaku Ultima IV diffractometer in Bragg-Brentano geometry, with Ni-filtered CuKα radiation (λ = 1.54178 Å). Diffraction data were acquired over the scattering angle 2θ from 15° to 75° with a step of 0.02° and acquisition rate of 2°/min. The XRD spectra refinement was performed with the software package Powder Cell. The TCH pseudo-Voigt profile function gave the best fit to the experimental data.

Scanning electron microscope (SEM) JEOL 840A equipped with an EDS detector was used to characterize the morphology and chemical composition of formed oxide coatings.

Micro-Raman scattering measurements were performed at room temperature in a backscattering geometry, using a Jobin-Yvon T64000 triple spectrometer system and Nd:YAG laser line of 532 nm as an excitation source. The incident laser power was kept less than 10 mW in order to prevent the heating effects.

UV-vis diffuse reflectance spectra were acquired using the Specord M40 Carl Zeiss spectrometer.

X-ray photoelectron spectroscopy (XPS) was used for the surface composition analysis of WO_3/TiO_2 coatings. XPS was carried out on a VG ESCALAB II electron spectrometer with a base pressure in the analysis chamber of 10^{-8} Pa. The X-ray source was monochromatized AlKα radiation (1486.6 eV) and the instrumental resolution was 1 eV. The spectra were calibrated using the C 1 s line (284.8 eV) of the adventitious carbon and corrected by subtracting a Shirley-type background.

2.3. Photocatalytic experiments

The photocatalytic activity of WO_3/TiO_2 samples was evaluated by monitoring the decomposition of Rhodamine 6G (R6G) and Mordant Blue 9 (MB9) under the irradiation of two different light sources: fluorescent and UV lamps. The photocatalytic measurements on R6G solution (initial concentration in water: 10 mg/L) have been performed using a 36 W visible fluorescent lamp (Hyundai eagle), whose emission spectrum, compared to sunlight spectrum, is given in Ref. [9]. The cuvette (3 mL) was placed at about 5 cm from the lamp. The evolution of the rhodamine concentration was followed by measuring the variation of the intensity of main absorption peak at ~525 nm. UV–vis absorption measurements as a function of the light exposure time were performed by using USB2000 spectrometer by Ocean Optics. The solution was placed in the dark for 60 min to reach the adsorption/desorption equilibrium before visible light exposure.

The photocatalytic activity of WO_3/TiO_2 samples under UV light irradiation was evaluated using aqueous solution of MB9 as a model pollutant. Batch type experiments were performed in an open thermostated cell (at 25 °C). The cell was equipped with a water circulating jacket to maintain the solution at room temperature. A mercury lamp (125 W) was used as a light source and was placed 13 cm above the surface of the dye solution. The initial concentration of MB9 in an aqueous suspension was 50 mg/L and the working volume was 25 mL. Before the lamp was switched on, the cell was kept in dark for 60 min in order to achieve the adsorption-desorption equilibrium. At regular time intervals the aliquots were taken and the concentration of the dye was determined by UV–vis spectrophotometer (Super Scan) at λ_{max} = 516 nm. The photocatalytic experiments were conducted at the natural pH of the dyes (pH = 7 in a case of R6 G solution and at pH = 6 in a case of MB9 solution). All photocatalytic measurements were repeated at least twice to check their reproducibility.

In order to detect the formation of free hydroxyl radicals ($OH^{\bullet}$) on the UV illuminated WO_3/TiO_2 surface, photoluminescence (PL) measurements were performed using terephthalic acid, which is known to react with $OH^{\bullet}$ radicals and produces highly fluorescent 2-hydroxyterephthalic acid. The experiment was conducted at ambient temperature. The WO_3/TiO_2 photocatalyst (TW300) was placed in open termostated cell filled with 20 mL of the 5×10^{-4} mol L^{-1} terephthalic acid in a diluted NaOH aqueous solution with