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WO_3 thin films for photoelectrochemical purification of water

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Abstract

Tungsten trioxide thin films on transparent substrates (glass and $F:SnO_2$ or ITO-coated glass) were prepared by layer-by-layer brush painting and spin-coating using organic precursors. Well-crystallized WO_3 with monoclinic structure was formed on all substrates after annealing at 500 °C or above. The dense semiconducting films are specular and transparent outside the band-gap. Their photoactivity in junctions with aqueous electrolytes extends up to 470 nm, with incident photon to current conversion efficiencies around 0.9 at 313 nm and up to 0.1 at 436 nm.

Films of 10 cm × 10 cm were used for the study of solute degradation reactions in a thin-film reactor under backside illumination. Dilute aqueous solutions of model substances for contaminants like oxalic acid were decomposed under continuous flow using broadband UVA illumination and electrical bias. Operation under solar illumination was also feasible. The advantage over operation without bias (conventional photocatalysis) prevailed for all decomposition reactions studied.

Keywords: Faradaic efficiency; IPCE; Oxalic acid; Degradation; Thin film; Tungsten trioxide

1. Introduction

In degradation of organic compounds using semiconductor oxides and light (photocatalysis; the topic was thoroughly reviewed by Hoffmann et al. (1995) and Mills and Le Hunte (1997)), most of the studies have been performed with powder suspensions. This approach has the drawback of requiring separation of the photocatalyst from the liquid after completion of the degradation process. The alternative to a suspension is to use the photocatalyst in immobilized form (films), e.g. realized in the form of coated rods and fibers by Hofstadler et al. (1994) and Peill and Hoffmann (1996), respectively, or coated on large, transparent beads (Kobayakawa et al., 1998). Titanium dioxide has emerged as the most widely studied photocatalyst, but it is only photosensitive in the UV. Tungsten trioxide might be an alternative since it also absorbs blue light. It is an extensively studied material owing to its potential application in various fields of science and technology viz. photocatalysis, smart electrochromic windows, switching devices, gas sensors etc. (Leftheriotis et al., 2003). Recently this material has drawn attention because of its high efficiency in photocatalytic degradation of organic compounds including toxins (Luo et al., 2002; Hepel and Hazelton, 2005), and a few reports were issued on photocatalytic studies of WO_3 films (Santato et al., 2001; Luo et al., 2002; O'Neill et al., 2004). The latter pointed out that only fully stoichiometric WO_3 is photocatalytically active. As tungsten trioxide is a semiconductor, photocatalysis on large enough particles or bulk material, including thin films in contact with electrolyte, can be understood as an electrochemical process (Neumann-Spallart and Enea, 1984; Desilvestro and Neumann-Spallart, 1985). Semiconducting catalysts, immobilized on an electrically conducting surface, can therefore be treated as electrodes, and application of an electrical bias increases the charge separation

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efficiency under illumination, which therefore leads to increased rate of reaction (oxidation of solutes in the case of an n-type semiconductor).

In pursuing research on photoelectrochemical detoxification of water using wide band-gap semiconductor photocatalysts such as TiO_2 and WO_3 (Waldner et al., 2003; Belaidi et al., 2004), we have recently investigated the photoelectrochemical properties IPCE (incident photon to current efficiency), spectral sensitivity, etc. of thin films of WO_3 deposited on transparent electric conductors (TCO) (Gaikwad et al., 2005) in view of their use in degradation reactions. Doctor-blading and various layer-by-layer methods such as dip coating, brush-painting (LBLP) and spin-coating (SC) using alkoxide precursors were compared; LBLP and SC deposited films on conducting glass were found to be the best and comparable with respect to photon to electron conversion efficiency. Electrode properties were maintained when the surface area was up-scaled to 10 cm × 10 cm.

In this study, we wanted to see whether the above described large, semitransparent WO_3 films can be used for photocatalytic solute degradation, whether the use of electrical bias leads to the predicted increase in conversion efficiency, and whether sunlight can be used for carrying out photoelectrochemical degradation reactions on WO_3.

2. Experimental

2.1. Chemicals and electrode preparation

Tungsten(VI) oxychloride ($WOCl_4$, Aldrich) and tungsten(V) ethoxide (Johnson Matthey) were used as precursors. All other chemicals were of analytical grade and used without further purification. Water was purified with a Millipore Simplicity 185 apparatus. F:SnO_2 coated glass (with a surface resistivity of 9 Ω (Solems, France)) and ITO/glass (13 Ω, Sztatecsny, Austria) were chosen as substrates. The size of the substrates was 10 cm × 10 cm. Electrodes were prepared by LBLP and spin-coating as described by Gaikwad et al. (2005).

2.2. Light sources

An array of fluorescent tubes (either Sylvania Lynx BL350 UVA or Osram Dulux S daylight-type broadband) was used for homogeneous illumination of the large surface reactor. Relative intensities of light emitted by these tubes as a function of wavelength (Fig. 1) were measured with an ocean optics fiber optic spectrometer, calibrated against a white light source of known color temperature. For measurements on small electrodes a medium pressure Hg lamp in combination with interference filters was used and actinometry was carried out by using a calibrated Hamamatsu S1337-1010BQ silicon photodiode. Solar irradiance was measured using a Kipp & Zonen CC20 with a pyranometer CM3, at the location N48° E16° (Vienna), under sunny winter conditions around noon it was found to be $710(\pm 50)\ \mathrm{W\,m^{-2}}$, integrated between 350 and 1500 nm (±5% points).

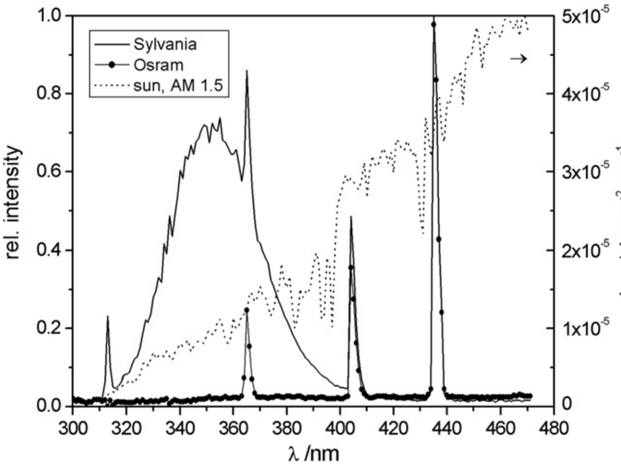

Fig. 1. Emission spectra of UVA (Sylvania Lynx BL350) and daylight (Osram Dulux S) fluorescent lamp arrays of 3 × 9 W each, and the standard solar spectrum AM1.5 (NREL).

2.3. Analytical

TOC (total organic carbon) was analyzed by a Shimadzu TOC 5000 analyzer. This parameter gives the sum of starting compound plus all organic intermediates; in the case of oxalic acid as educt there are no intermediates, so TOC can be taken as oxalic acid concentration. The TOC was calibrated, according to Shimadzu recommendations, by use of potassium hydrogenophthalate and the IC (inorganic carbon) by a mixture of sodium carbonate and sodium hydrogenocarbonate. CO_2 concentration in the gas phase was measured by a non-dispersive IR detector, Gascard II, Edinburgh Instruments.

2.4. Electrochemical characterization

Photoelectrochemical measurements were performed using a potentiostatic set-up (Wenking TG97 potentiostat, Bank Intelligent Controls) and a Keithley DAS1601 AD/DA data acquisition card. The WO_3/TCO served as working electrode, and Ag/AgCl was the reference electrode, except for the solute degradation experiments, where the potential was measured and applied vs. a polished stainless steel counter electrode kept at 1.2 mm distance to the working electrode in a two-terminal flow-through cell. The supporting electrolyte was 0.01 M $HClO_4$ unless otherwise specified (tests were also performed in the absence of supporting electrolyte). IPCE for small electrodes was calculated as follows (using the actinometric results obtained as described above):

$$\mathrm{IPCE} = \frac{i}{F \cdot P} \qquad (1)$$

with i = photocurrent density, F = Faraday constant, P = light intensity ($E\ \mathrm{s^{-1}\ cm^{-2}}$).