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Preparation and photoelectrocatalytic activity of a nano-structured WO_3 platelet film

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Abstract

A tungsten trioxide (WO_3) film was prepared by calcination from a precursor paste including suspended ammonium tungstate and polyethylene glycol (PEG). The ammonium tungstate suspension was yielded by an acid–base reaction of tungstic acid and an ammonium solution followed by deposition with ethanol addition. Thermogravimetric (TG) analysis showed that the TG profile of PEG is significantly influenced by deposited ammonium tungstate, suggesting that PEG is interacting strongly with deposited ammonium tungstate in the suspension paste. X-ray diffraction (XRD) data indicated that the WO_3 film is crystallized by sintering over 400 °C. The scanning electron microscopic (SEM) measurement showed that the film is composed of the nano-structured WO_3 platelets. The semiconductor properties of the film were examined by Mott–Schottky analysis to give flat band potential $E_{FB} = 0.30\,V$ vs. saturated calomel reference electrode (SCE) and donor carrier density $N_D = 2.5 \times 10^{22}\,cm^{-3}$, latter of which is higher than previous WO_3 films by two orders of magnitude. The higher N_D was explained by the large interfacial heterojunction area caused by the nano-platelet structure, which apparently increases capacitance per a unit electrode area. The WO_3 film sintered at 550 °C produced $3.7\,mA\,cm^{-2}$ of a photoanodic current at 1.2 V vs. SCE under illumination with a 500 W xenon lamp due to catalytic water oxidation. This photocurrent was 4.5–12.8 times higher than those for the other control WO_3 films prepared by similar but different procedures. The high catalytic activity could be explained by the nano-platelet structure. The photocurrent was generated on illumination of UV and visible light below 470 nm, and the maximum incident photon-to-current conversion efficiency (IPCE) was 47% at 320 nm at 1.2 V. Technically important procedures for preparation of nano-structured platelets were discussed.

Keywords: Tungsten trioxide; Photoelectrocatalysis; Platelet film; Water oxidation

1. Introduction

Design and development of nano-structured materials have expanded new research fields of materials and surface sciences since "nanotechnology" was propounded at the end of the last century [1,2]. Metal oxide semiconductors have been extensively studied for its fundamental science and a wide variety of application to photocatalysts, displays, batteries and solar cells [3–8]. Titanium oxide (TiO_2) is one of the semiconductors that have been studied most actively due to its attractive photocatalytic activities [6] without photocorrosion and its successful application to dye-sensitized solar cells [7,8]. Nano-crystalline TiO_2 is effective for a large surface area with high crystallinity kept, giving high photocatalytic activities. A nano-structured interfacial heterojunction between TiO_2 and an electrolyte solution is also important for dye adsorption and light harvest in dye-sensitized solar cells.

Since TiO_2 exhibits photocatalytic activity in being exposed to ultraviolet (UV) light ($>3.1\,eV$), TiO_2 has a disadvantage for converting visible light in solar light from the viewpoint of practical solar energy application. Tungsten trioxide (WO_3) is also an n-type semiconductor possessing a resistance to photocorrosion and a photocatalytic activity in acidic conditions. WO_3 has a more advantage for solar energy utilization than that of TiO_2 because the band gap energy (2.5–2.7 eV) of the former is

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lower than that of the latter. However, the photocatalytic and photoelectrochemical characteristics of WO_3 have not been studied as extensively as those of TiO_2.

WO_3 films have been prepared by several techniques, e.g., vacuum evaporation [9], chemical vapor deposition [10,11], sol–gel precipitation [12–15], spin coating [16], sputtering [17] and electrodeposition [18–22]. Although a sol–gel technique is one of the simple and low-cost procedures selected for a wide range of applications, there have been only a few reports on photoelectrochemical characteristics of the WO_3 film prepared by a sol–gel technique [12–15]. In previous procedure by a sol–gel technique, the precursor (tungstic acid) was obtained by passing an aqueous solution of sodium tungstate through a column filled with a proton exchange resin, followed by adding PEG to the solution to give viscous precursor solution. It was cast on a substrate and then annealed under oxygen atmosphere at 550 °C. Herein, we report that a WO_3 film composed of a nano-structured platelet is prepared by a simpler and easier procedure (without a cation exchange procedure) and that it produces a significant photoanodic current of a milliampere order under illumination with a 500 W xenon lamp due to catalytic water oxidation. The preparation and photoelectrocatalytic activity of the nano-structured WO_3 platelet film will be discussed.

2. Experimental

2.1. Materials

The purest grades of tungstic acid, ammonium tungstate pentahydrate (Kanto Chemical Co. Inc.), ammonia aqueous solution (Junsei Chemical Co., Ltd.), and polyethylene glycol (PEG) ($M_w = 20.000$, Wako Pure Chemical Ind., Ltd.) were purchased and used as received. An indium tin oxide (ITO)-coated glass with 10 Ω/sq of a sheet resistance was purchased from Kinoene Kogaku Kogyo Co., Ltd.

2.2. Preparations

Tungstic acid (yellow powder; 0.25 g, 1.0 mmol) was dissolved in a 30% ammonia aqueous solution (0.6 ml) to give a colorless solution containing a little bit of white precipitate (ammonium tungstate). Ethanol (1.0 ml) and PEG (0.78 g) were added to the solution, providing the viscous stable suspension of ammonium tungstate as a precursor paste. It was squeegeed on the ITO substrate by means of a doctor blade technique using scotch tape as a spacer, and then air-dried for 30 min followed by a calcination treatment at 300–550 °C for 90 min to form a WO_3 film. This film was abbreviated to the type-A film to distinguish from the other control film of types—B, C and D. For the type-B film, the same amount of tungstic acid (0.25 g, 1.0 mmol) was suspended in water (0.6 ml), and then ethanol (1.0 ml) and PEG (0.78 g) were added to obtain a precursor paste. For the type-C film, the same amount of tungstic acid (0.25 g, 1.0 mmol) was dissolved in a 30% ammonia aqueous solution (0.6 ml), and then PEG (0.78 g) was added without addition of ethanol to obtain a precursor paste. For the type-D film, commercially available ammonium tungstate was suspended in water (0.6 ml) and then ethanol (1.0 ml) and PEG (0.78 g) were added to obtain a precursor paste. For all the films of type—A–D, the precursor pastes were conditioned for tungsten atom concentration (0.63 mmol/ml) to be constant before the squeegee. The type-B, C and D films were formed from respective precursor pastes by the same calcination treatment as the type-A film.

2.3. Measurements

Thermogravimetric (TG) data were taken at 10 °C min^{-1} using a TG analyzer (Shimadzu, DTG-60). XRD data were recorded using an X-ray diffractometer (MAC Science, MX labo). SEM measurements were carried out using a scanning electron microscope (JEOL JSM-7400F) operated at an accelerating voltage of 2 kV. UV–visible diffuse reflectance (DR) spectra were measured using a UV–visible spectrophotometer (JASCO V-550) in a DR mode. Electrochemical experiments were conducted in a single compartment electrochemical cell equipped with the WO_3 film-coated ITO working electrode, a saturated calomel reference electrode (SCE) and a platinum wire counter electrode using an electrochemical analyzer (Hokuto Denko, HZ-3000). The capacitance was given at 45 mHz of a frequency and 10 mV of amplitude potential in alternating-current impedance measurements using the electrochemical analyzer interfaced with a frequency response analyzer (NF Electronic Instruments, S-5720c). A 500 W xenon lamp (Ushio, UXL-500SX) in a lamp house (SX-U1500XG) was used for photoelectrochemical measurements. A monochromic light with 8 nm of a bandwidth was given from the 500 W xenon lamp using a monochromator. All the electrochemical and photoelectrochemical experiments were carried out under argon atmosphere at 25 °C.

3. Results and discussion

Tungstic acid reacts with an ammonia aqueous solution to give a colorless ammonium tungstate solution. The titration of a 30% ammonia aqueous solution to the tungstic acid (1.0 mmol) showed that 0.6 ml (9.5 mmol) of the ammonia aqueous solution is required to give an ammonium tungstate solution by an acid–base reaction. The addition of ethanol to the ammonium tungstate solution yielded fine white deposit, which precipitates for a few minutes in the solution. However, in the presence of PEG, it dispersed stably in a suspension paste for at least a few weeks. Instead of PEG, ethylene glycol, glycerol and mannitol were used for preparation of suspension pastes. The paste using ethylene glycol or glycerol was inappropriate for squeegee on an ITO glass, whereas the paste using