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Fabrication of tungsten trioxide photoanode with titanium microfibers as a three dimensional conductive back contact

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ABSTRACT

Ti microfibers with a diameter of 20 μm were used as a three dimensional conductive back contact for a tungsten oxide (WO_3) photoelectrode. We coated the microfibers with WO_3 nanoparticles by a solution-based dip coating step and heat treatment at 650 °C. A high loading of WO_3 nanoparticles was achieved over a large surface area of the porous microfibers through the use of a high viscosity solution for the dip coating. The prepared WO_3-coated Ti microfibers exhibited enhanced photoelectrochemical properties. Visible light response was improved in the conductive Ti microfibers owing to increased absorption of visible light and efficient extraction of photoexcited electrons at the large interface.

1. Introduction

Photoelectrochemical (PEC) water splitting based on semiconductor electrodes has been extensively investigated owing to its potential for low-cost hydrogen production powered by solar energy. Recently, a new type of PEC cell inspired by a fuel cell reactor has been investigated for photoelectrolysis of water [1–7], composed of a membrane electrode assembly (MEA) with a proton exchange membrane. In this device structure, TiO_2 photoanodes coated on carbon microfibers are typically used [1–5], because TiO_2 is a common photoelectrode material and carbon fibers are used for fuel cells as a gas-diffusion layer and electrically conductive pathway for current collection. One limitation of carbon fibers is that they become easily damaged by heat treatment at high temperature due to their low thermal stability in air.

In this study, we focused on Ti microfibers as a thermally stable three-dimensional (3-D) conductive substrate for current collection, and fabricated WO_3 films by a combination of a dip coating technique and high temperature calcination at 650 °C. WO_3 can absorb visible light up to ~475 nm because its band gap (~2.6 eV) is narrower than that of TiO_2 [8]. Thus, a higher photocurrent may be expected from the use of WO_3 photoanodes under sunlight. There have been reports on PEC applications of TiO_2/WO_3 on stainless steel mesh [6], WO_3 on carbon microfibers [9], and TiO_2 nanotube arrays on Ti microfibers [7]. Here, for the first time, we prepared a WO_3 photoanode coated on Ti microfibers as a 3-D back contact. Our structure provides a highly porous substrate with a large specific surface area, high conductivity, and fast extraction of photoexcited electrons.

2. Experimental

We coated precursors for WO_3 on Ti microfibers by a dip coating method using ammonium metatungstate hydrate ($(NH_4)_6H_2W_{12}O_{40}{\cdot}6H_2O$, 16 mmol) as the WO_3 source [9–11] in a 10 g of aqueous solution of 20 wt% polyethylene glycol (PEG 20,000, average molecular weight 15,000–25,000). The Ti microfibers were dipped in the solution for 30 min at room temperature, lifted at a speed of 10 mm/s, and then calcined in air at 650 °C for 2 h to transform the coated precursor into WO_3. The obtained samples are denoted as WO_3/Ti-fibers.

For comparison, WO_3 particulate films were coated on a Ti sheet (purity 99.5%) and FTO-coated glass substrate (<10 ohms/sq) by a squeegee method from a paste prepared from 150 mg of commercial WO_3 powder (purity 99.99%, BET-specific surface area 6.0 $m^2\,g^{-1}$ [12]), 250 μL of pure water, 20 μL of acetyl acetone,

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and 0.1 g of Triton X-100. The coated films were calcined in air for 2 h at optimized temperatures of 650 °C for the Ti sheet and 550 °C for the FTO-coated glass substrate. The obtained films are denoted as WO_3/Ti-sheet and WO_3/FTO, respectively.

A three-electrode cell with an Ag/AgCl reference electrode and a Pt wire counter electrode was used to evaluate the PEC performance for water oxidation in aqueous solution at pH = 2.2 (0.2 mol/L Na_2SO_4, phosphate buffer). For methanol oxidation, a 10-vol% aqueous methanol solution was used. The WO_3 electrodes had a geometrical area of 1 cm^2 and were irradiated by a light-emitting-diode (LED, peak wavelength 385 nm, width ~ 12 nm) with an irradiance of 40 mW/cm^2. A 300-W xenon lamp with bandpass filters (band width ~10 nm) was used to measure the incident photon-to-current conversion efficiency (IPCE) at each wavelength.

3. Results and discussion

Fig. 1 shows pictures of the Ti microfibers (porosity 67%, thickness 0.1 mm, density 14 mg/cm^2) and the prepared WO_3-coated films. The Ti microfibers had a silver paper-like appearance. After calcination at 650 °C for 2 h, the color changed to grey owing to the formation of a thin oxidized layer. The part of the film coated with WO_3 appeared yellow. The loading of WO_3 per unit area was measured to be ~ 13 mg/cm^2 over the WO_3/Ti-fibers. The high loading was achieved by the dip-coating of a highly viscous solution containing PEG 20,000 together with the use of porous 3-D microfibers. The dip coating method was not effective for conventional 2D sheet substrates. Thus, a squeegee method was applied to the flat sheets, but a high loading was difficult to achieve because thick WO_3 layers peeled easily from the substrates. The light yellow appearance of the WO_3/FTO and WO_3/Ti-sheet were a result of the thinness of the WO_3 layers.

Fig. 2 shows scanning electron microscope (SEM) images of Ti microfibers and WO_3/Ti-fibers. The Ti microfibers exhibited high porosity owing to the 3-D network structures. The diameter of individual fibers was approximately 20 μm. For the WO_3/Ti-fibers, the surface of the Ti fiber was covered with a thick WO_3 layer. A porous network structure was observed, but some void spaces were filled by agglomerations of nanoparticles. The WO_3 coating was not homogeneous because of the high loading. High magnification images revealed that the WO_3 layer consisted of nanoparticles with a diameter of 100–300 nm. Abe et al. have reported that PEG 300 enabled homogeneous loading of fine WO_3 particles on carbon microfibers [9]. In the present study, the loading of WO_3 was much higher than that of previously reported for WO_3/carbon-fibers. The high loading also led to the formation of aggregates of WO_3 nanoparticles.

The purpose of study was to fabricate a highly efficient WO_3 photoelectrode for application to PEC cells. Fig. 3(a–c) shows the results of PEC water oxidation. The cyclic voltammograms show that an anodic photocurrent was clearly observed at applied

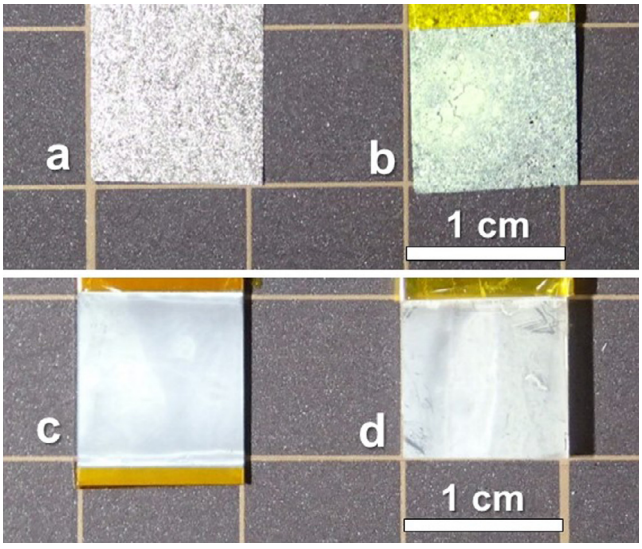

Fig. 1. Photographs of (a) Ti microfibers, (b) WO_3/Ti-fibers, (c) WO_3/FTO, and (d) WO_3/Ti-sheet. Orange parts of the image are polyimide masking tape.

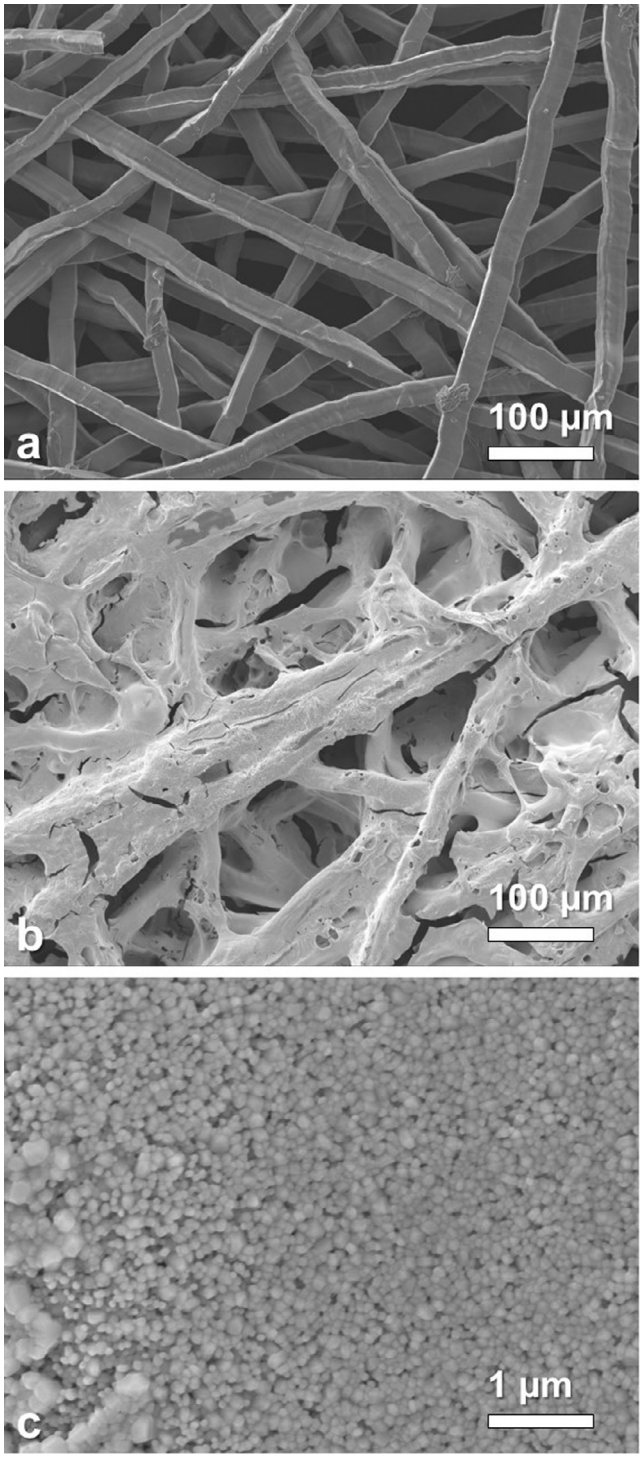

Fig. 2. SEM images of (a) Ti microfibers, and (b, c) WO_3/Ti-fibers.