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Short communication

Hematite modified tungsten trioxide nanoparticle photoanode for solar water oxidation

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ABSTRACT

Hematite (α-Fe_2O_3) film is electrochemically deposited onto the surface of tungsten trioxide (WO_3) nanoparticulate film. The synthesis of the WO_3 nanostructure is directed by surfactants for control of its morphology. The resulting composite shows visible light harvesting and is tested as photoanodes in heterojunction photoelectrochemical cells for the possibility of direct water splitting under visible illumination. The composite's structural and optical properties are characterized by FESEM, EDS, XRD, XPS, and UV–vis spectrometry; its photocurrent responses are also investigated under simulated solar illumination. Coupling WO_3 with hematite results in over 9 times greater photocurrent density than that shown by pure WO_3 in sodium sulfate electrolyte. This simple modification can significantly improve the performance of WO_3.

1. Introduction

Solar energy is a cleaner, renewable alternative to fossil fuels, with wide potential applicability. However, its direct use in such as solar thermal power or photovoltaic solar cells is still limited and large scale use of solar energy requires efficient energy storage. Since Fujishima and Honda's 1977 finding that a TiO_2 photoanode in a photoelectrochemical cell (PEC) could split water into hydrogen and oxygen under UV irradiation [1], solar hydrogen generation by water splitting has been considered one of the most suitable methods of solar energy conversion and storage [2]. However, such water splitting still faces many challenges, particularly because of its low efficiency. New materials with smaller bandgaps than TiO_2 have therefore been explored so as to increase solar absorption to include visible wavelengths. Examples of photoanodes tested for PECs include metal oxide semiconductors such as tungsten trioxide (WO_3) [3–6] and iron oxide (Fe_2O_3) [7]. Interfacial effects significantly affect charge transport and research has aimed to optimize electron transport pathways through the synthesis of nanostructured photoanodes incorporating such as nanotubes [8–11], nanowires [12,13], nanosheets [14], or nanorods [15–17].

Heterojunction photoanodes can also potentially improve cells' efficiency. Heterojunction electrodes contain a small-bandgap semiconductor, such as CdS or CdSe, and a large-bandgap semiconductor, such as TiO_2 [18–20]. Unfortunately, most low-bandgap materials suffer from poor long-term stability in aqueous solution under solar illumination. α-Fe_2O_3 has a favorable bandgap of 2.0–2.2 eV, is stable against corrosion in aqueous environments at pH > 3, and is inexpensive. It is therefore a promising light absorber for heterojunction photoanodes, but is limited by poor electrical conductivity and a short minority carrier diffusion length. α-Fe_2O_3 decorated TiO_2 nanotube arrays have been reported as photoanodes for PECs, though the enhancement of photocurrent was limited because the conduction energy band of TiO_2 is higher than that of α-Fe_2O_3, which hindered electron transfer from the α-Fe_2O_3 to the TiO_2 nanotube arrays after the absorption of photons. WO_3 is a promising alternative host material for heterojunction PEC as its conduction band is only slightly lower than that of α-Fe_2O_3 [3,21,22], allowing efficient electron transport across the interface between them. Therefore, the heterojunction of α-Fe_2O_3 and WO_3 was investigated in this study (Fig. 1).

Few papers have reported α-Fe_2O_3/WO_3 photoanodes for improving the efficiency of PECs [23,24], and no noticeable photocurrent enhancement has yet emerged. This work reports the synthesis of a transparent and nanostructured α-Fe_2O_3/WO_3 film prepared in two steps. Spherical WO_3 nanoparticles were grown as a film on FTO glass by a surfactant-assisted sol–gel reaction [25]. α-Fe_2O_3 was then electrodeposited onto the WO_3 film. Pure WO_3 and

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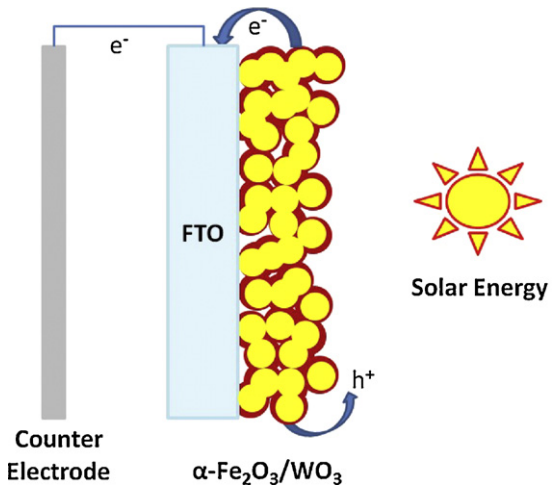

Fig. 1. Energy band diagram of α-Fe_2O_3/WO_3 film on FTO substrate.

pure α-Fe_2O_3 films were also synthesized and tested for comparison. The deposition conditions of the α-Fe_2O_3 were optimized with respect to photocurrent density, which was 9 times greater photocurrent density than that shown by pure WO_3 in sodium sulfate electrolyte.

2. Experimental

2.1. Synthesis of WO_3 nanostructured film

Nanostructured WO_3 films were deposited on transparent conducting glass substrates (F-doped SnO_2-coated glass, FTO, dimension: 1.5 cm × 1.5 cm, WOOYANGGMS, Siheung, Gyeonggi-do, Korea) using a precursor solution comprising a colloidal complex of peroxy-tungstic acid and polyethylene glycol 300, an organic stabilizer and morphology controlling agent [26]. The peroxy-tungstate precursor was prepared by mixing tungsten powder (W, 99.9%, Acros, Geel, Belgium) in hydrogen peroxide (30% H_2O_2, Junsei, Tokyo, Japan). 0.9 g tungsten was added to 10 ml H_2O_2. After 6 h, 25 ml IPA (2-propanol, Junsei, Tokyo, Japan) stabilizer and PEG 300 (polyethylene glycol 300, Aldrich, St Louis, Mo, United States) structure enhancer were added [27]. IPA can slow the condensation of tungstate [28] and can complex with tungsten oxoanions [29]. The nanostructured WO_3 films on the FTO were obtained by dropping 20 μl precursor onto the FTO substrate and drying it at room temperature for 20 min. Such dropping and drying were repeated twice more. The deposited precursor was then annealed at 550 °C for 30 min, resulting in monoclinic WO_3 (crystalline *m*-WO_3) with improved nano-crystallinity [30]. Samples were prepared with tungsten and PEG 300 at a 1:10 weight ratio.

2.2. Synthesis of α-Fe_2O_3/WO_3 nanostructured film

Fe was electrodeposited onto the WO_3 nanostructured film under a constant potential. The electrolyte was prepared by mixing 60 g ferrous sulfate ($FeSO_4 \cdot 7H_2O$, 98.0%, Junsei, Tokyo, Japan), 1.5 g ascorbic acid ($C_6H_8O_6$, 99%, Aldrich, St Louis, Mo, United States), 0.5 g amidosulfonic acid (H_2NSO_3H, 99.99%, Aldrich, St Louis, Mo, United States) and 15 g boric acid (H_3BO_3, 99.99%, Aldrich, St Louis, MO, United States) in 1 l distilled water [31]. A constant −0.5 V potential *vs.* Ag/AgCl was applied to the working electrode. Samples were then thermal annealed under air at 500 °C for 6 h to form crystalline α-Fe_2O_3/WO_3.

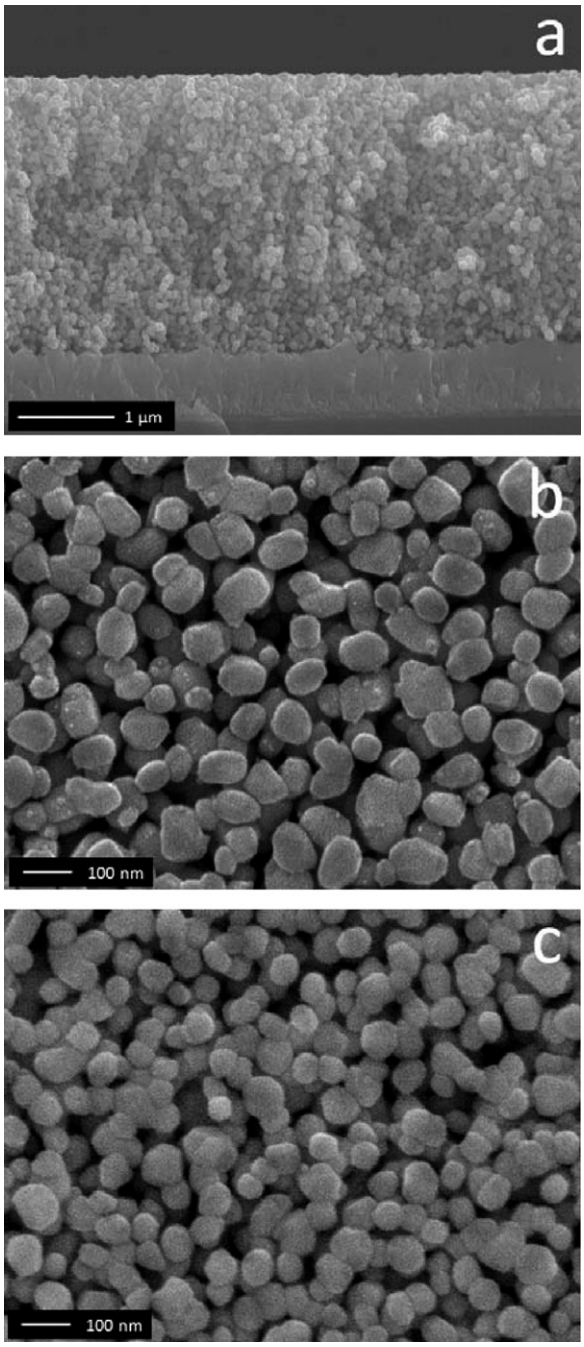

Fig. 2. FESEM images: (a) section and (b) top views of pure WO_3 film on FTO glass, (c) top view of α-Fe_2O_3/WO_3 film.

2.3. Characterization methods

Field emission scanning electron microscopy (FE-SEM, JSM-7000F, JEOL Co., Tokyo, Japan) was used to examine the samples' morphologies. Energy dispersive spectrometry (EDS, Oxford, INCA, Oxfordshire, United Kingdom) was used to identify constituent elements and their distributions. X-ray diffraction spectra were recorded to observe crystalline phases on a Siemens diffractometer D500/5000 in Bragg-Bretano geometry using Cu Kα radiation (D500/5000, Bruker, Billerica, MA, United States). X-ray photoelectron spectroscopy (XPS) was conducted on an AES-XPS instrument (ESCA2000, VG Microtech, West Sussex, United Kingdom) with an aluminum anode (Al Kα = 1486.6 eV). Optical properties were