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Enhanced solar water splitting of electron beam irradiated titania photoanode by electrostatic spray deposition

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ABSTRACT

Surface modifications are often made to titania films to improve its photocatalytic performance in water splitting. We herein introduced electron beam irradiation to enhance the photocatalytic activities of an electro-sprayed titania film for solar water splitting application. The film was fabricated by a facile and scalable electrostatic spraying deposition. According to SEM, X-ray diffraction, and Raman data, electron beam densified the film and improved its crystallinity. Absorbance data indicated that the band gap of the E-beam film reduced, which in turn covered the wider range of absorbed light. These modifications increased oxygen vacancies or defects, which enhanced mobility and separation of electrons and holes. As a result, the E-beam film exhibited a threefold increase in the photocurrent density, compared to that of the non-E-beam film. This electrosprayed titania film was used as a photoanode while the reference and counter electrodes involved in the generation of hydrogen were made of Ag/AgCl and platinum, respectively. The intensity of the UV light illumination used was 1 mW/cm^2.

1. Introduction

Photoelectrochemical (PEC) cells are capable of harvesting the highly abundant supply of sunlight to produce energy in the form of chemical energy stored within hydrogen, which is produced by water splitting. To trigger photocatalysis, semiconducting materials are needed that can absorb a level of energy equal to or higher than the material's band gap when exposed to photon energy. When this occurs, excited electrons (e^-) migrate to the conduction band, thus leaving behind holes (h^+) in the valence band of the semiconductor photoelectrode. Ultimately, these excited electrons travel to the cathode, where they undergo a reduction process, whereas the holes combine with water and produce oxygen at the anode. To achieve higher PEC performance, the top of the valence band (VB) should secure a higher potential than that of oxidation of H_2O/O_2 (1.23 vs NHE). Similarly, the bottom of the conduction band should secure a lower potential than that of reduction of H^+/H_2 (0 vs NHE) [1]. The performance of any PEC cell is therefore completely dependent upon the nature of the semiconductor material used as the photoelectrode. However, the quantum efficiency of this semiconductor is adversely affected by the recombination of holes and electrons. Consequently, in order to achieve better PEC water-splitting performance, the semiconductor photoelectrode should be modified in such a way that it restricts the recombination of electrons and holes.

Titania (TiO_2) has long been considered one of the most popular semiconducting materials for use in PEC water splitting, due largely to the pioneering work by Fujishima and Honda in 1972 [2]. Since then, titania has been widely accepted for its high physical and chemical stability, greater oxidizing capacity, nontoxic nature, and low price. Furthermore, the band gap energy of titania is suitable for the oxidation and reduction of water, with just a slight modification of the defect chemistry and oxygen stoichiometry all that is required to tune its electronic properties.

Park et al. have previously reported an improved absorption of visible light (>420 nm) after doping of carbon onto TiO_2 nanotube arrays [3]. Similarly, Zhang et al. modified sol–gel synthesized TiO_2 by nitrogen doping in order to improve its photocatalytic activity [4]. Adopting a slightly different approach, Maijenburg et al. successfully synthesized Ag/TiO_2 nanowires to achieve improved water splitting over empty TiO_2 nanotubes [5]. Kumar et al. reported the modification of the work function and surface potential of TiO_2 thin films by exposing them to dense electron excitation

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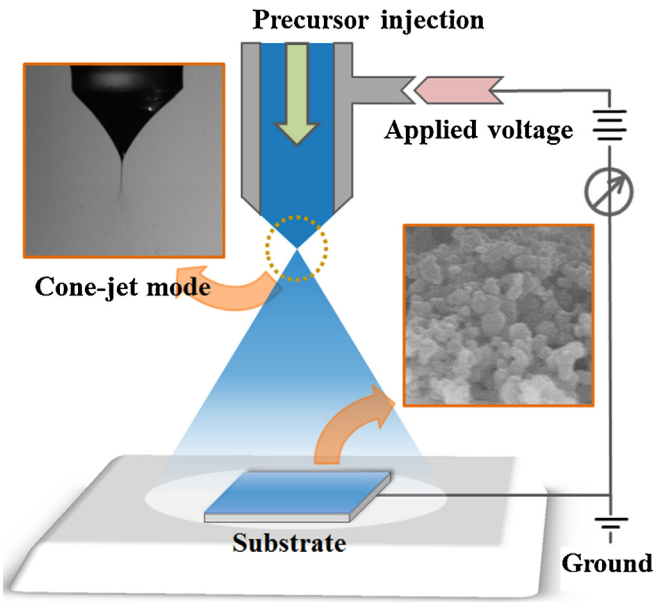

Fig. 1. A schematic for electrostatic spray deposition.

induced by a 100 MeV Ni ion beam [6]. Later, Yun et al. reported improved electronic and optical properties in nanomaterials following irradiation by energy electron beam [7–9]. Electron beam irradiation therefore presents a novel and potentially very valuable tool for the engineering and modification of materials at an atomic level. In this way, various functional properties and electronic structures can be achieved by tuning selected oxides with energy electron beam irradiation. Improvements in the electronic structure are made possible by the formation of defects such as oxygen vacancies in the bulk material.

In this study, TiO_2 thin-film photoelectrodes were prepared by electrostatic spray deposition (ESD), and then subjected to low-energy (0.2 MeV) electron beam irradiation in an effort to optimize their performance in PEC water splitting. As depicted in Fig. 1, ESD is an attractive option for preparing a uniform film as it yields extremely fine, self-dispersive, highly wettable, adhesive droplets [10]. Moreover, ESD is capable of producing pure materials with structural control at a nanometer scale. The crystallinity, surface texture, film thickness, and deposition rate can therefore all be easily controlled by adjusting the voltage, flow rate, precursor concentration, and substrate temperature [10]. In ESD, charged droplets are accelerated toward a substrate, thereby offering improved targeting and resulting in a high deposition efficiency and low material consumption [11–13]. To the best of our knowledge, there have yet been no reports pertaining to the effect of electron beams on electrosprayed titania films intended for use in PEC water splitting. Consequently, the changes in the physicochemical structure of TiO_2 films after electron beam irradiation and their subsequent mechanism of PEC water splitting are investigated herein in detail.

2. Experimental

2.1. Titania films

A spray solution was first prepared by mixing titanium tetraisopropoxide (TTIP, $Ti[OCH(CH_3)_2]_4$, 97%, Sigma–Aldrich) with deionized water, ethyl alcohol (C_2H_5OH, 99.9%, Duksan chemical), and DEG ($C_4H_{10}O_3$, Duksan chemical) to the amount of 1, 1.5, 50, and 50 ml, respectively. This solution was stirred at room temperature, and then the ethanol was evaporated by heating it to 80 °C.

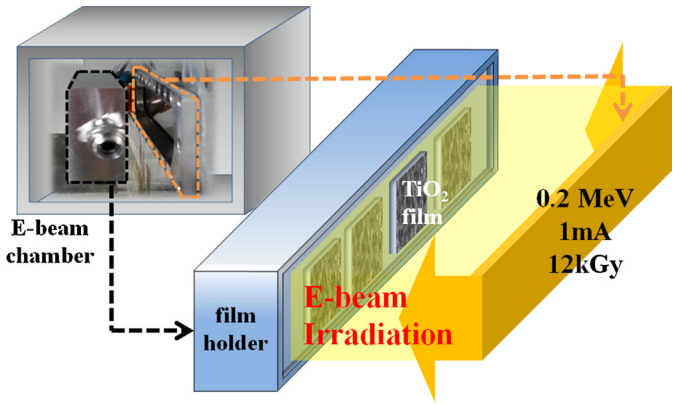

Fig. 2. A schematic for electron beam irradiation.

The resulting ethanol-free precursor was used to form a stable Taylor cone for ESD, being electrostatically sprayed at 1 ml/h onto an indium tin oxide (ITO)-coated conductive glass substrate at 230 °C for 20 min. Finally, the as-prepared films were annealed for 10 min at 500 °C in a closed furnace.

2.2. Electron beam irradiation

An electron beam typically consists of low-energy electrons, its irradiation on to a material inducing a variety of changes in its original properties. To this end, the electrostatically sprayed TiO_2 films were irradiated under ambient conditions with a low-energy (0.2 MeV, 1 mA) electron beam at the Korea Atomic Energy Research Institute (KAERI, Daejeon, Korea). For uniform deposition, titania films were mounted on a sample holder located at 2 cm downstream of the electron beam window. The irradiation time is proportional to the amount of electron beam. This irradiation is depicted schematically in Fig. 2, with each sample absorbing a dose equivalent to 12 kGy.

2.3. Characterization

The structural aspects of pure TiO_2 films and the low-energy electron beam-irradiated TiO_2 films were studied using X-ray diffraction (XRD, Rigaku, Japan, D/max-2500) with CuKα radiation over a 2θ range of 10–70°. Raman measurements were also performed using a confocal Raman spectrometer (NRS-3100) with a 514 nm laser excitation source. The surface chemical composition of the titania films was studied by X-ray photoelectron spectroscopy (XPS, Theta Probe base system, Thermo Fisher Scientific Co.), whereas UV–visible spectrometry (Optizen POP Mecasys Co. Ltd, Korea) was used to study their absorbance. The surface morphology of the films was studied by scanning electron microscopy (HR-SEM, XL30 SFEG, Phillips Co., Holland) at 10 kV, the film thickness being determined from an average of five different measurements so as to yield statistically reliable data.

For all photoelectrochemical measurements, a single cell with a three-electrode set-up was used. Fig. 3 shows a schematic of the PEC setup used, in which pure and electron beam-treated films were used as the working electrode (anode). To complete the set-up, Ag/AgCl rod was used as the reference electrode, and a platinum wire was used as the counter electrode (cathode). All of the electrodes were kept as close as possible to each other, and their locations were kept constant for all measurements. A solution of 1.0 M KOH (pH = 14) was used as the electrolyte, with this being purged with nitrogen to remove any dissolved oxygen prior to testing. A 400 W xenon arc lamp (Newport, Oriel Instruments, USA) was used to provide alight intensity of 1 mW/cm^2. A water filter