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Electrostatic spray deposition of transparent tungsten oxide thin-film photoanodes for solar water splitting

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ABSTRACT

Photocatalytic water splitting has been explored extensively as a promising way to capture and store solar energy. In this study, stable WO_3 thin-film photoelectrodes for water splitting applications were prepared with the simple, inexpensive, and scalable technique of electrostatic spray deposition. The physicochemical, structural, optical, and morphological properties of the WO_3 films were studied with X-ray diffraction, Raman spectroscopy, UV–visible spectroscopy, and scanning electron microscopy. The thickness of the films prepared was varied from 50 to 400 nm in order to establish a relationship between film thickness and water splitting performance. The photocurrent of the WO_3 thin films, measured in a 0.5 M Na_2SO_4 electrolyte solution against a standard Ag/AgCl reference electrode, increased with increasing film thickness. The film electrosprayed for 10 min exhibited a photocurrent density of 0.04 mA/cm^2. The photocurrent density was increased by 10-fold to 0.40 mA/cm^2 when the electrospraying time was increased to 60 min. Of all the films tested in this study, the film electrosprayed for 60 min, which had a thickness of 400 nm, showed the best photoelectrochemical cell activity.

1. Introduction

Photocatalytic water splitting is an attractive way to produce energy as it directly converts solar energy to chemical energy, and therefore, it could play a central role in a hydrogen-based energy economy [1]. In solar water splitting, water is split into elemental hydrogen and oxygen when an appropriate semiconductor electrode is immersed in an aqueous electrolyte and illuminated with sunlight [2]. This converts the solar energy into an inherently more storable form of energy. The semiconductor-assisted splitting of water was first reported by Fujishima [3] in 1972. The use of semiconductor photoelectrodes in photoelectrochemical water splitting has since attracted considerable attention [4–7]. Light absorption, charge generation, and charge separation are the three most important steps in the photoconversion of solar energy for water splitting. In addition to increasing the absorbance of light, improving the transport of charge carriers once they are generated and separated is critical for increasing photocatalytic activity. To achieve better water-splitting performance, a semiconductor material should possess a suitable band gap that enables the efficient absorption of visible light. It should also be non-toxic and possess high chemical stability [8]. During recent developments in the design of semiconductor photoelectrodes, n-type semiconductors, such as TiO_2, Fe_2O_3, ZnO, and WO_3, have been widely explored for their use in photoelectrochemical and photocatalytic applications.

Of the previously mentioned materials, WO_3, i.e., tungsten oxide, has been broadly investigated for various applications, such as photochromic materials (materials that exhibit reversible color changes) [9], gas sensing [10], dye-sensitized solar cells (DSSCs) [11], the degradation of organic dyes [12], and photocatalytic water splitting [13]. As an example of a building-integrated photovoltaic (BIPV) application, transparent WO_3 films can be installed in a water-filled window to produce energy (hydrogen) [14]. The use of WO_3 in photocatalytic and photoelectrochemical cell (PEC) applications is because of its suitable absorption of the visible portion of the solar spectrum, as well as good charge carrier mobility and chemical stability [15]. In addition, WO_3 has been successfully used to build heterojunction PECs [16]. The photoactivity of WO_3 in the visible region of the solar spectrum is credited to its indirect band gap of 2.7–3.0 eV. This band gap, which is lower than that of other semiconductor materials (especially TiO_2), makes WO_3 an attractive candidate for use as photoanodes in PECs. Another advantage of using WO_3 for photoanodes is its stability against corrosion

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and photocorrosion. In the literature, WO_3 nanostructures and thin films have been synthesized through various methods, including solvothermal techniques [17], hydrothermal techniques [18], chemical vapor deposition (CVD) [19], electrochemical anodization [20], sol–gel coating [21], atomic layer deposition [22], and electrostatic spray deposition (ESD) [23].

Of all these techniques, we used ESD for the synthesis of WO_3 thin films because of its advantages. ESD is an attractive option for preparing a uniform film as it yields extremely fine, self-dispersive, highly wettable, adhesive droplets. Moreover, ESD is capable of producing pure materials with structural control at the nanometer scale. The crystallinity, morphology, film thickness, and deposition rate can all be easily controlled by adjusting the voltage, flow rate, precursor concentration, and substrate temperature [24–26]. In ESD, charged droplets are accelerated towards a substrate, with the improved accuracy of this technique resulting in a high deposition efficiency and low material consumption.

Matei Ghimbeu et al. [23] have previously shown the fabrication of WO_3 thin films using ESD. However, they did not study the PEC water-splitting performance of their films. Therefore, in this paper, we report the use of ESD for the synthesis of WO_3 films and their PEC water-splitting performance. WO_3 films with high crystallinity were obtained by varying the post-annealing temperature between 450 and 600 °C. To determine the optimal PEC performance of the films, electrospraying times of 10, 20, 40, and 60 min were used to create four different WO_3 films. The fabricated films, which had various thicknesses, were tested in PEC experiments to measure the photocurrent density.

2. Experimental

2.1. Preparation of WO_3 photoelectrodes

WO_3 thin films were prepared on indium-doped tin oxide (ITO)-coated glass substrates with ESD. The spray solution was prepared by mixing tungsten (VI) ethoxide ($C_{12}H_{30}O_6W$) in absolute ethanol (Alfa Aesar) with polyethylene glycol ($C_{2n}H_{4n+2}O_{n+1}$). The WO_3 thin films were deposited using the operating conditions listed in Table 1. Prior to the deposition of the films, the ITO-coated glass substrates were first cleaned by ultrasonication in an ethanol bath and then dried.

2.2. Electrostatic spray deposition

In ESD, the atomization of the spray solution is caused by electrical forces. In order to initiate atomization, the nozzle is kept at a high potential, which provides the necessary electrical shear stress [27]. The particle size is controlled by adjusting the flow rate of the spray solution and voltage applied to the capillary nozzle. The center of the downward-facing nozzle was aligned with the center of the substrate (nozzle-to-substrate distance = 45 mm, cone angle = 40°), and the tungsten oxide solution was deposited onto a $2.5 \times 2.5\ \text{cm}^2$ area of the ITO substrate. The operating conditions, viz. flow rate, were adjusted in order to generate the smallest droplets. A voltage supply wire was attached to the charging needle (anode), and the substrate (cathode) was grounded, as described in Fig. 1a [24–26]. The electrospraying time was varied from 10 to 20, 40, and 60 min, which resulted in increasing the film thickness. Any higher thickness of the 60 min spraying case resulted in surface cracking and delamination due to the stress generated during the film growth.

Table 1
ESD operating conditions.

Properties	Conditions
Substrate	Indium tin oxide (ITO)-coated glass
Nozzle-to-substrate distance [mm]	45
Substrate temperature [°C]	80
ITO-coated substrate dimensions [cm^2]	0.25×0.25
E-spraying flow rate [μL/h]	80
Deposition times [min]	10, 20, 40, 60
Film thickness [nm]	90, 140, 270, 400
Annealing temperatures [°C]	450, 500, 550, 600

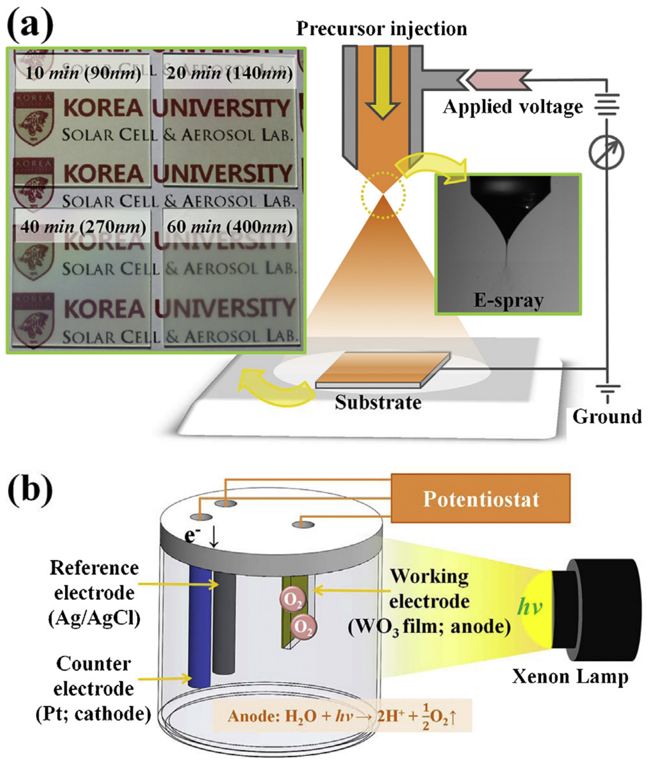

Fig. 1. (a) ESD setup. (b) Water splitting setup.

2.3. Characterization of WO_3 photoelectrodes

The physicochemical properties of the prepared WO_3 electrodes were assessed using various characterization tools. Structural aspects were studied with X-ray diffraction (XRD, Rigaku, Japan, D/max-2500, CuKα radiation) over a 2θ ranging from 20 to 80°. Raman spectroscopy measurements were performed with a confocal Raman spectrometer (NRS-3100) containing a laser excitation source (514 nm). UV–visible (UV–vis) spectroscopy (Optizen POP, Mecasys Co. Ltd., Korea) was used to determine the absorbance of the films. The morphology of the WO_3 thin films was studied with high-resolution scanning electron microscopy (HR-SEM, XL30 SFEG, Phillips Co., Holland) at 10 kV. The thickness of the films was determined from the HR-SEM images.

2.4. Photoelectrochemical measurements

A PEC water splitting setup was used to carry out the PEC experiments. For all of the PEC measurements, a single cell with a three-electrode setup was used, as depicted in Fig. 1b. In this setup, the WO_3 is the working electrode, Ag/AgCl rod is the reference electrode, and a platinum wire is the counter electrode. All of the electrodes were kept as close together as possible and their positions were kept constant for all measurements. The electrolyte was a 0.5 M Na_2SO_4 solution, which was purchased from Sigma–Aldrich. Nitrogen was used to remove any dissolved oxygen from the electrolyte solution before testing. Artificial sunlight from a xenon arc lamp (Newport, Oriel Instruments, USA) was used to illuminate the