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Dual-functional zinc oxide aggregates with reaction time-dependent morphology as the dye-adsorption layer for dye-sensitized solar cells

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ABSTRACT

High surface area and light scattering abilities are dispensable for a well-performed photoanode of dye-sensitized solar cells (DSSCs) to respectively provide abundant active sites for dye adsorption and enhance the light path for electron excitation. In this study, an energy-saving and cost-effective low-temperature (80 °C) aqueous solution method is applied to synthesize dual-functional ZnO aggregates which are composed of small nanocrystallites with the diameter of 20 nm. The reaction time plays a significant role in controlling the morphology of ZnO nanostructures. The ZnO aggregates are randomly oriented at the early stage and the flower-like morphology gradually forms when the reaction time reaches 4 h, while the well-defined structure is further destroyed when the reaction time is increased to 8 h. The growth mechanism is proposed to discuss the formation of ZnO nanoflower. The ZnO nanoflower-based DSSC achieves a light-to-electricity conversion efficiency (η) of 4.41%, which is higher than that for the cell with commercial ZnO nanoparticles on its photoanode (3.42%) under AM 1.5G simulated sunlight with an intensity of 100 mW/cm^2. The electrochemical impedance spectroscopy (EIS) is also applied to analyze the electron transport parameters to understand the kinetics of electron transport in the ZnO films. The low-temperature (150 °C) fabrication process for preparing the highly-performed ZnO film also enables the future applications of flexible DSSCs with polymeric substrates.

1. Introduction

Dye sensitized solar cells (DSSCs) have drawn much attention in the last two decades because of their appealing properties, including transparency and multicolor options, potentially low production costs, and compatibility with flexible substrates [1–6]. A critically important component of DSSC is the photoanode, which consists of a mesoporous oxide semiconductor film covered by dye molecules and plays a pivotal role in converting light into electrical energy. Desirable properties of a well-performed photoanode film include large interfacial surface area, as well as strong light scattering and fast electron transport abilities. Nanocrystallite aggregates composed of submicrometer-sized assemblies with nano-sized crystallites is a promising class of nanomaterial to provide all these desirable features [7]. The nano-sized crystallites can provide large interfacial surface area for dye uptake, and the aggregates can improve the optical absorption *via* generation of light scattering [8–10]. Besides, the aggregates can enhance the electron transport with its well-interconnected and densely-packed nanocrystallites, [11] and the relatively open structure of the aggregate-based films can also facilitate the diffusion of ions in the electrolyte during solar cell operation [12,13]. Successful applications of aggregates to DSSCs have been reported for both ZnO [5,6] and TiO_2 nanostructures [11–16]. Zhang et al. fabricated a DSSC employing poly-dispersed ZnO aggregates on its photoanode to attain an overall power conversion efficiency (η) of 5.4%, which is more than double of the η obtained for cell with dispersed ZnO nanoparticles (2.4%) [10]. Sauvage et al. utilized a single layer of mono-disperse mesoporous TiO_2 beads with the $TiCl_4$ post-treatment on the photoanode of a DSSC to achieve an η higher 10% [11]. Most of the literatures focus on the nanocrystallite aggregates based on the spherical shape [7], but the investigations of the aggregates in other morphologies are less common. To our knowledge, there is only one example for the ZnO nanostrawberry aggregates reported recently [17]. Since the surface structure, particle size and shape, as well as the porosity of the dye-adsorbed layer in the photoanode are important factors to determine the performance of the pertinent DSSCs [18], investigation of the ZnO aggregates with various morphologies and properties is highly desirable. One of our previous studies reports the synthesis of a novel burger-like aggregate nanostructure assembled from ZnO nanocrystals and the application on the photoanode of DSSCs. The resulting DSSC achieved a higher η of 4.03%, as compared with that of the cell with a commercial ZnO nanoparticle-based photoanode (3.07%), due to the enhanced dye adsorption and prominent light scattering abilities of the aggregates for the former case [19]. Also, it is believed that the

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reaction time plays an important role on the morphology of the ZnO nanocrystalline aggregates. Therefore, it is worthy to study the morphology change of ZnO aggregates with the reaction time and the influences of the morphology on the performance of the pertinent photoanode of the DSSCs.

The present study investigates the ZnO nanocrystalline aggregates with various morphologies, synthesized *via* a novel energy-saving and cost-effective low-temperature (80 °C) aqueous solution method. It was found that the reaction time plays a significant role in controlling the morphology of the ZnO nanostructure. The morphology and the crystalline structure of the nanocrystalline aggregates were respectively characterized by field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). The aggregates obtained at various reaction times were fabricated in the photoanode of DSSCs, and the corresponding photovoltaic performances were compared. At the same time, the DSSC based on the commercially available disperse ZnO nanoparticle was served as a control. The structural, optical, and charge transfer properties for the flower-like ZnO based photoanode of a DSSC as well as the underlying mechanisms of the charge transport were discussed.

2. Experimental

2.1. Materials

Lithium iodide (LiI) and 1, 2-dimethyl-3-propylimidazolium iodide (PMII) were obtained from Merck. Acetonitrile (ACN) was bought from J. T. Baker. Chenodeoxycholic acid (CDCA), dimethylformamide (DMF), iodide (I_2), sodium hydroxide (NaOH), tert-butylpyridine (TBP), tert-butanol (TBA), and $Zn(NO_3)_2 \cdot 6H_2O$ were acquired from Sigma-Aldrich. H_2PtCl_6 was purchased from Showa.

2.2. Synthesis of ZnO nanocrystalline aggregates

ZnO nanocrystallite aggregates were synthesized using an aqueous solution method performed at a low temperature (80 °C). Equal volumes of 0.05 M $Zn(NO_3)_2 \cdot 6H_2O$ and 1.0 M NaOH aqueous solutions were heated to 80 °C and thoroughly mixed. Upon mixing, the originally clear solutions turned into a milky white colloidal solution, which was allowed to react at 80 °C for 2 to 8 h. The as-synthesized solution was centrifuged at 3500 rpm for 30 min. After centrifugation, precipitated aggregates were collected and dried. Finally, the dried precipitate was ground to fine white ZnO nanocrystallite aggregates.

2.3. Fabrication of dye-sensitized solar cells

The ZnO pastes were prepared using a solvent composed of TBA and distilled water (volume ratio of 2:1) and dispersing the commercial ZnO nanoparticles (approximately 20 nm) (UniRegion Bio-Tech) or the as-synthesized ZnO aggregates in the solvent (weight ratio of 3:8). The mesoporous ZnO films were fabricated by applying the ZnO pastes onto the fluorine-doped tin oxide (FTO) substrates (Nippon Sheet Glass, 8–10 Ω/□, 2.2 mm-thick) as the photoanodes by doctor blading using an adhesive tape as a frame and spacer (0.25 cm^2). The photoanodes were calcined at 150 °C for 1 h to remove organic materials in the films and to increase the crystallinity of ZnO. After cooling to the room temperature, the ZnO electrodes were immersed into a dye solution composed of 0.5 mM D149 (Mitsubishi Paper Mills Limited) and 1 mM CDCA in a mixed solvent of ACN and TBA (volume ratio of 1:1). Because higher η can be achieved for the ZnO-based DSSC using the D149 dye to sensitize the ZnO film than that for the cell sensitized using the N719 dye. The organic D149 dye has smaller size and therefore higher dye-loading amount can be achieved with this sensitizer as compared with the larger size of the ruthenium-based N719 dye, as reported in the previous literature [20]. Also, the ZnO film is easy to be destroyed by the acid environment, so the organic D149 dye is more suitable for sensitizing the ZnO film as compared with the N719 dye which would produce the acid environment during sensitizing. The dye adsorption time was varied from 1 to 4 h depending on the film thickness. The electrodes loaded with D149 were then washed with acetonitrile and dried in the air before cell assembly. The counter electrode of DSSCs was made by decomposing H_2PtCl_6 onto FTO glasses at 400 °C for 20 min. The ZnO photoanode and the Pt counter electrode were sandwiched together with a 60 μm-thick hot-melting spacer in between, and the space between the electrodes was filled with an acetonitrile-based electrolyte containing 0.6 M PMII, 0.05 M I_2, and 0.5 M TBP.

2.4. Characterization

The surface morphology of ZnO nanostructures was characterized using FEI Nova230 field emission scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM, H-7100, Hitachi, Japan). X-ray diffraction (XRD) patterns were obtained by using a diffractometer (PANalytical X'Pert PRO) with Cu Kα radiation. The BET (Brunauer–Emmitt–Teller) surface area was obtained from nitrogen adsorption–desorption measurement (ASAP-2010, Micromeritics). The ZnO film thickness was measured by a microfigure measuring instrument (Kosaka Laboratory, Surfcorder ET3000). The dye loading of the ZnO films was estimated by measuring the absorbance of the DMF solution containing the desorbing dye molecules from the ZnO films using an ultraviolet–visible (UV–vis) spectroscopy (V-570, Jasco). The incident photon-to-current conversion efficiency (IPCE) was measured as a function of wavelength from 350 to 800 nm by using a monochromator (Forter Tech). The η were measured under a white light source (Yamashita Denso, YSS-100A), which gives an irradiance of 100 mW/cm^2 (the equivalent of AM1.5) on the surface of the solar cell. The irradiance of simulated light was calibrated using a silicon photodiode (BS-520, Bunko Keiki). The evolution of the electron transport process in the cell was investigated using the electrochemical impedance spectroscopy (EIS), and the impedance measurements were performed under AM 1.5G illumination. The applied DC bias voltage and AC amplitude were respectively set at the open-circuit voltage (V_{OC}) of the cell and 10 mV between the working and the counter electrodes. The frequency ranges from 10^{-2} to 10^5 Hz. The EIS spectra were recorded using an electrochemical analyzer (Autolab PGSTAT30, Eco-Chemie) and analyzed using the Z-view software with the aid of an equivalent circuit.

3. Results and discussion

3.1. The characterization of ZnO nanocrystallite aggregates

Typical FE-SEM images of the prepared ZnO nanocrystallite aggregates films are shown in Fig. 1. All the ZnO aggregates are composed of similar nanocrystallites with the size of 20 to 50 nm in diameter. An irregular shape of the ZnO aggregates was obtained for the reaction time of 2 h (Fig. 1(a)), while at a reaction time of 4 h, the aggregates converted into a flower-like architecture (Fig. 1(b)). Each of the flower-like aggregates, *i.e.*, nanoflower, shows a dome-shaped core similar to a cauliflower head surrounded by 4, 5, or 6 cone-shaped petals radiating from the core, forming a star-like nanoflower. The diameter of the core is approximately 150 to 200 nm, which is similar to the length of the cone-shaped petals estimated from the point of attachment to the apex. The overall dimension of the nanoflower structure ranges from 400 nm to 600 nm, which is comparable to the wavelengths of the visible light. Therefore, the nanoflower structure is expected to have the ability to generate light scattering, and at the same time to provide high interfacial surface area. To demonstrate the porous features of the nanocrystallites aggregation for the nanoflowers more clearly, a geometrical structure of an individual aggregate is schematically