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Construction of 3-dimensional ZnO-nanoflower structures for high quantum and photocurrent efficiency in dye sensitized solar cell

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ABSTRACT

3-dimensional ZnO nanoflower were obtained on FTO (F:SnO_2) substrate by hydrothermal method in order to produce high efficiency dye sensitized solar cells (DSSCs). We showed that nanoflowers structures have nanoscale branches that stretch to fill gaps on the substrate and these branches of nano-leaves provide both a larger surface area and a direct pathway for electron transport along the channels. It was found that the solar conversion efficiency and quantum efficiency (QE) or incident photon to current conversion efficiencies (IPCE) is highly dependent on nanoflower surface due to high electron injection process. The highest solar conversion efficiency of 5.119 and QE of 60% was obtained using ZnO nanoflowers/N719 dye/I^-/I^-_3 electrolyte. In this study, three dimensional (3D)-nanoflower and one dimensional (1D)-nanowires ZnO nanostructures were also compared against each other in respect to solar conversion efficiency and QE measurements. In the case of the 1D-ZnO nanowire conversion efficiency (η) of 2.222% and IPCE 47% were obtained under an illumination of 100 mW/cm^2. It was confirmed that the performance of the 3D-nanoflowers was better than about 50% that of the 1D-nanowire dye-sensitized solar cells.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention in the last decade due to low cost and relatively efficient photovoltaic energy conversion [1–3]. The highest efficiency, to the best of our knowledge, reported on DSSCs was produced by Gratzel et al. and it was obtained 11% on nanoporous TiO_2 by using ruthenium complex dye, containing I^-/I^-_3 redox couple electrolytes and platinum counter electrode [2–4]. Although the conversion efficiency for TiO_2 are much higher than that achieved with ZnO based cells (0.3–6%), ZnO nano-semiconductor materials are considered as an alternative to TiO_2 due to its ease of crystallization and anisotropic growth [5]. ZnO nanostructures are one of the most promising semiconductor materials for optoelectronic and photonic applications due to its wide, direct band gap (3.37 eV), a large exciton binding energy (60 meV) and a huge magneto-optic effect [6,7]. Many different ZnO nanostructures have been synthesized under specific experimental conditions and investigated for DSSC applications due to the large specific surface area offered by these nanostructures [8]. The large specific surface area is one of the most important requirements for the photo-electrode films in DSSCs mainly because of the need to maximize dye molecule adsorption on semiconductor materials [9]. Therefore, it was reported that the surface structure, high surface area and the porosity are all important factors for obtain high solar conversion efficiency in DSSCs [10,11].

Especially, three-dimensional nanoflower and one-dimensional nanowire have attracted great interest for DSSC applications due to their unique optical, electronic, mechanical properties [12–15]. However, the uses of ZnO nanoflowers consisting of outstretched branches have been also reported for high efficiency in DSSC [16]. This is based on the consideration that the one-dimensional structures may not capture the photons completely due to the existence of intervals inherent in the morphology [16]. Therefore, nanoflower structures have nanoscale branches that stretch to fill these intervals and, provide both a larger surface area and a direct pathway for electron transport along the channels from the branched petals [5–17].

In this study, ZnO nanoflowers were growth on FTO substrate by hydrothermal method. X-ray diffraction (XRD) studies of the ZnO nanoflowers showed a high crystallinity and preferred orientation along the (0 0 1) plane of the wurtzite structures. Scanning electron microscopy (SEM) images showed that the nanoflowers can be obtained with average diameters of 10–50 nm and in the

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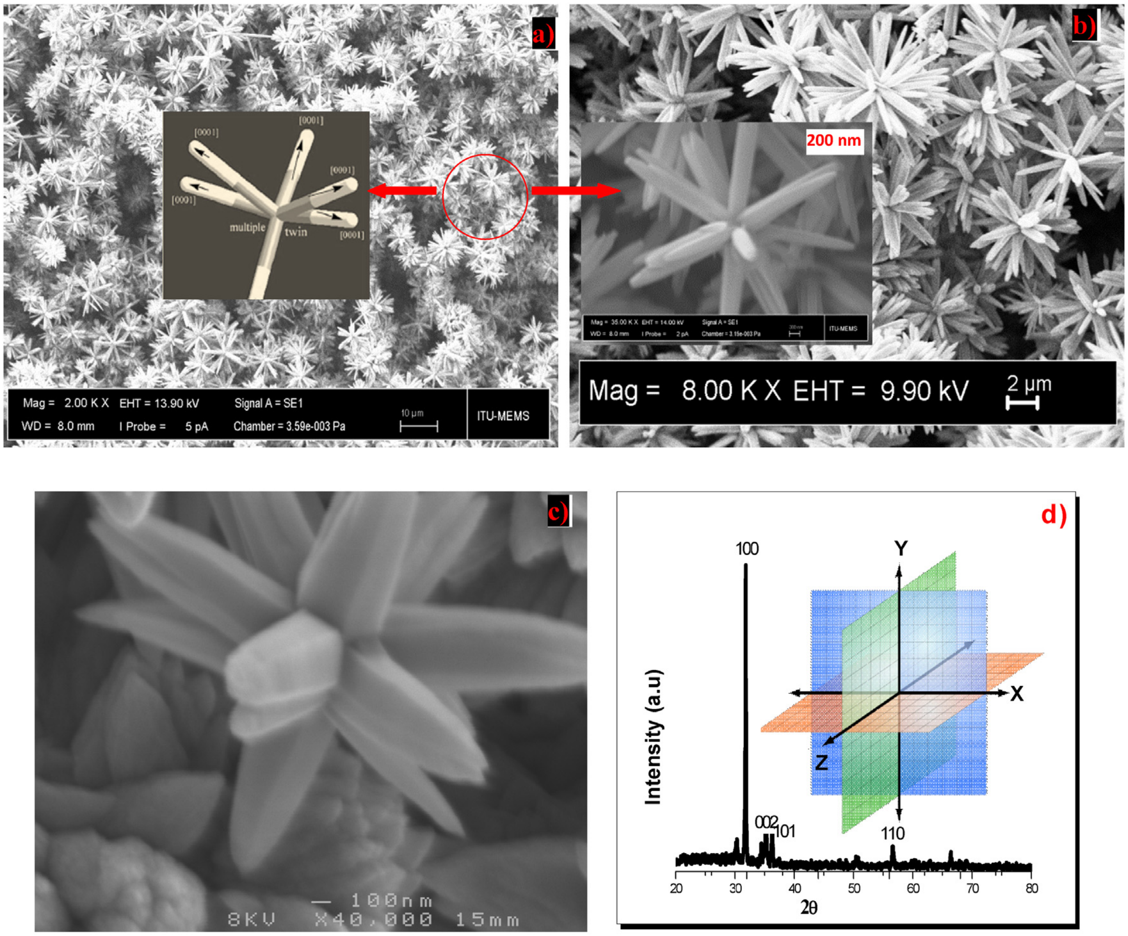

Fig. 1. (a–c) SEM images, (d) XRD characterization of ZnO nanoflowers with different magnification by using 10 Mm $Zn(NO_3)_2.6H_2O$, 24 h, 175 °C, pH 10 on FTO substrate.

range of 1–5 μm in size. Raman spectra of the ZnO nanoflowers showed that the peaks at around 582 cm^{-1} to be related to the E_1 mode of the ZnO nanoflowers. The room temperature photoluminescence (PL) measurements confirm that the nanoflower samples have near band edge emissions and broad deep level emission. The UV–Visible absorbance spectrums of the ZnO nanoflower show a strong absorption edge between 360 and 400 nm and high transmittance of higher than 92%. As a result, wide band gaps ZnO nanoflowers were successfully used as photoanode in DSSCs and it was compared with one-dimensional nanowire in terms of solar conversion efficiency.

2. Experimental section

2.1. Preparation of ZnO nanoflowers

ZnO nanoflowers were grown on FTO (SnO_2:F), substrate by hydrothermal method using ammonia as the base source. The growth was carried out at 175 °C for 24 h with Zn $(NO_3)_2$ as a source of Zn^{2+} ions. First of all, FTO substrates were cleaned carefully by dipping for 2 min each in Propan-2-ol, de-ionized water, methanol and de-ionized water, in sequential manner. After the cleaning process, 10 mM $Zn(NO_3)_2·6H_2O$ (aq) solution was prepared and pH of the solution was adjusted to ~10 using ammonia solution. Then, the FTO substrates were immersed into the solution and then heated to 175 °C for 24 h (Fig. 1). We also produced one dimensional ZnO nanowire structures [11] in order to compare solar conversion efficiency with nanoflowers structures. After the growth step, the substrate was rinsed using de-ionized water and then dried by N_2 blowing. The morphology of the nanostructures was analyzed using a JEOL–6400 scanning electron microscopy (SEM). The crystal structure was analyzed by X-ray diffraction (XRD) (Rigaku D/Max-IIIC diffractometer) with Cu-Kα radiation of 1.54 Å, within the 2θ angle ranging from 20–80 and the photoluminescence (PL) measurements were conducted with the RF 5301 PC Shimadzu spectrofluorometer at room temperature. The absorption and transmittance measurements were carried out by PerkinElmer UV–Visible Lambda 2S spectrometer. The Raman scattering measurements were performed using a micro Raman Renishhaw 2000 system with an excitation source of 514.5 nm at room temperature.

2.2. Solar cell construction and testing

DSSCs base on ZnO nanoflowers were obtained by N719 dye onto the surfaces of the nanostructures grown on FTO substrates. Substrates were heated to 100 °C before immersing them into 0.5 mM ethanolic dye solution for 30 min. The counter electrode was an Pt:FTO substrate and the electrodes were separated by 20 mm polypropylene spacer and pressed together with binder clips. Electrolyte, which consisted of 0.5 M tetrabutylammonium iodide, 0.05 M I_2(Iodine), and 0.5 M 4-tertbutylpyridine in acetonitrile, was introduced between the electrodes by capillary forces. Active electrode area was typically 0.25 cm^2. Current density–voltage (J–V) characteristics were recorded using a Keithley 175A digital multimeter using 0.01 V/s voltage ramp rate.

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