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Short Note

Indoline-dye immobilized ZnO nanoparticles for whopping 5.44% light conversion efficiency

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ABSTRACT

Using indoline D102-dye, a whopping 5.44% light-to-electrical conversion efficiency owing to higher current density and open circuit voltage is explored for the ZnO nanoparticles (NPs)-based photoelectrode. The ZnO NPs/D102 dye structure has been designed onto indium-tin-oxide, electrons extractor, conducting and transparent substrate. The ZnO NPs of minimum [0 0 2] direction orientation compared to that of [1 0 0] and [1 0 1] directions, an indication of good charge transporting ability, with agglomerated grains of about 5–10 nm in diameters were immobilized in D102 dye for 1 h for dye loading. Low charge transport resistance and nearly 60% incident photon-to-current conversion efficiency were obtained. The results suggest that D102 dye can be potentially used for obtaining high performance ZnO-based dye-sensitized nanostructured solar cells.

1. Introduction

As the incessant quest for clean, sustainable, alternative renewable energy gathers enormous euphoria within the scientific community, interest of researchers and industrialists in solar photovoltaic cells is increasing progressively. In the search of a promising photoelectrode, dye-sensitized nanostructured solar cells (DNSCs)-based on nanostructured metal oxides including TiO_2, ZnO, SnO_2, etc., with a prospect of low-cost photovoltaic energy conversion, have attracted much attention in recent years [1–4] wherein, photo-excitation takes place in the dye molecules, and the photo-generated charges are then separated at the dye/oxide interface, and therefore, electrons are injected into the conduction band of semiconductor oxide, then diffuse through the semiconductor oxide to the collecting electrode. Surface area and the nanostructure of preferred wide band gap metal oxides and extinction coefficients of sensitizing dyes are essentially and critically important to get higher light-harvesting efficiency for higher solar-to-electrical conversion efficiency. The electron transport in the semiconductor oxide is dominated by diffusion; therefore, it is necessary to reduce the charge traps in the semiconductor oxides for enhancing electron transport kinetics to obtain higher current density and minimum recombination centers. Different proposed alternatives include the use of wider band gap energy metal oxides as capping layers or blocking layers for stopping reverse electrons, hopping-free one dimensional nanostructures and cocktail dyes [5,6], etc. In spite of novelty in nanostructure on account of its ease of crystallization and anisotropic growth, high direct band gap energy, high exciton energy, ZnO is one of the mostly suffered metal oxides. Very few groups have succeeded so far in achieving more than 5% light conversion efficiency based on ZnO nanostructures [7–9]. The factors that determine the efficiency of DNSCs are the photocurrent density (J_{sc}), the open circuit potential (V_{oc}), fill factor (*ff*), and the intensity of the incident light (J_{sc}) [10]. In general, the J_{sc} and V_{oc} are related to the rate of electron injection to the photoelectrode and the energy difference between the Fermi level of the photoelectrode and the Nernest potential of the redox couple in the electrolyte, respectively. Recent studies conclude that the J_{sc} and V_{oc} are greatly influenced by the number of carboxylic groups (protons) existing in the dye to anchor the photoelectrode and therefore, so far such investigations dealing with the relationship between the molecular structures of the dyes and the J_{sc} and V_{oc} were subjected to the ruthenium-based N3 dye and its derivatives, such as N749 and N719, which are characterized by as high as four protons per molecule [11,12]. Using a dye of relatively high

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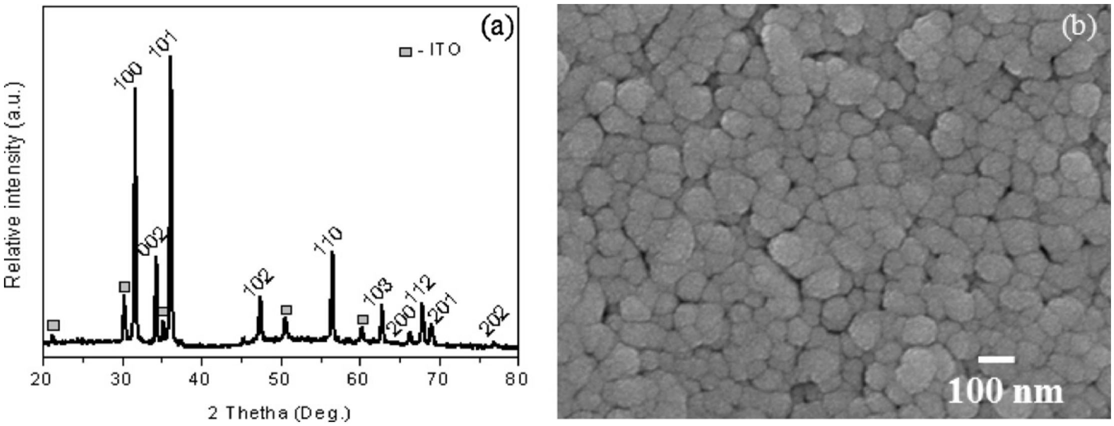

Fig. 1. (a) X-ray diffraction pattern confirming the formation of ZnO and (b) the SEM image revealing the nanometer sized angular grains.

extinction coefficient of minimum surface aggregation impact and CdS NPs immobilization for dual photosensitization, DNSCs performance of ZnO NPs-based electrodes can be improved immensely [13–15]. However, the variations observed in the V_{oc} and J_{sc}, and therefore, efficiency of DNSCs constituted with metal-free organic dyes having a single carboxylic group [16–21], have not been explored to a larger extent. In this communication, ZnO NPs-based DNSCs using an indoline D102 dye is explored. In brief, structural and morphological aspects of ZnO NPs are presented in the preceding part and in the later; Nyquist plot obtained from impedance spectroscopy measurement, incident photon-to-current collection efficiency (IPCE), and the J_{sc} and V_{oc} characteristics are investigated. The D102 dye structure (inexpensive on account of its ruthenium free structure), commercially available, was used for immobilizing ZnO NPs electrodes of different thicknesses for optimal performance.

2. Experimental details

Nanostructured ZnO NPs electrodes of various thicknesses were prepared by application of NPs dispersion, obtained from Alfa Aesar, Germany, onto indium-tin-oxide (ITO) conducting and transparent substrate by spin method. The ZnO-solvent solution was filtered to remove dust, typically with a 0.45 μm filter before spinning. The plate is spun in at least two stages by simple spin-coating apparatus. During the first stage, the plate is spun at a low to moderate speed of 500–1000 rpm for 5–10 s to evenly spread the solution. In brief, ZnO electrodes deposited onto ITO were prepared from commercial ZnO paste composed of nanoparticles with approximate nanoparticle size of 20 nm and wurtzite structure (discussed later). The paste was mixed with 30% water and stirred overnight to obtain a colloidal suspension of ZnO. The thickness of the coating is then determined and controlled during the second stage by spinning the coating at a higher speed, between 1500 and 3000 rpm for anywhere between a few seconds and a minute. The ZnO NPs films of 2, 4, 6, 8, 10 (±0.2) μm were prepared. A Sloan Dectak profilometer was used to measure the thicknesses of all films. These were further annealed at 573 K for 60 min to remove organic contents, if any, and to improve the crystallinity, respectively. The X-ray diffractometer (XRD) and the scanning electron microscope (SEM) image was used for the structural elucidation and surface morphology confirmation. Using LOT-ORAL solar simulator, current density–voltage, *J–V* characteristic after standardizing with Si photodiode to 100 mW/cm^2 was measured. The Sandwich-type cells (1 cm^2) were prepared by sealing together the ZnO-coated electrode which was further scratched to obtain an active area of 0.25 cm^2; with the counter electrode using a transparent film of Surlyn 1472 polymer. The electrolyte was then introduced through holes drilled in the counter electrode, which were sealed immediately with microscope cover slides and additional strips of Surlyn to avoid leakage unless otherwise stated. It is scientifically recommended to use a photo-mask to cover the photo-cell in order to define the accurate active area, but in our case we scratch the entire film to limit the active area to only 0.25 cm^2 and the non-active region is meticulously sealed using a non-reflecting Surlyn polymer tape. The impedance spectroscopy measurement (EIS) was performed using BAS-Zahner IM6 Impedance analyzer. For IPCE measurement, cell of maximum conversion efficiency performance was standardized with UV filtered Si diode before actual measurement wherein light was focused from the glass side.

3. Results and discussion

Fig. 1a shows the ZnO X-ray diffraction pattern wherein the *c*-axis growth, i.e. compared to neighboring (1 1 0) and (1 0 1) peaks (0 0 2) reflection plane showed relatively weak intensity which is related to the relative growth rates of various faces as intermolecular bonding preferences or dislocations, supersaturation, temperature, solvents and surfactant, sculptures the surface morphology and the structural related aspects of any domain [22]. A weak (0 0 2) reflection plane in the ZnO NPs XRD pattern suggested, indirectly, the presence of higher oxygen vacancies. In general, oxygen vacancies and interstitial zinc atoms have strong influence on the electronic properties of ZnO as electrons in ZnO are located in the conduction band and/or shallow traps [23]. In short, higher the number of oxygen vacancies lower is the resistivity. Fig. 1b presents the high resolution SEM image of ZnO NPs wherein surface texture was smooth and uniform without pinholes, cracks and defects over the whole respective surface image. Individual ZnO crystal was close to 100 nm in diameter. Several small spherical crystallites of 20–30 nm in diameters were agglomerated to form relatively bigger island. These irregular (sizes and shapes) crystallites would be practically important for light scattering and dye-absorbing effect to enhance DNSCs performance. Fig. 2a shows the chemical structure of the D102 dye. Very strong absorption coefficient (55,800 L mol^{-1} cm^{-1} at 491 nm), about four times stronger than the ruthenium N3 dye (13,900 L mol^{-1} cm^{-1} at 541 nm), was obtained [24]. The higher extinction coefficient of dye and mesoporous ZnO NPs of angular sizes would be interesting when used in DNSCs applications. For J-V characteristics, 15 mL of methoxyacetonitrile (98%) containing 0.6 M 1-hexyl-2-3-dimethylimidazolium iodide (C6DMI), 0.1 M lithium iodide (LiI), 0.05 M iodide (I_2), and 0.5 M 4-*tert*-butylpyridine (*t*-BPy) solution was used as an electrolyte. All measurements were carried