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Crystallographic phase-mediated dye-sensitized solar cell performance of ZnO nanostructures

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A facile fabrication of ZnO nanostructures with different crystallographic phases on indium tin oxide glass substrates by using an aqueous solution growth method at low temperature is explored. Electron charge transportation in ZnO crystallographic phases is probed for dye-sensitized solar cells. Due to the decrease in the electron lifetime from 5.5 to 1.36 ms the ZnO electrode primed with nanoparticles and sensitized with ruthenium dye (N3) delivers light conversion efficiency of up to 1.33%, which is higher than electrodes made up of nanoplates (0.81%), nanorods (0.50%) and microrods (0.28%).

Keywords: ZnO crystallographic phases; Dye-sensitized solar cells (DSSCs); Impedance analysis; *J–V*; IPCE

Dye-sensitized solar cells (DSSCs) using sensitizing dye molecules linked to wide band gap mesoporous metal oxides have attracted a great deal of attention [1]. In general, DSSCs are composed mainly of abundantly available and non-toxic metal oxides, a monolayer of dye molecules and an electrolyte. Light harvesting is a key factor for improving the efficiency of DSSCs. The molar extinction coefficient, surface coverage of the sensitizing dye and the total surface area of the metal oxide electrode are the main factors determining the light absorption and, thereby, the power conversion efficiency of DSSCs [2,3]. In addition to the development of suitable dyes, electron transport through mesoporous oxides needs to be probed in detail, with the specific intention of finding materials of higher electron mobility ensuring longer electron lifetime, and it is also necessary to determine the intrinsic material composition and the properties of the loading dye. ZnO is a uniquely sensitive material that belongs to the group IIb–VI compound semiconductors whose intrinsic properties depend strongly on their crystallographic phase, orientation, surface treatment and nanostructure form. Apart from micro- and nanorods of the same orientations, a variety of nanostructures including nanoparticles (NPs), nanowires (NWs), tetrapods, hierarchical structures, nanoflowers, nanotips, nanosheets, nanotubes and branched nanostructures have been widely employed in recent years. The growth of ZnO can be deduced from its crystal lattice structure or the nucleation sites of the substrate surface, and the concentration and electrostatic interaction between the cations (Zn^{2+} and $ZnOH^{+}$) and anions (OH^{-}) influences growth along polar or non-polar facets [4]. The most prominent ZnO rods are composed of a polar metastable phase and a stable non-polar Zn-terminated (Zn-rich) phase. These phases influence the material surface characteristics, including the charge transfer kinetics and dye-loading properties, in addition to surface defects which are affected by the preparation conditions [5].

The electron transport of ZnO NPs can be increased by about two orders of magnitudes and the electron mobility by several orders of magnitudes when a thin film of ZnO NPs is deposited on vertically aligned ZnO NWs [6]. Furthermore, the unidirectional growth of ZnO nanostructures with fewer surface traps enables a faster and more direct electrical pathway for the

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collection of the electrons [7]. To investigate the relationship between the ZnO phase and DSSC performance, electron lifetime values for NRs, microrods (MRs), nanoplates (NPls) and NPs were calculated. Ruthenium(II) *cis*-di(thiocyano) bis(2,2′-bypyridyl-4,4′-dicarboxylic acid) (N3) dye was applied for a fixed, i.e. 45 min, period of time [8].

Various ZnO nanostructures, including NPs, NRs, NPls and MRs, were produced via different procedures [9–11]. In brief, a commercially available ZnO NPs dispersion, electrodeposited NPls, chemically deposited NRs and MRs electrodes were presented as the dye-loading agents. The film thickness of the NPs electrode was varied by dilution with distilled water in the ZnO dispersion and by dip coating, i.e. qualitative dilution of ZnO dispersion can form a thin film via a dip-coating process. It is worth mentioning here that the growth conditions for NPls, MRs and NRs were stringent and the film thickness was ~1–1.5 μm. The nanostructural evolution of ZnO NPs, NPls, NRs and MRs was monitored by scanning electron microscopy (SEM) with a Cambridge Stereoscan 250-MK unit. The Zn:O ratio in the ZnO nanostructures was confirmed by energy-dispersive X-ray analysis using an attachment on an EM-912 transmission electron microscope. Film thickness was measured with a surface profilometer (DEKTAK 3) by electromechanically moving the samples beneath a diamond-tipped stylus. For structural elucidation, X-ray diffraction (XRD) patterns were recorded. The electrochemical impedance spectroscopy (EIS) measurements were performed using a BAS-Zahner IM6 impedance analyzer. For the solar cells, an electrolyte solution consisting of 15 ml 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) was used. The soaking time for all the electrodes was 45 min and the DSSCs measurements were performed at a photo-intensity of 100 mW cm^{-2} (0.25 cm^2) using a solar simulator. The incident photon-to-current conversion efficiency (IPCE) was measured using a Polaronix® K3100 spectral IPCE measurement system (South Korea); prior to the sample measurement, the equipment was calibrated with a standard silicon photodiode.

The crystallographic phases of ZnO nanostructures are shown in Figure 1. The (0 0 1) plane observed in the peripheral phase of the hexagonal rods appears the region more likely to absorb the dye molecules. The ZnO nanostructures for DSSCs consist of a non-stoichiometric excess of oxygen ions compared to zinc ions. In the growth of NPls, the Cl^- ions from the KCl electrolyte used in the electrodeposition process prevent growth from the basal plane and, consequently, the vertical stacking of ZnO hexagonal platelets is promoted. These platelets are more horizontally stacked. Figure 2a–d presents different ZnO nanostructures employed in this study. The NPs are not exactly spherical as seen in the inset of Figure 2a, but are the agglomeration of many small spherical crystallites with diameters ranging from 20 to 30 nm. These irregular crystallites are important for light scattering and dye absorption to enhance DSSCs performance. The NPls morphology of the ZnO grown against the indium tin oxide (ITO) substrate surface is shown in Figure 2b. The horizontal in-plane top width of the individual ZnO NPls (inset) is 100–150 nm. The vertical placement of the individual plate makes it difficult to visualize at the bottom even under high-resolution scanning [12]. The ZnO NRs of 100–120 nm in diameter and MRs of 500–600 nm in diameter, respectively, are clearly distinguished from one another (Fig. 2c and d). Uniformly distributed ZnO NWs are grown randomly with the evolution of a neck-like structure at their tips (Fig. 2c, inset). MRs composed of horizontally stacked hexagonal plates are perpendicular to the substrate surface (Fig. 2d, inset). Under the influence of non-covalently bonded intermolecular forces, such as hydrogen bonding, van der Waals interactions or electrostatic forces, the nuclei will become clustered and possibly rearrange into crystallographically organized configurations, ensuring the formation of various nanostructures [13].

The intensity of the XRD for the (0 0 2) reflection plane varies (Fig. 3), indicating that there must be a change in the structural, optical and electrical properties of ZnO phases. The intensity of the (0 0 2) plane is systematically increased from NPs to the MRs. Due to fewer oxygen ions, and a lower ionic diffusion resistance, i.e. a higher charge transfer resistance, the ZnO NPs phase was confirmed to have a weaker (0 0 2) reflection plane intensity compared to that of other phases. Wurtzite-type hexagonal ZnO rods have six prismatic faces in addition to the polar basal $(0 0 \bar{1})$ and peripheral polar metastable (0 0 1) plane (*c*-axis growth) [5,14]. In the

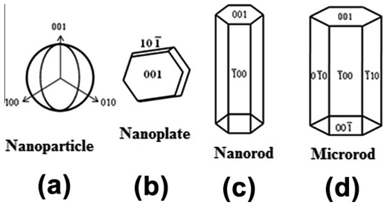

Figure 1. Crystallographic phases of ZnO: (a) NPs, (b) NPls, (c) NRs and (d) MRs.

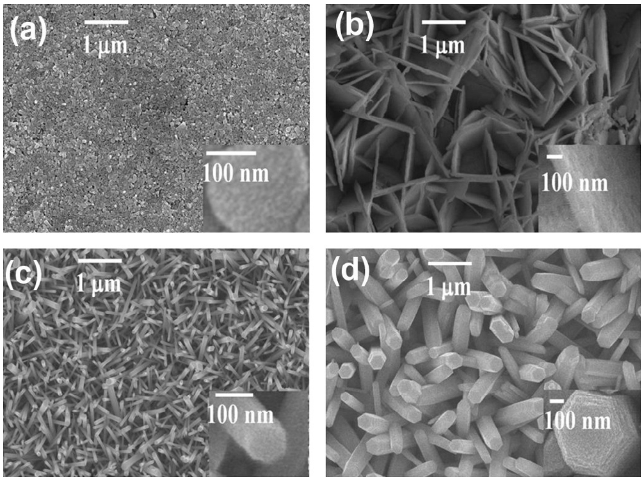

Figure 2. SEM images of ZnO: (a) NPs, (b) NPls, (c) NRs and (d) MRs; inset shows a magnified version.