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One-pot synthesis of intercalating ZnO nanoparticles for enhanced dye-sensitized solar cells

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ABSTRACT

In this letter we report a facile one-pot synthesis of intercalated ZnO particles for inexpensive, low-temperature solution processed dye-sensitised solar cells. High interconnectivity facilitates enhanced charge transfer between the ZnO nanoparticles and a consequent enhancement in cell efficiency. ZnO thin films were formed from a wide range of nanoparticle diameters which simultaneously increased optical scattering whilst enhancing dye loading. A possible growth mechanism was proposed for the synthesis of ZnO nanoparticles. The intercalated ZnO nanoparticle thin films were integrated into the photoanodes of dye-sensitised solar cells which showed an increase in performance of 37% compared to structurally equivalent cells employing ZnO nanowires.

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1. Introduction

Recently there has been much effort towards the development of dye-sensitised solar cells (DSSCs) due to their high power conversion efficiency and vacuum-less processing [1]. DSSCs typically consist of TiO_2-based dye/electrolyte/catalysts sandwiched between two transparent conductive electrodes. One of the key technological innovations behind enhanced DSSC performance is the replacement of traditional sol–gel based TiO_2 films with commercially available TiO_2 nanoparticles [2]. Although TiO_2 nanoparticles are widely available and chemically stable they suffer from low electron mobility [3]. Consequently, several alternative nanoparticles have been considered, such as SnO [4] and ZnO [5]. Amongst the proposed, ZnO is perhaps the most promising due to its similarly wide band gap (3.34 eV), inexpensive solution-based synthesis methods, and the wide range of morphologies its nanoscale crystals can adopt [6] such as nanowires [7], nanoflowers [8], and tetrapods [9] many of which have been previously employed, to varying degrees of success, in DSSCs.

Nanoparticle-based DSSCs outperform nanowire-based devices due to the significantly enhanced surface area of the photoanode, resulting in greater dye uptake [1,2]. During construction of the working electrodes, TiO_2 nanoparticles are typically annealed at ~450 °C to stimulate increased intercalation. Intercalation creates additional conduction pathways for the transfer of the photogenerated charge carriers. This increase in interconnectivity is typically absent in ZnO-based nanostructured films. In fact, it has been shown that ZnO infusion can occur only at sintering temperatures above 700 °C [10], which greatly exceeds the glass transition temperature of most optically transparent substrates. In this study, a one-pot synthesis of highly intercalated ZnO nanostructures for DSSCs is presented. A possible growth mechanism is proposed as well as a demonstration of the integration of the intercalated ZnO in a low-cost DSSC platform.

2. Experimental

The intercalating ZnO nanostructured thin films were synthesised through a two-step, one pot process. 0.1 M of zinc acetate dehydrate was dissolved in ethanol and agitated at 60 °C for 2 h. This precursor solution was centrifuged to collect the synthesised ZnO nanoparticles, re-dispersed into equimolar aqueous 25 mM zinc nitrate: hexamine (HMTA), and refluxed at 90 °C for 2 h. 0.25 cm^2 photoanodes were fabricated by the doctor blade method [2] on fluorine doped tin oxide (FTO) glass substrates, yielding a thickness of ~15 μm. ZnO photoanodes were dye-sensitised by immersion into a 5×10^{-4} M ethanoic solution of ruthenium-based N719 dye, for 2 h. After dye impregnation, samples were thoroughly rinsed in ethanol to remove excess dye. Counter electrodes were fabricated by spin coating Pt solution (Dyesol) onto FTO glass substrates, which were subsequently baked at 450 °C in air for 10 min. Two small holes

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were drilled on the Pt coated FTO for electrolyte injection. DSSCs were constructed by sandwiching a Suryn sheet between the ZnO and Pt electrodes. DSSCs were sealed by hot compression with a redox couple electrolyte of 0.1 M LiI, 50 mM I_2, 0.6 M 1,2-dimethyl-1,3-propylimidazolium iodide, and 1 M tert-butylpyridine, with 3-methoxypropionitrile injected into the cavity. The injection holes were sealed with Suryn sheet.

Current density–voltage (J–V) characteristics were measured using a Keithley 2400 source-measure unit, under illumination (100 mW/cm^2), provided by a solar simulator (Science-tech.). For comparison, DSSCs were fabricated using hydrothermally synthesised ZnO nanowire-based photoanodes, as reported in detail elsewhere [11].

The morphology and chemical composition of the deposited ZnO nanoparticles were observed using an environmental scanning electron microscope (FEI Quanta 400 F) equipped with an energy dispersive spectroscope (EDS). The crystalline orientation of the films was studied by X-ray diffractometry (Philips, PW1830) using a Cu Kα radiation source. The detailed morphology of the synthesised ZnO nanoparticles was evaluated using a Philips CM-200 TWIN transmission electron microscope (TEM) operated at 20 kV.

3. Results and discussion

Fig. 1a and b presents SEM micrographs of the synthesised ZnO nanomaterial. The synthesised ZnO nanoparticles form clusters that are up to 300 nm in diameter (± 79.8 nm (1 S.D.)). Conventional TiO_2 based DSSCs often employ optical scattering layers to enhance light scattering. This increases the overall power conversion efficiency. Such additional processing not only adds significant cost per unit cell, but also time to the fabrication process. In the present study, such additional scatter-site formation is not required as it is implicitly provided by the larger ZnO particles. A typical TEM image of the synthesised ZnO nanoparticles is shown in the inset of Fig. 1b. The nanoparticles consist of interconnected ZnO nanoparticles around 50–300 nm in diameter. Note that smaller ZnO particles, 5–10 nm in diameter, are also highly interconnected. The EDS chemical composition of the synthesised ZnO is shown in Fig. 1c. The intercalated thin film is

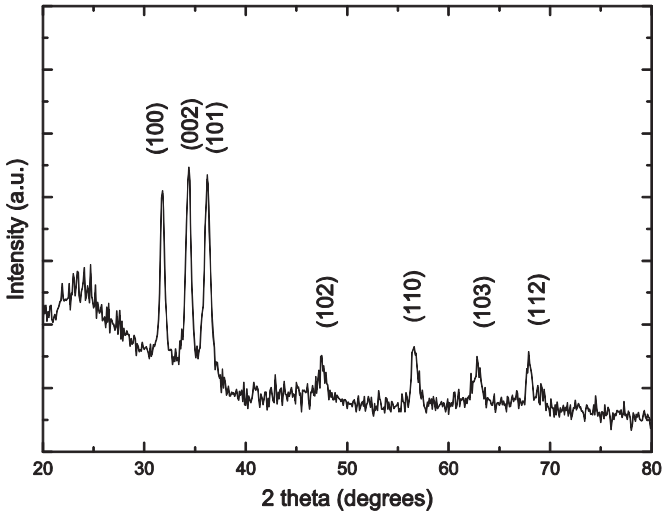

Fig. 3. XRD spectrum of the intercalated ZnO thin film.

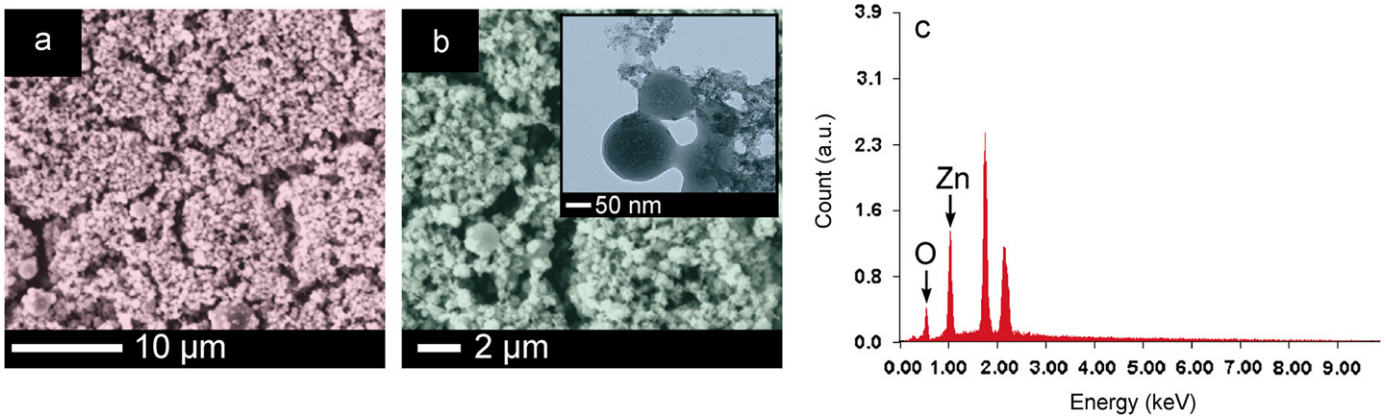

Fig. 1. Morphology of the intercalated ZnO thin films. (a) A scanning electron micrograph of an intercalated ZnO thin film at low magnification (scale bar: 10 μm). (b) An SEM micrograph at higher magnification highlighting the variation in nanoparticle size within the film (scale bar: 2 μm). The inset shows the corresponding TEM image (scale bar: 50 nm). (c) EDS compositional analysis of the film.

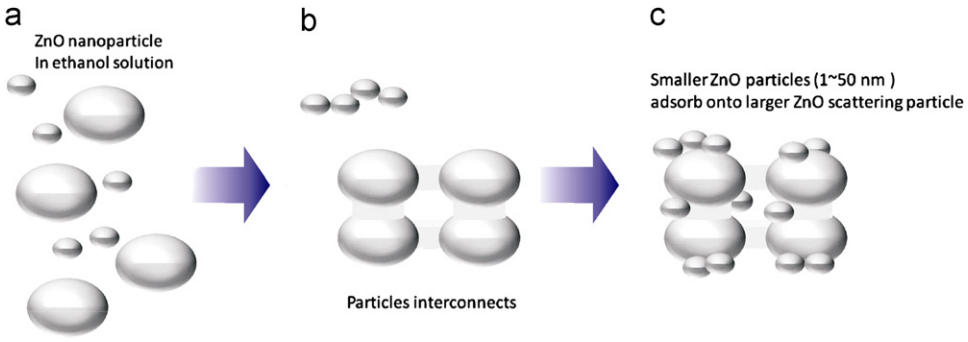

Fig. 2. Proposed growth mechanism of the intercalated ZnO thin films. (a) Initial formation of the ZnO particles, (b) larger ZnO particles bind from the seed layer growing ZnO and (c) smaller ZnO nanoparticles adsorb onto the larger ZnO particles, increasing film connectivity.

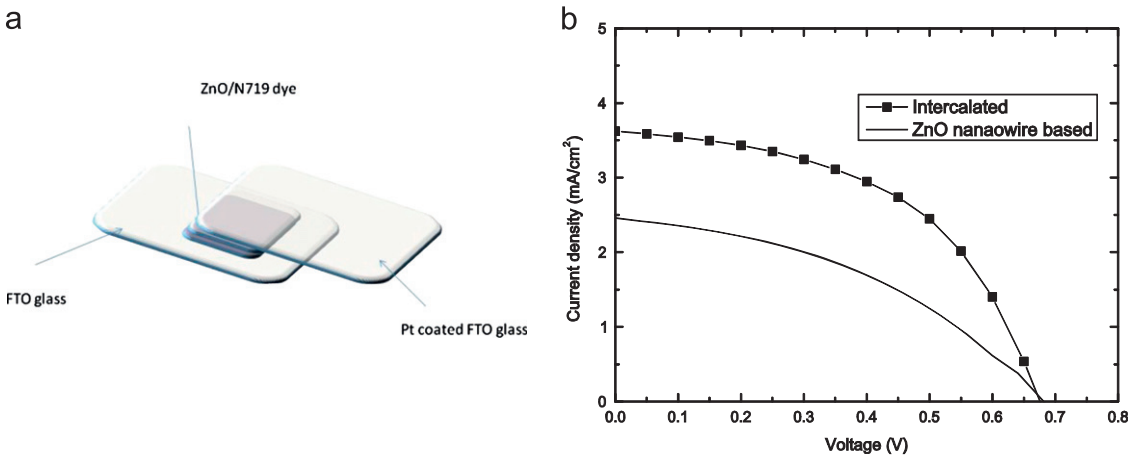

Fig. 4. Intercalated ZnO integration in DSSCs. (a) Illustration of the DSSC construction and (b) *J–V* of an intercalated ZnO photoanode DSSC (■) compared to a ZnO nanowire cell of nominally equivalent construction.

Zn-rich with a Zn:O ratio of around 52.1:47.9. This is consistent with previous studies which have shown that hydrothermally synthesised ZnO tends to exhibit oxygen vacancy defects [12].

Fig. 2 depicts one possible formation mechanism for our interconnected ZnO. As the zinc acetate dissolves, ZnO particles of various sizes form. Usually chelating agents, such as monoethanolamine or diethanolamine, are employed to prevent such precipitation. However, in our case this is beneficial toward enhanced intercalation. After centrifugation and collection the ZnO particles were added to a zinc nitrate/HMTA solution, which has been employed in the past for ZnO nanowire growth [11]. The zinc nitrate functions as a Zn source, whilst the HMTA preferentially absorbs onto the (010), (100) and (110) surfaces, leaving the *c*-axis for (002) ZnO growth. In the present study, the zinc nitrate/HMTA solution functions as the intercalent between the ZnO nanoparticles, without the need for high temperature (>300 °C) processing. These larger particles increase light scattering within the photoanode and consequently increase cell efficiency [13]. On the contrary, smaller particles increase dye loading, also key to achieving high cell efficiency. However, the specially engineered intercalation reported herein provides a means to achieve a simultaneously enhanced number of conduction pathways between the ZnO nanoparticles as well as high dye-loading without the creation of cell-degrading interfacial potential barriers.

Fig. 3 shows the crystalline orientation of the as-deposited ZnO nanoparticles, determined by XRD. The dominant peaks agree with the hexagonal phase of the bulk wurtzite ZnO crystal, showing a lattice constant $a=3.25$ and $c=5.21$ Å. The sharp peaks indicate polycrystalline ZnO formation without significant impurities due to complete burnout of organic compounds.

Fig. 4b depicts the photocurrent density–voltage (*J–V*) transfer characteristics of a fabricated device, 0.25 cm^2 in size, where the cell fabrication details are illustrated in Fig. 4a. The short-circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (*FF*), and power conversion efficiency (η) of the fabricated device were 3.64 mA/cm^2, 0.68 V, 0.49 and 0.92%, respectively, whereas DSSCs manufactured using ZnO nanowires exhibited $J_{sc}=2.44$ mA/cm^2, $V_{oc}=0.68$ V, $FF=0.41$, and $\eta\sim0.67\%$. Thus, when compared with ZnO nanowire-based cells, increased intercalation improves DSSC performance by around 37%. Although η for the intercalated ZnO film did not reach the same level of performance as those of TiO_2 based DSSCs the data presented demonstrates that low-temperature methods do indeed offer a viable route to achieving beneficial intercalation between ZnO nanoparticles, and may ultimately facilitate a paradigm shift in DSSC fabrication toward platforms based on ubiquitous, inexpensive, flexible and low-temperature polymeric substrates. Work is on-going to improve overall power conversion efficiency.

4. Conclusion

A one-pot synthesis method to grow porous and highly interconnected ZnO nanoparticles has been demonstrated. The proposed strategy ensures formation of intercalated nanoparticles that offer multiple conduction paths whilst remaining highly porous for optimal dye absorption. This polymer-compatible, low-temperature method produced nanoparticles of various sizes that efficiently scatter incident light which increased DSSC efficiency. Intercalated ZnO DSSCs showed a 37% increase in performance compared with DSSCs employing ZnO nanowire-based photoanode.

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