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Ultra-rapid synthesis of highly porous and robust hierarchical ZnO films for dye sensitized solar cells

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ABSTRACT

Dye sensitized solar cells are a promising third generation solar cell technology bearing considerable commercial potential. Here, we present the synthesis of robust, aerogel-like ZnO nanoparticle films with extremely high porosity. These film morphologies enable synthesis of stable cells with linearly increasing photocurrent up to a working-electrode thickness of 200 μm. Optimized films led to more than 100% efficiency enhancement with respect to more dense film morphologies made by wet-deposition of the same ZnO nanoparticles. These results suggest that optimization of the semiconductor-electrolyte nano-interface by a hierarchical multi-scale morphology has the potential to minimize electron-holes recombination enabling efficient thick cells with substantially higher surface area for dye absorption.

Dye sensitized solar cells (DSSC) are an established solar cell technology (O'Regan and Gratzel, 1991) with the potential to enable large-scale fabrication of low-cost flexible devices. A first breakthrough in cell design was the utilization of a nanostructured mesoporous TiO_2 film as charge collector for the photogenerated electrons (O'Regan and Gratzel, 1991). This increased the solar energy conversion efficiency of DSSC from less than 1 (Matsumura et al., 1977) to more than 7% (O'Regan and Gratzel, 1991) owing to a 780 fold increase in surface area available for dye adsorption. Improvement of dye composition (Mathew et al., 2014) and film morphology (Wang et al., 2004) have, since then, led to over 80% incident photon to current conversion reaching 13% (Mathew et al., 2014) solar energy conversion.

Alternative semiconductor film morphologies have the potential to further enhance the performance of both dye- and perovskite based DSSC. In the last decades, the working electrode composition and main structural parameters have been extensively investigated for dye-based devices. Poor light absorption in the red domain (Wang et al., 2004) and high electron-hole recombination in thick films (Ferber et al., 1998; Grätzel, 2003) have been key issues limiting development of highly efficient cells. Incorporation of large scattering ZnO nanoparticles in high specific surface area films has successfully increased light absorption and conversion efficiency (Zhang et al., 2008). Minimization of electron-hole recombination has been attempted by substitution of TiO_2 with better electron-conducting ZnO (Zhang et al., 2009). The latter is a wide bandgap semiconductor sharing similar optical and energy-band structure ($E_g = 3.3$ eV) but having more than an order of magnitude higher electron mobility (Hutson, 1959). Typically, ZnO-based devices have achieved lower conversion efficiency than TiO_2 due to poor chemical stability. Nevertheless, ZnO nanowire films have demonstrated a considerable increase (Law et al., 2005) in collection efficiency of photogenerated electrons. The low conversion efficiencies ≈ 0.5–1.5% of nanowire devices have so far been attributed to surface area (Law et al., 2005).

Higher internal film surface for dye adsorption can be achieved by increasing the specific surface area of the film components. For example, aerogel-templated ZnO films made of high surface area mesoporous structures have led to up to 2.4% efficiency (Hamann et al., 2008). Analogous improvements have been reported for hierarchically ZnO films (Chou et al., 2007; Zhang et al., 2008). Alternatively, light absorption can be enhanced by increasing the working electrode thickness. This is particularly challenging as, generally, electron-holes recombination increases rapidly with increasing film thickness (Grätzel, 2003). Usually for ZnO films (Zhang et al., 2009), the benefits of higher light absorption (by thicker films) level-off rapidly against the swell in recombination losses leading to optimal thickness of 5–20 μm. Nevertheless, the validity of these observations may be limited to specific film morphologies. In particular, DSSC working-electrodes are typically assembled by wet-methods leading to average porosities of 50–65% (Grätzel, 2003). These low porosity may not ensure sufficient electrolyte ion exchange rates in thick films (Ferber et al., 1998).

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First attempts to utilize highly porous morphologies have led to full functioning DSSC up to film thicknesses of 320 µm with, however, very low conversion efficiencies (ca. 1%) (Hsu et al., 2008).

Recently, flame-made ultraporous networks of ZnO nanoparticles have been reported (Nasiri et al., 2015a, 2015b) as a highly performing super-structural design for visible-blind UV-photodetectors. Such films were rapidly synthesized by flame spray pyrolysis of nanoparticle aerosols and direct deposition (Tricoli et al., 2012) resulting in 95–98% film porosity (Mädler et al., 2006; Nasiri et al., 2015a, 2015b). Among other advantage, this dry-approach allows the rapid deposition of multi-layer structures (H. Kim et al., 2006) with competitive process time (Tricoli et al., 2008) and low production costs (Strobel and Pratsinis, 2007). Furthermore, flame-made nanoparticles feature very high specific surface area as endorsed by their efficient application as gas sensors (Tricoli et al., 2010a, 201b), functional coatings (Tricoli et al., 2009a, 2009b), UV photodetectors (Nasiri et al., 2015a, 2015b), tissue engineering (Nasiri et al., 2016) and battery electrodes (Chew et al., 2009). A major limitation of flame-made films is, however, their poor mechanical stability (Tricoli et al., 2008) that so far has not enabled fabrication of satisfactorily stable DSSC (Tricoli et al., 2012). Further optimization of highly porous film key structural properties has the potential to improve the absorber-semiconductor interface offering a competitive alternative working-electrode morphology for both dye- and perovskite-based cells.

Here, we report the one-step flame-synthesis and aerosol-deposition of hierarchical ZnO nanoparticle films as a promising electrode morphology for dye sensitized solar cells. Atmospheric flame spray pyrolysis is used to produce a concentrated aerosol of highly crystalline ZnO nanoparticles featuring high specific surface area and dye loading capacity. The aerosols are directly deposited on FTO substrates leading to the ultra-rapid self-assembly of highly porous nanoparticle layers (Nasiri et al., 2015a, 2015b). The film key structural properties and growth dynamics are investigated as a function of the aerosol deposition time up to a film thickness of 200 µm. The solar energy conversion performance of these hierarchical films is assessed by DSSCs assembly and critical comparison with denser films made by the same flame-made ZnO nanocrystals.

Highly concentrated aerosols of agglomerated ZnO nanoparticles were produced by atmospheric, not-enclosed flame spray pyrolysis (Fig. 1) of zinc salts dissolved in a combustible solution. Nanoparticles (Fig. 1, inset) were collected from the gas-phase on water-cooled glass-fiber filters placed downstream of the burner. The collected ZnO powders were highly crystalline with a pure wurtzite structure (Fig. 2a) and a crystal size (d_{XRD}) of 19.4 nm. This is in line with the TEM analysis indicating a polydisperse size distribution with a particle diameter between 5 and 40 nm (Fig. 1, inset). The ED patterns support these results (Fig. 2a, inset) indicating the presence of both large (bright spots) and small (diffuse rings) crystals. The ZnO particles had also a polydisperse morphology with mostly spherical and some elongated rod-like structures (Fig. 2b, inset). This is in good agreement with previous reports suggesting that flame-synthesis of ZnO promotes growth along the wurtzite 100 plane (Height et al., 2006; Nasiri et al., 2015a, 2015b). Nitrogen adsorption analysis revealed a large specific surface area of 53 $m^2 g^{-1}$ and a dense primary particle surface structure with no measurable porosity. This results in an equivalent-sphere diameter of 20 nm suggesting formation of mainly monocrystalline particles in line with the TEM and XRD analysis. The structural properties of these flame-made agglomerates are comparable to that of highly performing wet-made ZnO aggregates previously applied to the fabrication of DSSC working electrodes (Zhang et al., 2008).

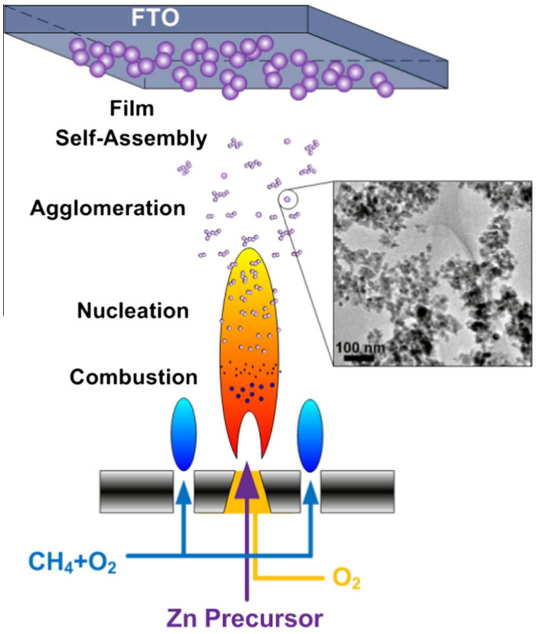

Fig. 1. Schematic of ZnO nanoparticles synthesis (inset) and direct film self-assembly by flame spray pyrolysis of combustible zinc naphtenate solutions.

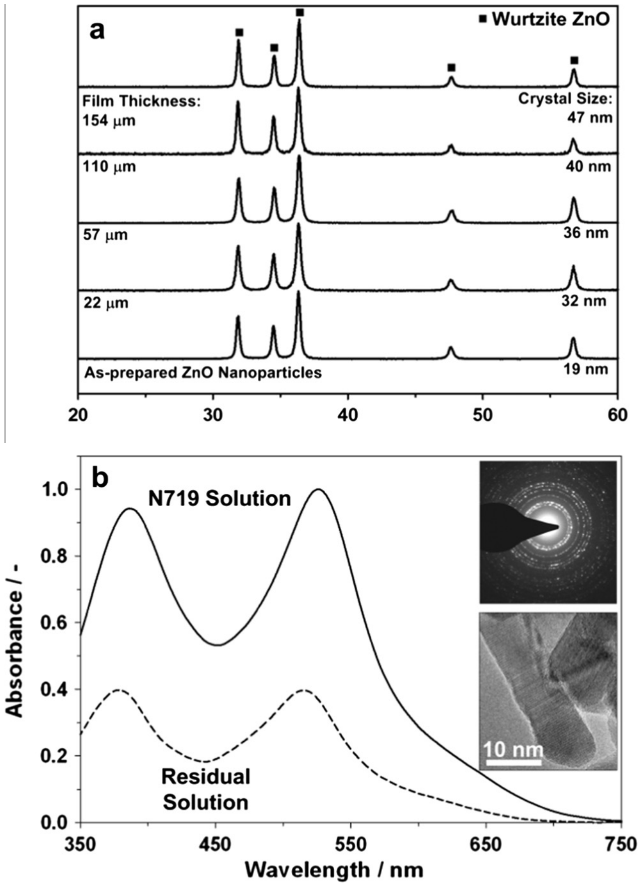

Fig. 2. (a) XRD of flame-made ZnO nanoparticles, and (b) UV-vis absorption spectra of a N719 (1.5×10^{-4} mol l^{-1}) ethanol solution (continuous line) and its residual (broken line) upon impregnation of the same ZnO nanoparticles revealing a dye-adsorption capacity of 1.6 dye molecules nm^{-2}. The top and bottom insets present the TEM analysis of these crystalline flame–made ZnO nanoparticles.