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Hierarchical growth of TiO_2 nanosheets on anodic ZnO nanowires for high efficiency dye-sensitized solar cells

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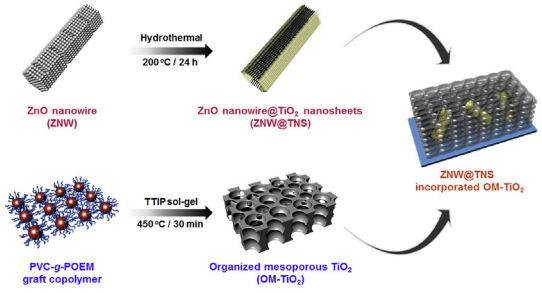
HIGHLIGHTS

- An effective route to hierarchical core-shell structures is demonstrated.
- Anodic ZnO nanowire core was surrounded by TiO_2 nanosheets shell (ZNW@TNS).
- High efficiency of 7.5% is achieved for ZNW@TNS quasi-solid-state DSSCs.
- It is due to the improved light scattering, surface area and electron transport.
- Solid-state DSSC with single component polymer exhibits high efficiency of 7.2%.

GRAPHICAL ABSTRACT



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ABSTRACT

We present a novel route to hierarchical core-shell structures consisting of an anodic ZnO nanowire core surrounded by a shell of TiO_2 nanosheets (ZNW@TNS). This material combines the beneficial properties of enhanced electron transport, provided by the nanowire core, with the high surface area and chemical stability of the TiO_2 shell. Quasi-solid-state dye-sensitized solar cells (qssDSSCs) are prepared using different quantities of either the bare ZnO nanowires or the hierarchical nanowire structures and the effect on cell performance is examined. It is found that whilst the addition of the bare ZnO nanowires results in a decrease in cell performance, significant improvements can be achieved with the addition of small quantities of the hierarchical structures. Power conversion efficiencies of up to 7.5% are achieved under 1 Sun, AM 1.5 simulated sunlight, with a ~30% increase compared to non-hierarchical mesoporous TiO_2 films. A solid-state DSSC (ssDSSC) with a single component solid polymer also exhibits excellent efficiency of 7.2%. The improvement in cell performance is related to the improved light scattering, surface area and electron transport properties *via* the use of reflectance spectroscopy, BET surface area measurements and electrochemical impedance spectroscopy.

1. Introduction

Dye-sensitized solar cells (DSSCs) are an attractive photovoltaic

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technology for application in a wide range of markets due to their low cost, aesthetic appeal and compatibility with flexible substrates [1]. Since their first report in 1991 by Grätzel et al. they have attracted significant interest from the research community, leading to power conversion efficiencies of over 14% [2–4]. Key to the success of DSSCs is the mesoporous TiO_2 scaffold that provides a high surface area for dye-adsorption and allows conduction of photo-generated electrons to the collecting electrode. Many different attempts have been made to improve the performance of DSSCs by modifying, or finding alternatives to, the mesoporous TiO_2 layer. These include the introduction of light scattering layers to improve light absorption [5], the use of templating polymers to form ordered porous networks [6,7] and the introduction of a wide range of different nanostructures to improve charge transport or increase surface areas [8].

The use of one-dimensional nanostructures, such as nanowires, has commonly been proposed as a route to enhanced electron transport within DSSCs, particularly when high electron mobility materials such as ZnO are used [9–12]. However, improvements in charge transport have often been accompanied by significant losses in light absorption due to the low surface areas of crystalline nanowires compared to nanoparticles [13,14]. To enhance the surface areas of one-dimensional nanostructures, hierarchical structures have been investigated, which typically involve the growth of high surface area nanostructures onto the nanowire surface. Such approaches have shown promise in enhancing cell performances compared to the use of bare nanowires structures [15–20].

Another successful route has been to combine two different materials, forming core-shell nanostructures [21]. Here the one-dimensional nanomaterial at the core is a high electron mobility material, such as ZnO or SnO_2, and the shell is TiO_2, which provides the best compatibility with commonly used dyes and electrolytes [22–25]. Recently, TiO_2-ZnO nanowire or nanosheet composite has been also reported as an efficient photoanode for DSSCs [26–30]. We have previously demonstrated that the use of hierarchical nanostructures consisting of a TiO_2 nanosheet shell surrounding a SnO_2 nanotube core can provide significant enhancements in cell performance when employed in solid state DSSCs (ssDSSCs) [31]. By using the hierarchical nanostructures as additives within an organized mesoporous TiO_2 film, power conversion efficiencies of up to 7.7% were achieved, some of the highest reported for ssDSSCs.

Herein, we report the formation of novel hierarchical nanostructures consisting of a polycrystalline ZnO nanowire core surrounded by a shell of TiO_2 nanosheets and their application within quasi solid-state DSSCs (qssDSSCs). The polycrystalline ZnO core is produced *via* the rapid electrochemical anodization of zinc foil and can be modified with TiO_2 nanosheets through a simple solvothermal growth method [31,32]. The synthesis based on electrochemical anodization is a simple and time-saving process compared to the combined process of electrospinning and calcination, which was used for the synthesis of SnO_2 nanotubes [31]. Through addition of small quantities of the hierarchical nanowire structures to an organized mesoporous TiO_2 film power conversion efficiencies were increased from 5.8% to 7.5% which are among some of the highest reported efficiencies for qssDSSCs. The improvements in cell performance are attributed to the enhanced light scattering, improved electron transport and increased surface areas of the hierarchical nanowires.

2. Experimental section

2.1. Materials

Poly(vinyl chloride) (PVC, M_n ~ 55,000 g/mol), poly(oxyethylene methacrylate) (POEM, M_n ~ 500 g/mol), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%), copper (I) chloride (CuCl, >99%), hydrochloric acid (HCl, 37%), titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol), chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, ≥37.50% Pt basis), 1-methyl-3-propylimidazolium iodide (MPII), poly(ethylene glycol) (PEG, M_n ~ 10,000 g/mol), iodine (I_2, ≥99%), lithium iodide (LiI, 99.9%), diethylenetriamine (DETA), titanium (IV) chloride ($TiCl_4$, 99.9%), benzyl alcohol (anhydrous, 99.8%), sodium bicarbonate ($NaHCO_3$, ACS reagent > 99.7%) and acetone (>99.5%) were all purchased from Sigma-Aldrich and were used as received without further purification. Zinc foil (99.98%, 0.25 mm thickness) was purchased from Alfa-Aesar, and Fluorine-doped tin oxide (FTO) conductive glass (TEC8, 8 Ω $sq.^{-1}$, 2.3 mm thick) was purchased from Pilkington, France, and washed before using, with ethanol, acetone, and ethanol under sonication for 30 min in sequence, respectively.

2.2. Synthesis of ZnO nanowires

ZnO nanowires (ZNW) were produced by the electrochemical anodization of zinc foil, full details of which have been previously published [32,33]. Prior to anodization, zinc foils were annealed at 300 °C for 1 h in air followed by degreasing with acetone in an ultrasonic bath for 10 min. The clean zinc foil was applied as the anode in a two-electrode cell with a stainless steel plate held parallel to the anode at a distance of 10 mm acting as the cathode. The active area of the zinc anode was controlled using kapton tape, exposing a 13.5 cm^2 area on one side of the zinc foil. The anodization was conducted in an aqueous electrolyte of $NaHCO_3$ (0.05 M) with constant stirring. The temperature of the electrolyte was controlled at 20 °C using a jacketed beaker linked to a refrigerated circulating bath. Anodizations were undertaken for 15 min at a constant voltage of 5 V provided by a DC power supply (Agilent, E3634A) to give rise to uniform nanowire films with a typical film thickness of 50 μm. After anodization, the anodic films were washed thoroughly with deionized water to remove any excess electrolyte from the surface. The foils were then dried under a gentle flow of argon gas and annealed at 300 °C for 1 h in air using a ramping rate of 1 °C min^{-1}. Finally, the nanowire films were scraped from the substrates to form a powder.

2.3. Synthesis of ZnO nanowire@TiO_2 nanosheets

ZnO nanowires coated with TiO_2 nanosheets (ZNW@TNS) were synthesized by a hydrothermal reaction using TTIP and DETA as the precursor and structure directing agent of TiO_2 nanosheets, respectively [31]. 0.1 g of ZNW was dispersed in 40 ml of isopropyl alcohol (IPA) under sonication for 30 min. Next, 0.3 ml of TTIP and DETA were added into the ZNW dispersion and further stirred for 30 min to prepare a homogeneous solution. It was transferred to a Teflon-lined autoclave and kept at 200 °C in an oven for 24 h. After cooling down to room temperature, the white product was collected *via* centrifugation at 9000 rpm or *via* natural precipitation for 24 h. It was further washed with ethanol several times, dried at 80 °C in a vacuum oven for 24 h and annealed at 450 °C for 30 min to remove the organic residue. For the fabrication of photoanodes, the ZNW@TNS collected by natural precipitation method was used.

2.4. Device fabrication

First, a compact blocking layer was deposited on the FTO glass by spin-coating a 0.1 M titanium diisopropoxide bis(acetylacetonate) solution in n-butanol and annealing at 450 °C for 30 min. The organized mesoporous (OM) TiO_2 was constructed on the blocking layer with an amphiphilic graft copolymer, PVC-*g*-POEM, as the