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In situ hydrothermal growth of hierarchical ZnO nanourchin for high-efficiency dye-sensitized solar cells

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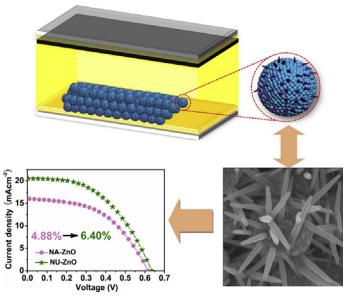
HIGHLIGHTS

- Hierarchical 1D ZnO nanoarchitecture is grown on a multi-scale ZnO seeded layer.
- Light harvesting and charge transport are simultaneously maximized.
- A superb photo-to-current conversion efficiency of 6.40% is obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

The ability to fabricate 1D nanotexture photoanodes with a high degree of multifunctionalities by structural and morphological control still represents a vital issue towards boosting the ultimate photoelectric conversion efficiency of DSCs. In this work, we report an innovative experimental design for in-situ hydrothermal growth of hierarchical ZnO nanourchin on multi-scale ZnO (i.e. nanocrystalline aggregate) seeded layer as photoanode for use in high-efficiency DSCs. It is found that this fascinating 1D nanoarchitecture can simultaneously achieve three favorable characteristics which are generally incompatible with one another in a mono-layer photoelectrode: large dye adsorption amount, strong light scattering and direct electron transport networks, hence leading to a significant improvement of solar cell performance ranging from light harvesting capacity to electron collection efficiency. An enhanced conversion efficiency of 6.40% for hierarchical ZnO nanourchin-based DSC is achieved, with a significant efficiency improvement of 31.1% in comparison with ZnO nanocrystalline aggregate-based DSC, and also far higher than reported efficiency of pure 1D ZnO-based cell.

1. Instruction

One-dimensional (1D) nanostructured metal oxides are of great interest because of their unique physical properties that make them the most fascinating functional materials for applications in photocatalysis, gas sensors, electrochromic devices, light-emitting diodes, field emitters, and energy conversion and storage systems [1–10]. Among these applications, 1D nanoarchitectures of ZnO with direct electric pathways are particularly attractive as photoanodes of dye-sensitized solar cells (DSCs) due to their high electron mobility (~205–1000 $cm^2\ V^{-1}\ s^{-1}$), increased electron diffusion length (~100 μm), and easy tailoring of the nanostructure via a mild wet-chemical method compared with conventional TiO_2 [8,11,12]. However, the low internal surface area of simple 1D

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nanostructures constrains the energy conversion efficiency to relatively low levels i.e. 1.5% for ZnO nanowire DSC and 2.4% for ZnO nanorod DSC [8,13]. As such, nanostructures combining multi-scale hierarchical configurations have been successively developing for boosted surface area and energy conversion efficiency [14–18]. A prominent example reported by Ko et al. is the fabrication of nanoforest of hydrothermally grown hierarchical ZnO nanowires by using a simple engineering of nanocrystalline seeds [14]. They demonstrated a significant enhancement in nanowire-based cell conversion efficiency, but the full sun efficiency was still considerably low, only 2.63%, again due to insufficient surface area of the nanowire network. Therefore, how to fabricate 1D ZnO nanostructures with substantially large surface area for dye adsorption and light harvesting is believed to the key step in achieving high-efficiency DSCs. In our previous work, we reported on the synthesis of ZnO nanocrystalline aggregates (NA-ZnO) with or without doping elements and films consisting of these materials as photoanodes for ruthenium- or indoline-based DSCs [19–23]. We demonstrated that hierarchically structured ZnO electrode films possessed large internal surface area for dye adsorption and strong light-scattering for optical absorption. Considering that 1D ZnO nanoarchitectures can be readily obtained from the single-scale ZnO seeds via a wet chemical process, we thus imagine if there is any possibility of using NA-ZnO with large surface area as a seed layer to fabricate hierarchical 1D electrode films and consequently to boost power conversion efficiency of DSCs.

Herein, we report an innovative experimental design to photoanode tailoring by which the photovoltaic performance of DSCs can be boosted. Our strategy exploits a new class of hierarchical ZnO 1D nanoarchitecture photoanode film synthesized for the first time via in-situ hydrothermal growth on a multi-scale structured seed i.e. NA-ZnO (see Scheme 1). In schematic diagram, the most fascinating model for illustrating the novel multifunctional 1D nanostructure is perhaps a sea urchin, in which each nanoparticulate in an aggregate is analogous to the foot of urchin spine and omni-directional nanorod resembles the spine. In contrast to a zigzag electron transport pathway occurring in NA-ZnO photoanode, a directed electron pathway along the long axis of the nanorods in a randomly intercalated 3D structure may be discerned in hierarchical ZnO nanourchin (NU-ZnO) photoanode (Scheme 1). In such hierarchical 1D ZnO nanourchin, the primary submicrometer-sized NA-ZnO seeded layer that makes up of nanocrystallites exhibits large internal surface area and strong light-scattering property. Apart from this, we hypothesize that the ZnO nanorods in-situ grown on the surface of NA-ZnO may endow two extra prominent advantages to this architecture i.e. eminent charge transport and strengthened light-scattering effect (see Fig. S1). Various morphological characterizations and photovoltaic performance measurements towards the nanourchin-like ZnO photoanode verified the hypothesis. As a result, an enhanced conversion efficiency of 6.40% for NU-ZnO-based DSC was achieved, with a significant efficiency improvement of 31.1% in comparison with NA-ZnO-based DSC, and also far higher than reported efficiency of pure 1D ZnO-based cell.

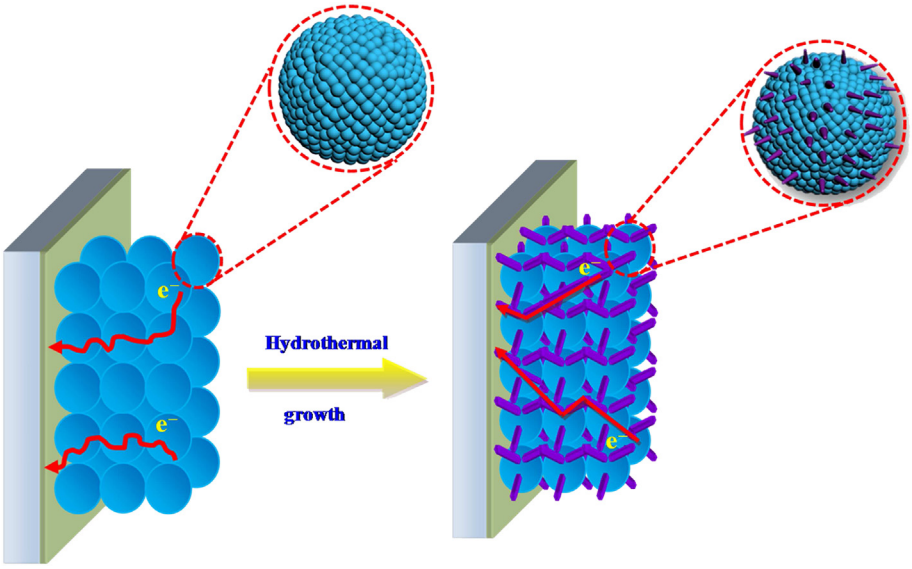
2. Experimental

2.1. Materials

Anhydrous lithium iodine (LiI), Iodide (I_2), 1, 2-dimethyl-3-propylimidazolium iodide (DMPII), Zinc acetate dihydrate ($(CH3COO)_2Zn$) and chloroplatinic acid (H_2PtCl_6) were purchased from Sigma. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine ($(CH_2)_6N_4$) and 4-tert-butylpyridine (TBP) were received from Aladdin. Acetone, diethylene glycol ($(HOCH_2CH_2)_2O$), sodium hydroxide (NaOH), acetonitrile and anhydrous ethanol (analytical grade purity) were obtained from Beijing Chemical Works and were used without further purification. Indoline dye D205 was obtained from Shanghai Green Technology Co. Ltd. All solutions used in this work were prepared with 18.2 MΩ cm^{-1} water produced by a reagent water system (Easy pure II, Barnstead).

2.2. Preparation of NU-ZnO photoanodes and DSCs

The synthesis of NU-ZnO on conductive substrate was performed following a simple two-step method. NA-ZnO was synthesized by the solvothermal process of zinc salt in polyol medium at 160 °C [19,20,22,23]. NA-ZnO films were constructed onto the FTO and ITO (for XRD and SEM characterization) by means of a doctor-blade method following by calcination at 350 °C for 60 min to obtain the ZnO seeded layer. NU-ZnO photoanodes were prepared by suspending the as-prepared NA-ZnO seeded substrate in a



Scheme 1. In-situ preparation of NU-ZnO film and electron diffusion transport in the NA-ZnO film and NU-ZnO film; and schematic diagrams that illustrate the microstructure of aggregated ZnO and nanourchin-like ZnO.