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RAPID COMMUNICATION

CdS/CdSe co-sensitized TiO_2 nanowire-coated hollow Spheres exceeding 6% photovoltaic performance

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Abstract
The development of an effective anode material with hierarchical multi-dimensional architecture is conducive to further improve the cell performance of photovoltaic devices. Herein we introduce an intriguing three-dimensional (3D) hierarchically branched hollow sphere-nanowire hybrid TiO_2 photoanode for promising CdS and CdSe quantum dots co-sensitized solar cells application. The demonstrated 3D hierarchically hybrid photoanode owns a considerably high specific surface area while maintaining roomy space and providing ample porosity for efficient electrolyte infiltration. Moreover, the outstanding light scattering ability of such multi-dimensional architecture leads to an enhancement of light utilization efficiency and thus significantly enhanced short-circuit photocurrent. The control over the pore size of TiO_2 hollow spheres and the optimizations on the newly developed chemical bath deposited (CBD) cuprous sulfide (Cu_2S)/FTO counter electrode eventually yields power conversion efficiency as high as 6.01% for CdS/CdSe based quantum dot-sensitized solar cells (QDSSCs).

Introduction

Under the backdrop of the rapid energy depletion and aggravated environmental issues, the exploitation of clean energy alternatives and the development of cost-effective energy utilization techniques have drawn intense attentions in both scientific and industrial domain. Among various types of clean energy, solar light is considered as the most promising option and thus numerous researches have been focused on this field for a few decades. As a representative of the third generation photovoltaic technology, the dye-sensitized solar cells (DSSCs) possess significant advantages in its low

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production cost, easy fabrication technique, environmentally friendly characteristics and relatively high light-to-electricity conversion efficiency [1-3]. On top of that, the quantum-dot sensitized solar cells (QDSSCs), which derive from the DSSCs, gradually exhibit their superiority in recent years and showcase their great potential in practical application in the near future. The QDSSCs own a similar device structure and working principles as DSSCs, except the dyes were replaced by proper semiconductor quantum dots (QDs) such as CdS, CdSe, CdTe, PbS, Sb_2S_3, $CuInS_2$ [4-10]. Compared to metal complex or pure organic dyes, the quantum dots provide better photostability, high molar extinction coefficients, easily tailored band gap and a potential of multiple-exciton generation known as Auger effect [11]. All aforementioned advantages lead to a theoretical maximum thermodynamic conversion efficiency up to 44% [12]. However, the conversion efficiency of QDSSCs to date, which is 4-6% for liquid-junction, still witnesses a great gap between the practical devices and theoretical models.

Metal oxide anode material has been believed to play a key role in the photovoltaic performance of sensitized solar cells. Generally, the most wildly used nanoparticles (NPs) with size of 10–30 nm could provide sufficient specific surface area for sensitizers anchoring, however, would also suffer from the poor light utilization efficiency and charge transportation and collection efficiency. One-dimensional (1D) nanostructures such as nanowires [13-17] and nanotubes [18] are considered as the promising candidates as compared to stereotyped NPs, because they could offer direct pathways for electron diffusion and thus efficiently and effectively facilitate electron transport and suppress the charge recombination. On the other hand, the well-organized spheres or aggregates, which have been widely used in many energy-related fields, [19,36] can also be recognized as competitive candidate due to their enhanced optical properties. Notably, the hollow spheres with well-defined morphology, remarkable light scattering ability and commodious void space for electrolyte infiltration, have been proven to greatly enhance the photovoltaic performance of DSSCs in many cases [23-28]. The excellent light scattering ability contributes to the fully utilizing incident light and thus improves the photocurrent. Nevertheless, fewer successful cases have been witnessed in QDSSCs based on hollow structured photoanode. The CdS/CdSe sensitized macroporous SnO_2 photoelectrode showed ~4% in efficiency for QDSSCs [32]. To overcome the intrinsic drawback (low surface area) of macroporous and nanowire array structure, the composite photoelectrode composed of macropore and nanowire will potentially exhibit larger surface area, fast electron transportation and superior light scattering ability which may contribute to the enhancement of photovoltaic performance [37]. Recently, several hierarchical macropore-nanowire composites such as TiO_2-TiO_2, [37,38] TiO_2-ZnO, [39] ZnO-ZnO, [40] Zn_2SnO_4-ZnO [41] have been designed for high efficiency DSSCs or QDSSCs. However, up to date, there is no report on the macroporous oxide-TiO_2 nanowire composite for QDSSCs application.

Herein, we introduce a CdS/CdSe co-sensitized 3D hierarchically branched TiO_2 hollow sphere-TiO_2 nanowire (HBTHSs) photoanode to construct high efficiency QDSSCs. This HBTHSs composed of numerous epitaxial nanowires on the nano-embossed hollow spheres can provide sufficient surface area for QDs loading, ordered pathway for fast electron transport and superior light scattering capability for enhanced light utilization efficiency. The existed pores and voids within the hollow spheres and between the adjacent nanowires also greatly contribute to the efficient electrolyte infiltration, which is in favor of the contact in QDs/electrolyte interface and the diffusion of S_n^{2-} ions. Moreover, a simple and facile chemical bath deposition process was employed to *in-situ* synthesize cuprous sulfide directly onto the FTO glass as the counter electrode. Further optimizations of the pore size of TiO_2 hollow spheres scaffold and the thermal treatment process of Cu_2S counter electrode leads to an optimized and impressive efficiency of 6.01%.

Experimental section

Preparation of TiO_2 hollow sphere (THSs) films

The THSs was prepared through a template-assisted method with the polystyrene (PS) spheres as the sacrificial templates. To control the pore size of THSs, different sizes of the PS spheres were synthesized in an emulsifier-free system [26,42]. In a typical process, 4 ml of PS suspension with sphere diameter of 220, 400, 560 or 750 nm (approximately 1 mg/ml, PS sphere dispersed in absolute ethanol) was mixed with 15 ml absolute ethanol and then sonicated for 5 min. Afterwards, 0.4 mL butyl titanate was mixed with the above PS suspension under vigorous stirring at 70 °C for 30 min in a round bottom flask. Then 10 ml Water/Ethanol (v/v=1:9) mixed solution was slowly added to the flask and kept refluxing at 70 °C for 12 h. The as-obtained PS@TiO_2 suspension was then rinsed with ethanol and distilled water, and was dried at 70 °C. To form a viscous THSs paste, 1.0 g THSs-TiO_2 samples were stirred for 24 h in the mixtures of 8.0 mL ethanol, 0.2 mL acetic acid, 3.0 g terpineol and 0.5 g ethyl cellulose to form slurry, and then the mixtures were sonicated for 5 min in an ultrasonic bath. A thin compact layer of TiO_2 was coated onto the FTO glass (7 Ω/square, America) by spin-coating of the synthesized TiO_2 colloid solution followed by annealing process at 500 °C for 30 min. Then the THSs paste was screen-printed onto the TiO_2 compact layer-coated FTO glass and calcined at 500 °C for 1 h to remove the PS templates and increase the TiO_2 crystallinity.

Fabrication of the 3D hierarchical branched nanowires-coated TiO_2 hollow spheres (HBTHSs) photoelectrode

The HBTHSs were fabricated through a hydrothermal process modified from our published methods [13,37]. 0.35 g $K_2TiO(C_2O_4)_2$ was dissolved in the 20 mL mixture solvent containing diethylene glycol (DEG) and deionized water in a volume ratio of 17.5: 2.5 under constant stirring for 30 min. Then the solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and a piece of as-prepared FTO@THSs was placed at an angle against the wall of the Teflon-liner with the films side facing down. The hydrothermal reaction was maintained at 180 °C for 6 h and naturally cool down to room temperature. The as-prepared FTO@HBTHSs was taken out and rinsed with deionized water, ethanol and dried in air.