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Controlled growth, properties, and application of CdS branched nanorod arrays on transparent conducting oxide substrate

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ABSTRACT

Controlled growth of single-crystalline CdS branched nanorod arrays (B-NRs) on fluorine-doped tin oxide (FTO) substrate is achieved by growing the branches on the pre-formed CdS straight nanorod arrays (NRs) via the hydrothermal approach. The branches are formed by epitaxial growth from the backbones, and no seeds or catalysts are involved in the synthesis process. The microstructures of the CdS B-NRs can be easily tuned by varying the reaction parameters. The structures of CdS B-NRs are characterized in detail by field-emission scanning electron microscopy (SEM), X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) with focused ion beam (FIB) cutting of the materials. The properties and application of the CdS B-NRs are assessed by UV–vis absorption spectroscopy, photoelectrochemical cells and hybrid photovoltaic devices. Experimental results show that, compared to the straight NRs counterparts, the CdS B-NRs fabricated in this work exhibited significantly stronger light absorbability, remarkably enhanced photocurrents in photoelectrochemical cells, and an improvement of up to 92% in power conversion efficiency for hybrid solar cells. This work demonstrates clearly the advantages of the branched nanostructures over the straight one in device applications.

1. Introduction

Branched semiconductor nanostructures have recently attracted great attentions [1], and the controlled growth of such hierarchical nanostructures is of particular interest and challenging [2]. The formation of nanowire or nanorod branches on pre-formed nanowires or nanorods can enlarge the surface areas, enhance the light absorbability, and provide more charge transportation channels, which may find important technological applications, e.g., in optoelectronics and water splitting [3]. At present, the most popular strategy in controlled synthesis of semiconductor branched nanostructures is sequential nucleation and growth [3], namely, branched nanostructures which are fabricated by secondary or multiple nucleation and subsequent growth of nanobranches on pre-formed one-dimensional nanostructures. A number of successful cases have been reported in fabrication of semiconductor branched nanowires or nanorods over this strategy via vapor–liquid–solid (VLS) [4–11] and solution–liquid–solid (SLS) processes [12]. For example, Dick et al. [4] have firstly synthesized GaP nanowires using Au as catalysts on a GaP (111) substrate, and then re-seeded the nanowire surfaces with Au catalysts again to further grow GaP and InP branches. This VLS growth is typically carried out at high temperatures ($>800^{\circ}$C), thus restricting its applicability in choice of substrates, such as transparent conducting oxides (TCO) that are playing an important role in optoelectronic devices. Dong et al. [12] have employed SLS approach to prepare the colloidal ZnSe homobranched nanowires and CdSe–ZnSe heterobranched nanowires using Bi nanoparticles as the catalysts over a similar strategy. However, device applications of the colloidal products could be seriously limited due to its random distribution and to the fact that the organic surfactants capping the nanostructures can severely degrade the charge transport. Moreover, both the VLS process and the SLS growth need metallic catalysts, thus introducing impurities in the products, which is often detrimental to device performance. Most recently, solution synthesis has been demonstrated to be an effective strategy to prepare branched ZnO [13–15], TiO_2 [16] and $ZnO/TiO_2/CuO$ [17] hierarchical nanomaterials on TCO. For example, Ko et al. [13] have for the first time fabricated ZnO nanowire arrays on fluorine-doped tin oxide (FTO) via the hydrothermal process, then a seed layer of ZnO nanoparticles was deposited on the surface of the ZnO nanowires to guide the succeeding growth of ZnO branches. ZnO nanoforests were hence formed on FTO substrate and their application in dye-sensitized solar cells (DSSCs) was demonstrated. Furthermore, via the sequential nucleation and growth approach, Cho et al. [16] have obtained TiO_2 branched nanorod arrays on FTO using TiO_2 polymeric sol as the seeds via a

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two-step hydrothermal growth. The TiO_2 branched nanorod arrays were then served as the anode of photoelectrochemical cells, showing performances superior to the bare nanorod arrays without branches. Yin et al. [17] have achieved the fabrication of hybrid oxide branched nanostructures on FTO by a very similar route: CuO nanobranches were successfully grown on TiO_2-coated vertical ZnO nanowire arrays and the composites were applied as the photoanode materials for water splitting. However, the above-mentioned hydrothermal approaches need to deposit a layer of seeds on the pre-formed backbones before the secondary growth of the branches. The resulting branches are growing with random orientation, and it is not trivial to achieve good controllability over the seed deposition on the pre-formed nanorods. Moreover, the studies are mainly focused on oxides. It still remains a challenge to develop a facile approach to prepare non-oxide semiconductor branched nanostructures on TCO substrate for device applications.

Cadmium sulfide (CdS) is an important II–VI semiconductor with well-known applications in lasers, light-emitting diodes, solar cells etc. [18–20]. A number of reports have described the growth of CdS branched nanostructures in colloidal systems [21–26]. In contrast, only a few studies on CdS straight nanorod arrays on substrates have been reported [27–31]. For examples, Qian et al. and Jiang et al. have independently synthesized CdS nanowire arrays on Cd-foil substrate via a solvothermal route [27–28], Xu et al. have employed porous anodic aluminum oxide (AAO) as the template to fabricate vertical CdS nanorod arrays on tin-doped indium oxide (ITO) through electrodeposition [29], Sung et al. have obtained CdS nanowire arrays by the SLS process on FTO with Bi catalysts [30], and Chen et al. have demonstrated a facile one-step and nontemplate hydrothermal approach to fabricate CdS nanorod arrays on the ITO substrate [31]. Up to now, only one study has described the growth of CdS branched nanorod arrays on TCO substrate [32], where CdS branched nanorod arrays were fabricated via a one-step hydrothermal approach employing cadmium sulfide and thiourea as starting agents. Unfortunately, the branched nanorod arrays so obtained were sparse on ITO, and the growth was incontrollable, thus limiting their performance in device applications.

We herein report a facile hydrothermal approach for preparing CdS branched nanorod arrays (B-NRs) on FTO substrates in a highly controlled way. The synthetic approach involves the epitaxial growth of the CdS branches from the pre-formed CdS straight nanorod arrays (NRs) on the FTO under identical growth conditions in a two-step growth. An apparent advantage of this approach is that the secondary seed layers or catalysts, which are widely employed in fabricating branched nanostructures previously, are not involved in our synthesis. Also, the structures of the backbones and the branches of the CdS B-NRs can be easily tuned by varying the reaction parameters. Furthermore, the present synthesis is carried out under mild conditions and can be easily scaled up. We have thus presented a facile approach to CdS B-NRs on TCO in a device scale with high controllability. The growth mechanism of CdS B-NRs is suggested. Experimental results show that, compared to the straight CdS NRs, the CdS B-NRs exhibit higher light absorbability, better photoelectrochemical performance as the Photoanode in photoelectrochemical cells, and superior photovoltaic performance as the building blocks of hybrid solar cells.

2. Experimental

2.1. Materials and chemicals

Cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O > 99.0\%$) acetone ($(CH_3)_2CO$, analytically pure), 2-propanol ($(CH_3)_2CHOH$, analytically pure), and ethanol (CH_3CH_2OH, analytically pure) were bought from Tianjin Kemiou Chemical Reagent Co., Ltd. thiourea ($CH_4N_2S > 99.0\%$) and sodium sulfate anhydrous (Na_2SO_4, analytically pure) were obtained from Tianjin Bodi Chemical Co., Ltd. Glutathione ($C_{10}H_{17}N_3O_6S$, analytically pure) was provided by Huzhou Longs Biochem Co., Ltd. 1,2-dichlorobenzene ($C_6H_4Cl_2$, analytically pure) was supplied by Sigma-Aldrich. P3HT (poly(3-hexylthiophene) was obtained from Rieke Metals, Inc., Mw=48,000 g/mol).

2.2. Synthesis of CdS B-NRs

CdS B-NRs were prepared by a two-step hydrothermal process. Firstly, CdS straight NRs were synthesized on FTO coated glass similar to the reported method [31]. The FTO coated glass was initially cleaned by sonication in acetone, 2-propanol, and ethanol, subsequently rinsed with deionized water, and finally dried in a nitrogen stream. The FTO coated glass substrate was then placed in a sealed Teflon reactor with 60 mL of aqueous solutions containing cadmium nitrate, thiourea and glutathione with a molar ratio of 1:1:0.6 (the concentration of cadmium nitrate is 48 mmol/L, namely, 0.89 g cadmium nitrate, 0.22 g thiourea and 0.53 g glutathione) at an oven of 200 °C for 3.5 h. The surface of the resulting CdS NRs was cleaned by the oxygen plasma treatment using a Diener Plasma Cleaner at 180 W under oxygen flow of 35 sccm for 15 min, or it can also be cleaned by 1–10 vol% HCl solution for 30 s, then rinsed extensively with deionized water. Subsequently, the CdS B-NRs were produced by repeating the hydrothermal growth process in a fresh aqueous precursor solution, and were finally rinsed extensively with deionized water.

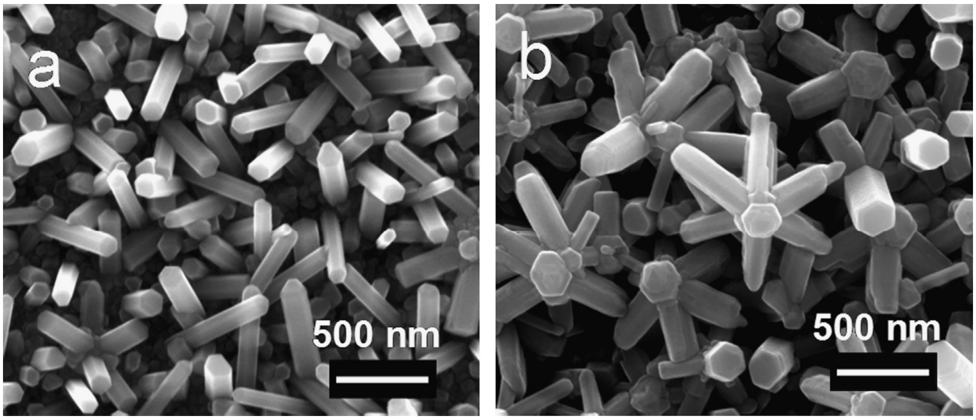

Fig. 1. High-magnification SEM images of (a) CdS straight NRs and (b) CdS B-NRs.