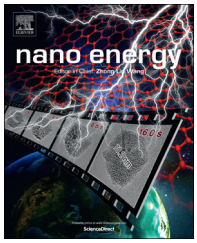
Nano Energy (2014) 9, 15–24

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/nanoenergy



RAPID COMMUNICATION

A family of vertically aligned nanowires with smooth, hierarchical and hyperbranched architectures for efficient energy conversion

Wu-Qiang Wu, Hua-Shang Rao, Hao-Lin Feng, Hong-Yan Chen, Dai-Bin Kuang*, Cheng-Yong Su

MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, KLGHEI of Environment and Energy Chemistry, Lehn Institute of Functional Materials, State Key Laboratory of Optoelectronic Materials and Technologies School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, PR China

Received 15 March 2014; received in revised form 28 May 2014; accepted 22 June 2014
Available online 1 July 2014

KEYWORDS
Solar cells;
Nanowires;
TiO_2;
Hierarchical;
Hyperbranched;
Energy conversion

Abstract
A powerful full solution-based process was demonstrated to synthesize various vertically aligned TiO_2 wires/rods self-assembled arrays nanostructures on conductive substrates via a simple hydrothermal growth system. Demonstrated samples included a family of high-quality and high-crystallinity anatase nanowire arrays with smooth, hierarchical or hyperbranched architectures, thanks to oriented attachment and crystallization as well as a self-assembly growth mechanism. The proposed hyperbranched arrays, consisting of long TiO_2 nanowire trunks, short TiO_2 nanorod branches as well as tiny TiO_2 nanorod leaves (recall a tree with luxuriant foliage) and thus possessing a microscopic feature size, overcome typical shortages of insufficient dye adsorption for conventional 1D smooth nanowire arrays or prototype hierarchical nanowire arrays when applied to DSSC, which achieved for the first time similar dye uptakes (*i.e.* 90.10 nmol cm^{-2} *vs* 88.62 nmol cm^{-2}) as nanoparticle counterparts under the same thickness. Dye-sensitized solar cell fabricated with an ~8 μm long novel hyperbranched nanowire arrays photoelectrode yields an impressive power conversion efficiency (PCE) of 8.11%, which was much greater than that of anatase TiO_2 nanoparticle (20 nm in diameter) counterpart due to synergistic effects of high dye uptakes and superior broadband light scattering for improved light harvesting as well as fast charge transport for efficient charge collection for the former.

*Corresponding author. Fax: +86 20 8411 3015.
E-mail address: kuangdb@mail.sysu.edu.cn (D.-B. Kuang).

http://dx.doi.org/10.1016/j.nanoen.2014.06.019
2211-2855/

Introduction

In recent years, the assembly of various vertically aligned nanomaterials has attracted intense attention because of their promising wide range of applications in solar cells, Li-ion batteries, sensing, optoelectronics, photocatalytics, water splitting, field emission, etc. [1-7]. To date, various types of one-dimensional (1D) TiO_2 nanostructures including nanowires, nanorods, nanotubes, and nanofibers have been extensively employed as promising alternatives of most commonly TiO_2 nanoparticles for dye-sensitized solar cells (DSSCs) as they offer a direct transport pathway for photogenerated electrons, thereby efficiently enhancing charge transport, hampering charge recombination and markedly improving the charge collection efficiency [8-16]. Generally, improved electron transport and reduced charge recombination are two crucial characteristics for ideal nanomaterials when applied in energy-related applications [17].

Despite their undisputed advantages of efficient charge transport, the power conversion efficiency of DSSCs using normal 1D nanostructured photoanode is still lower than the standard mesoporous TiO_2 nanocrystalline photoanode mainly due to severe limitations in dye-loading capacity, which results from insufficient surface area and considerable free space between adjacent 1D nanostructures [5,18]. In this sense, lower photocurrent is generated compared to the nanoparticles' counterparts [19]. Moreover, photoanodes with prominent light trapping and scattering architecture can guarantee a high photon-recycling, which can also lead to higher generated currents [20-28]. A common strategy for improving the performance of TiO_2 nanowire-based DSSCs is to decorate nanowires with a large number of smaller dendritic nanorod branches [29-36]. These hierarchical structures with anisotropic branches increase the nanowire surface area for anchoring more dye molecules and thus boost the power conversion efficiency of DSSCs. Recently, we reported the pioneer fabrication of our first generation of hierarchical anatase TiO_2 nanowires for DSSCs application [29]. Although interesting results were obtained, performances still lagged behind the standard nanocrystalline TiO_2 photoanode with similar film thickness due primarily to their insufficient roughness factor and relatively low dye-loading capability. Another approach to increase the surface area of nanowire is to prolong its length. In this regard, we demonstrated the second generation of ultra-long anatase TiO_2 nanowires up to $\sim$47 μm, which showed a better photovoltaic performance than the TiO_2 nanoparticle photoelectrode with similar dye-loading [37]. Building on previous observations and experiences, nanowire array still has plenty of space for further decoration with an increased packing density of the branches and even luxuriant foliage. Although the nanowire array is able to couple superior light-trapping, scattering and prominent electron transport, the roughness factor is much lower than the nanoparticles photoanode at similar film thickness.

Herein, we develop a facile, green and cost-effective strategy to synthesize the hyperbranched anatase TiO_2 nanowires (HBTNW) on FTO glass substrates. Such a novel morphology is formed by multiscale combination of elongated 1D features – recall a wide-spreading tree having trunk, branches and leaves simultaneously – namely, a 1D long vertical TiO_2 nanowire trunk coated with numerous 1D slender TiO_2 nanorod branches on which tiny 1D TiO_2 nanorod leaves were anchored. For comparison, smooth TiO_2 nanowires (STNW) and hierarchical TiO_2 nanowires (HTNW) were also synthesized in the same hydrothermal system containing potassium titanium oxide oxalate dehydrate (PTO), diethylene glycol (DEG) and water by carefully adjusting the hydrothermal parameters. It is worth noting that all nanowires with various morphologies were produced in a PTO/DEG/water hydrothermal system, which provided low cost, great simplicity as well as high reproducibility. Interestingly, the tree-like hyperbranched TiO_2 nanowires with higher hierarchical level resulted in a synergistic effect of high dye-loading for improved optical absorption, superior light scattering ability for enhanced broadband scattering and light harvesting, as well as fast charge transport, in turn yielding higher J_{sc} and V_{oc} and thus markedly enhanced power conversion efficiency (PCE) of 8.11% with respect to the reference anatase TiO_2 nanoparticles photoanode (6.32%). To the best of our knowledge, no reports have been demonstrated on the hydrothermal synthesis of a family of vertically aligned TiO_2 nanowires with comparable smooth, hierarchical and hyperbranched architectures for DSSCs applications.

Experimental

Synthesis of various TiO_2 arrays architectures

Firstly, TiO_2 blocking layer was spin-coated on an FTO glass substrate (2.5 cm × 3 cm), which was cleaned with acetone, ethanol and water, respectively. Vertically aligned TiO_2 nanowire arrays were fabricated on the surface of the TiO_2-coated FTO in a surfactant-free hydrothermal reaction in three cheap commercially available components: potassium titanium oxide oxalate dehydrate (PTO), diethylene glycol (DEG) and water. To fabricate a family of vertically aligned anatase TiO_2 nanowire arrays, a certain amount of PTO was dissolved in a mixed solution containing DEG and deionized water. After stirring for 30 min, the mixture solution was transferred to a 50 mL Teflon-lined stainless steel autoclave. Then TiO_2-coated FTO glass was placed at an angle against the wall of the Teflon-liner with the conducting side facing down. The hydrothermal synthesis was carried out at 160 °C or 180 °C for 9 h. After reaction, the samples were rinsed with water and ethanol several times and then heated to 550 °C for 1 h in air to remove the possible organic residual and improve the crystallization of TiO_2. Specifically, to synthesize the smooth (STNW) or hierarchical (HTNW) TiO_2 nanowires, 0.35 g PTO was dissolved in a mixed solution containing 17.5 mL DEG and 2.5 mL deionized water, followed by hydrothermal reaction at 160 °C (STNW) or 180 °C (HTNW) for 9 h, respectively. To fabricate the hyperbranched samples (HBTNW), the as-prepared hierarchical TiO_2 nanowires (HTNW) were immersed in another precursor solution with different DEG/water volume ratios (0.35 g PTO was dissolved in a mixed solution containing 15 mL DEG and 5 mL deionized water) and the reaction was kept at 180 °C for 9 h.

TiO_2 nanoarrays solar cells assembly

To fabricate DSSCs, all of the TiO_2 nanowire arrays on FTO glass were used as photoelectrodes. The TiO_2 films were