Solar Energy Materials & Solar Cells 151 (2016) 169–178

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Self-assembled hybrid polyvinylcarbazole–titania nanotubes as an efficient photoanode for solar energy harvesting

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ARTICLE INFO

Article history:
Received 9 October 2015
Received in revised form
4 February 2016
Accepted 6 March 2016
Available online 31 March 2016

Keywords:
Nanotubes
Crystal phase
Titania
Conducting polymer
Electron microscopy
DSSC

ABSTRACT

This paper presents a novel photoanode system of self-assembled hybrid Polyvinylcarbazole (PVK)–titania nanocomposites (PVTs) using template guided polymerization in a mixed phase of rutile–anatase titania nanotubes. Mixed crystalline phase of titania was prepared by aminolysis process through a controllable capping mechanism. During vinyl carbazole (VK) addition, the charges present on the surface of titania adsorb VK molecules and act as a template during propagation and allow the growing PVK molecular chains adhere along the walls of the titania nanotubes via the combination of various non-covalent interactions. UV–vis spectral band of PVT exhibited broad band with red shift revealing its synergistic effect of harvesting photons. Morphological and XRD studies revealed the preservation of tubular shape and mixed phase of rutile–anatase in PVT nanotubes. Dye sensitized solar cells (DSSCs) were fabricated with PVTs as photoanode using N719 dye as the photo-sensitizer. Conduction mechanism of the excited charge carriers in the device was studied by electrochemical impedance analysis. The presence of mixed anatase–rutile titania phase enhanced the electron transfer thereby reducing the charge recombination which is manifested from the studies made using individual phase of titania. PVT based cell characteristics were optimized to be $V_{oc}=0.83$ V, $J_{sc}=12.01$ mA/cm^2, FF=30.22 with an overall power conversion efficiency of $\eta=3.03\%$ which suggests that the present strategy can be exploited for the development of efficient photoanode systems.

1. Introduction

Systematic design and development of conducting polymer-inorganic metal oxide hybrid nanocomposites is receiving great attention in the photovoltaic research community due to its unique properties in enhancing the device performance. Preparation of hybrid nanocomposites through self-assembly of organic and inorganic precursors at the molecular level by controlling morphology and inter-phase continues to be a challenge because the synergism between these components are expected to enhance the properties that are superior to the individual constituents. Harnessing the benefits of the constituent requires excellent tuning of the spatial assembly of the individual domains and interfaces [1,2].

Among the nanostructured semiconducting oxides, titania on the nanometer scale have been widely studied semiconductor for different applications such as hybrid solar cells, memory devices, photocatalysts and so forth [3]. TiO_2 is mainly studied in two crystalline phases: anatase and rutile. Anatase is the most regarded photoactive phase of TiO_2 which has a band gap of ~3.2 eV while rutile is the most thermodynamically stable phase, generally which has a band gap of ~3.0 eV. Nanocrystalline form has been explored extensively as photoanode in DSSCs due to its wide band gap, high surface area for improved dye loading, and facile synthetic procedures. The lack of efficient electron transfer through the FTO/TiO_2 interface is poor in titania based DSSC which may lead to the back transfer electron to the redox ion in electrolyte and may limit the photo conversion efficiency in DSSCs [4]. Interesting synergistic effect exists between anatase and rutile in mixed-phase than their individual phases of TiO_2; henceforth it is widely chosen as an active component in the area of photocatalysis and photovoltaics. The most popular example is Degussa P25 consisting of 80% anatase and 20% rutile, which is now commercially available photo catalyst. The enhancement in the activity for Degussa P25 is attributed to the transfer of photo excited electron from high energy conduction band of rutile to lower energy conduction band of anatase at the junction formed between these two types of crystalline lattices. This effectively retards the charge recombination rate and leading to

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http://dx.doi.org/10.1016/j.solmat.2016.03.007
0927-0248/

effective electron–hole separation which will lead to higher device performances.

Among the various synthetic strategies developed, the solution phase synthetic route based on hydrolysis and condensation is mostly reported. The high reactivity of tetrafunctional titanium alkoxide can be chemically modified by using carboxylic acid such as oleic acid as chelating ligands to decrease the number of TiOR groups available for ligand substitution exchange. Chemical modification using carboxylic acid can decrease the furious hydrolysis by ligand substitution exchange which will reduce the precursor availability and the reaction will be more controllable process to improve the crystallization and shape of the nanoparticles. They are generally prepared by seeded growth, hydrothermal process and also organogelators as template [5,6]. Semiconducting oxides with controllable shape and crystalline phase can be prepared by using capping agents and also adjusting the calcinations temperature. Recently our group demonstrated the formation of nanocubes of rutile titania and hierarchical self-assembled porous ZnO spheres using bio surfactant as capping agent [7,8]. In the present work, we have employed 3-pentadecylphenyl sulfonic acid (3-PDPSA), a derivative of cardanol which is derived from cashew nut shell liquid, an abundantly available renewable resource material obtained as a byproduct from cashew industry.

Since the breakthrough of the photoconduction of poly (N-vinylcarbazole) (PVK) in 1957, it has become one of the best photo-conducting polymers for electronic and optical applications because of its effective hole-transport ability and relatively high thermal stability [9–12]. Titania and PVK–titania have been widely studied in fabrication of nanodevices such as solar cells, memory devices, photo detector etc. [3,13–15]. The control of energy or charge transfer process between the n-type semiconducting nanoparticle and p-type conjugated molecules is based on the degree of their spectral overlap and the distance between the two systems. Jin et al. fabricated photovoltaic device using PVK and zinc sulfide and obtained high open-circuit voltage of 1.65 V [16]. Zou et al. developed titania-graphene composites using reduction hydrolysis technique for fabricating DSSCs with an efficiency of 4.3% [17]. Buschbaum et al. reported layered PVK–titania nanocomposites for UV active photovoltaic devices [15]. Nandi et al. have recently reported polypyrrole–zinc oxide and polyaniline–zinc zinc sulfide nanocomposites for DSSC applications. DSSC based on the nanoscale morphology of hybrid nanocomposites showed an efficiency of 2.53–3.38% which was higher than that of pure ZnO/ZnS nanoparticles [18,19]. The dissociation of electron–hole pairs at interface and subsequent efficient electrons transfer to nanoparticles suggested that the hybrid p–n type nanocomposite systems are promising material. All these reports revealed that the use of nanocomposite systems with PVK will enhance the optical absorption and the mixed phase of titania can decrease the recombination rate through efficient interface charge separation/transfer and also advantages such as the large surface area to volume ratio, nanostructured percolation pathways from titania in the tubular shape will further improve the device performance.

This paper presents the preparation of semiconducting mixed phase of rutile–anatase titania nanotubes through aminolysis method in presence of bio-based capping agent by a single process. PVT nanocomposites were prepared through chemical oxidative emulsion polymerization of VK with different percentage of titania. They were characterized for its optical, thermal, electrochemical properties and compared the properties with individual anatase, rutile titania and PVK alone. DSSCs were fabricated using the prepared material as photoanode and studied its photoconversion efficiency.

2. Experimental

2.1. Materials

Titanium (IV) isopropoxide TTIP (97%) Aldrich Chemicals, 3-PDPSA prepared from cashew nut shell liquid as reported earlier [20], hexadecane, octadecylamine (ODA), hexane, acetone, ethanol, and pure distilled water were used as received. N-vinylcarbazole (Aldrich) was used without further purification. Anhydrous ferric chloride ($FeCl_3$) was chosen as initiator.

2.2. Synthesis

Mixed phase of nanotitania was prepared using modified strategy adopted by [21]. PVT nanocomposites were prepared through chemical oxidative polymerization using $FeCl_3$ as initiator.

2.2.1. Preparation of mixed phase of titania nanotubes

PDPSA (2.61×10^{-4} mol, 0.1 g) dispersed in hexadecane (6 mL) was taken in a round bottom flask and degassed at 80 °C for 1 h. Then TTIP (0.01 mol, 2.97 mL) was added and heated at 80 °C for 20 min and later at 180 °C for 20 min. Then octadecylamine (ODA) (7×10^{-3} mol, 1.88 g) was added with vigorous stirring for 1 h. It was then diluted with hexane (10 mL) and precipitated with acetone (20 mL). The precipitate was isolated by repeatedly washing with hexane and centrifuging. The precipitate was then dried under vacuum at 80 °C for 2 h followed by calcination at 800 °C for 8 h for obtaining white powder of mixed phase of nanotitania.

2.2.2. Preparation of PVT hybrid nanocomposites

0.1 g N-vinyl carbazole (5.17×10^{-4} mol) in 20 ml of chloroform was sonicated for 20 min. Titania was separately dispersed in chloroform and sonicated well and then the monomer solution was added to it and stirred well. Then the oxidative initiator $FeCl_3$ (0.25 g, 0.00154 mol) dispersed in chloroform was drop wise added to this mixture and stirred well. Color of solution changed to dark green. The reaction was carried out in ice cold condition for 24 h in inert atmosphere. The supernatant liquids were carefully decanted and the dark solution was subjected to centrifugation process. Centrifugation was repeated three times in order to ensure the complete removal of excess unreacted monomer, excess oxidant etc. Nanocomposites with different compositions are prepared by varying the amount of titania as shown in Table S1. They are designated as PVT1 (0.025 g), PVT2 (0.05 g) and PVT3 (0.075 g).

2.2.3. Preparation of anatase titania

TTIP (1.25×10^{-2} mol, 3.7 mL) was added to 100 mL of pure distilled water under vigorous stirring at room temperature. Then the solution was kept in a sonication bath for 1 h, followed by aging for about 36 h to form titania nanoparticles. The sample was isolated by repeated centrifugation and washing using water and finally dried in vacuum at 70 °C. Further, the samples were annealed at 800 °C for 8 h for complete removal of unreacted precursors to obtain white powders of nanotitania.

2.2.4. Preparation of rutile titania

TTIP (1×10^{-2} mol, 2.97 mL) was added to 100 mL 3 M HCl and stirred at room temperature for 1 h. The hydrothermal reaction was then conducted and refluxed for 24 h at 100 °C. Then the solution was cooled to room temperature and repeatedly washed several times with ethanol and distilled water. Further the samples were dried under vacuum at 50 °C for 4 h. Finally, the samples were annealed at 800 °C for 8 h for complete removal of unreacted precursors to obtain white powders of nanotitania.