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Novel triple-layered photoanodes based on TiO_2 nanoparticles, TiO_2 nanotubes, and β-$NaYF_4$:Er^{3+},Yb^{3+}@SiO_2@TiO_2 for highly efficient dye-sensitized solar cells

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ABSTRACT

Based on TiO_2 nanoparticles (TNPs), open-ended TiO_2 nanotube arrays (TNTs), and highly uniform double-shell β-$NaYF_4$:Er^{3+}, Yb^{3+}@SiO_2@TiO_2 submicron-sized plates (NYFEY@S@T), novel triple-layered photoanodes were developed for highly efficient dye-sensitized solar cells (DSSCs). For triple-layered photoanodes, 0-D TNPs were grown as a first layer on fluorine-doped tin oxide (FTO) glass substrate with the thickness of 6 μm to create a good contact and high specific surface area for loading the greater amount of dyes. To improve the dye-sensitized solar cells (DSSCs) efficiency, the 1-D TNTs were deposited as a second layer with five different thicknesses (9, 14, 24, 32, and 46 μm) due to their favorable electron transport rate. However, the photoelectric conversion efficiency of TNPs and TNTs layers is still low because of inefficiency of scattering and upconverting. Further, the 2-D NYFEY@S@T/TNPs (85% TNPs+15% NYFEY@S@T was also deposited onto the top surface of the TNTs film as a scattering and upconverting layer with the thickness of 7 μm. The short-circuit current density (J_{SC}) of 17.47 mA cm^{-2} and an efficiency (η) of 9.11% were achieved for the DSSCs with TNPs/TNTs/NYFEY@S@T-TNPs photoanode with the TNTs layer thickness of 24 μm and NYFEY@S@T content of 15 wt%, which were increased significantly by 38.1% and 16.6% in comparison with that of the DSSCs with single TNPs and bilayer TNPs/TNTs photoanodes. The obtained results indicated that significant enhancement in the performance of the DSSCs with TNPs/TNTs/NYFEY@S@T-TNPs photoanode is attributed to the peculiar triple-layered structure allowing the loading of more dye molecules, good light scattering and upconverting, and longer electron lifetime.

1. Introduction

Owing to the growing global energy crisis and global warming, solar cells have been regarded as one of the renewable energy sources [1]. Since the first report appeared in 1991, the dye-sensitized solar cells (DSSCs) have attracted widespread attention in the photovoltaics field as a cost-effective technology complementary to the conventional silicon-based solar cells [2–5]. The DSSCs work based on a peculiar photo-electrochemical principle – a contact is created between a nanocrystalline TiO_2 film sensitized with light-harvesting absorbers, electrolyte containing I^{3-}/I^- redox couple and a Pt counter electrode. One of the key points of the Grätzel cell is the use of randomly dispersed 0-D TiO_2 nanoparticles (TNPs) as the conventional photoanode in DSSCs because of their large specific surface area to ensure sufficient loading of dye molecules. However, a poor electron transport rate and inefficient light scattering ability within 0-D small-sized nanoparticles in the disordered network limited the efficiency improvement. Therefore, considerable efforts have been devoted to fabricate other efficient nano- and micro-structured titania-based photoanodes, such as ordered meso-structured titania [6], 1-D nano-structured titania [7–11] and 2-D submicron-structured titania [12,13]. Among these nano- and micro-structures, 1-D TiO_2 nanotubes (TNTs) have been exploited as alternatives for use in DSSCs as they offer a continuous pathway for photogenerated electrons to transport along the long axis of nanotubes and a largely reduced amount of grain boundaries, thereby efficiently enhancing charge transport and markedly improving the charge collection efficiency [14,15]. Unfortunately, it is worth noting that despite the advantageous characteristics noted above, the device efficiency of DSSCs using the 0-D TNPs and 1-D TNTs composite photoanodes remains low due primarily to their

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incapable upconversion and size-dependent light scattering effects. Therefore, an upconverting and scattering layer must be introduced into the composite photoanodes for enhancing the performance of DSSCs.

It is well-known that another principal factor limiting the photoelectric conversion efficiency of DSSCs is the incapacity of utilizing the near-infrared (NIR) and infrared photons. To overcome this limitation, Er^{3+} and Yb^{3+}-codoped β-$NaYF_4$ upconversion phosphors (UCPs), which can transform near infrared photons into visible photons, have been considered as one of the promising UCPs and have been applied in DSSCs [16–20]. However, the surface defects and ligands of the upconversion crystallite in the TiO_2 photoanode film would act as an electron trapping center and lead to charge recombination at the surface, which is the major limitation for their application in DSSCs [16,20]. Nevertheless, the coating of nano- or submicron-sized UCPs with SiO_2 and TiO_2-based insulating layer to form a core-shell architecture can additionally support to overcome this issue to some extent [12,13,21]. In previous study, 2-D core/double-shell structured (CDS) β-$NaYF_4$:Er^{3+},Yb^{3+}@SiO_2@TiO_2 (NYFEY@S@T) hexagonal sub-microprisms were applied as a scattering and upconverting layer to reduce the recombination, and an enhancement of 29.4% was obtained [22,23],and it was pointed out that overcoming the challenge of electron trapping will allow a full utilization of the up-converted light. Compared to nano-sized UCPs, the 2-D CDS upconversion submicron particles in the device not only possess the virtue of broadened the absorption range but also benefits the potential applications based on submicron-sized UCPs owing to the function of size-dependent scattering effect in light harvesting [16,22,23]. The experimental results of the aforementioned 2-D CDS UCPs are indeed interesting but hexagonal submicron-sized prisms could neither be grown directly on FTO substrate to offer an intimate interfacial contact nor produced a direct electron-transporting path, increasing consequently the electron–hole recombination probability.

Taking into account all the above-mentioned facts, in order to develop the well-performing photoanode, several criteria such as large specific surface area for dye adsorption, fast electron transport, and effective light scattering and upconverting effects should be concurrently satisfied. However, the discovery of a single 0-D, 1-D or 2-D material with a certain structure that fulfills the above conditions is still considered to be greatly difficult [24,25]. Consequently, the structure design and the materials should be studied together, that is to say, large specific surface area of 0-D TNPs, fast electron transport rate of 1-D TNTs and scattering/upconverting property of 2-D CDS submicron-sized particles can be combined together, and the multidimensional composite materials can be an ideal candidate for highly effective photoanodes due to their multifunctional application.

In this paper, we, for the first time, demonstrate the design and preparation of novel triple-layered photoanodes based on 0-D TiO_2 nanoparticles, 1-D TiO_2 nanotubes, and 2-D β-$NaYF_4$:Er^{3+},Yb^{3+}@SiO_2@TiO_2 for highly efficient dye-sensitized solar cells. For triple-layered photoanodes, 0-D TNPs were directly grown as a first layer on fluorine-doped tin oxide (FTO) glass substrate with the thickness of 6 μm to create a good contact and high specific surface area for loading the greater amount of dyes. To improve the dye-sensitized solar cells (DSSCs) efficiency, the 1-D TNTs were deposited as a second layer, and the effect of five different thicknesses (9, 14, 24, 32, and 46 μm) on electron transport rate and electron lifetime was studied. The 2-D NYFEY@S@T/TNPs (85% TNPs+15% NYFEY@S@T) was then deposited onto the top surface of the TNTs film as a scattering and upconverting layer with the thickness of 7 μm.

2. Experimental

2.1. Synthesis of 0-D TNPs

The 0-D TNPs were synthesized by hydrolysis technique [26,27] from tetrabutyl titanate (97 wt%, Sigma-Aldrich). In the synthesis process, tetrabutyl titanate was hydrolyzed with ethanol aqueous solution under strong stirring at pH=3 and then dried at 80 °C for 2 h.

2.2. Growth of 1-D TNTs arrays

Prior to the fabrication of the 1-D TiO_2 nanotubes, the Ti foils (0.2 mm thickness, 99.6%, Strem Chemicals) were cleaned by ultrasonication in acetone (> 99.5%), isopropyl alcohol (> 99.7%, Sigma-Aldrich), and deionized water (Millipore Milli-Q Plus purification system, 18.2 MΩ cm). The growth of TNT arrays was carried out by a direct anodic oxidation of the Ti foil in electrolyte consisted of 98 mL of ethylene glycol (99.8% Sigma-Aldrich), 0.33 g of NH_4F (> 98%, Sigma-Aldrich), and 2 mL of deionized water by applying 60 V dc potential for several hours. After the anodization, 120 V dc potential was applied for a few minutes to collect the TNT arrays.

2.3. Fabrication of 2-D NYFEY@S@T core/double-shell-structured submicroplates

Monodispersed β-$NaYF_4$: Er^{3+}, Yb^{3+} submicron-sized plates were fabricated by a modified hydrothermal reduction technique [28]. In a typical synthesis, an aqueous solution (20 mL) of $Y(NO_3)_3{\cdot}6H_2O$ (99.8%, Sigma-Aldrich), $Yb(NO_3)_3{\cdot}6H_2O$ (99.9%, Sigma-Aldrich) and $Er(NO_3)_3{\cdot}5H_2O$ (99.9%, Sigma-Aldrich) with the molar ratio of Y/Yb/Er=78:20:2) was mixed with 10 mL aqueous solution of $C_6H_8O_7$ (4.0029 g) (99%, Sigma-Aldrich) and NaOH (2.5 g) (97%, Sigma-Aldrich) under magnetic stirring for 30 min to form a homogeneous solution. Subsequently, aqueous solution (40 mL) of NaF (1.05 g) (> 99%, Sigma-Aldrich) was introduced into the above solution and stirred for 30 min, resulting in a complex. Then, the pH of the suspension was adjusted to 1.5 by dropwise addition of dilute HNO_3. After stirring for another 30 min, the well-homogenized suspension was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed, and maintained at 200 °C for 3 h. After natural cooling to room temperature, the white-colored precipitates were separated by centrifugation and washed with deionized water and ethanol several times and then dried at 80 °C for 12 h. The white-colored precipitates were then re-dispersed in aqueous ethanol solution and coated with silica to form NYFEY@S core-shell structure by the modified Stöber method [29,30]. The as-prepared NYFEY@S powders were collected by centrifugation and dried at 80 °C for 12 h for further usage. The NYFEY@S powders (0.2 g) were dispersed in 60 mL of isopropanol by sonication. Then, 0.05 mL of diethylenetriamine (DETA) and 0.2 mL of deionized water were added into the suspension, followed by magnetic stirring for 1 h at room temperature, and 0.1 mL of tetrabutyl titanate was added into 5 mL of isopropanol to form a transparent solution that was also added into the suspension slowly. After stirring for 30 min, the mixed suspension was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed, maintained at 220 °C for 3 h, and cooled naturally to room temperature. The resulting white-colored 2-D NYFEY@S@T powders were separated by centrifugation, washed with ethanol and deionized water repeatedly, and dried in vacuum at 80 °C for 12 h.

2.4. Fabrication of triple-layered photoanodes and DSSCs

Fig. 1 represents a simple schematic illustration of the fabrication of triple-layered TNPs/TNTs/NYFEY@S@T-TNPs films. First, 0-D TNPs-based paste was coated on FTO glass substrate by a doctor blade method, and then the 1-D TNTs with five different thicknesses (9, 14, 24, 32, and 46 μm) were grown on the TNPs-based layer. Afterwards, the 2-D NYFEY@S@T/TNPs (85% TNPs+15% NYFEY) paste was also deposited onto the top surface of the TNTs film, dried under ambient conditions and sintered at 500 °C for 30 min. All the prepared photoanodes were soaked in anhydrous ethanol containing commercially available N719 (0.5 mM, *cis*-diisothiocyanato-bis (2,2′-bipyridyl-