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Performance optimization in dye-sensitized solar cells with β-$NaYF_4$:Yb^{3+},Er^{3+}@SiO_2@TiO_2 mesoporous microspheres as multi-functional photoanodes

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ABSTRACT

The β-$NaYF_4$:Yb^{3+},Er^{3+}@SiO_2@TiO_2 (N@S@T) mesoporous microspheres have been successfully synthesized via a simple evaporation-driven oriented assembly method (EDOA) and applied as multifunctional photoanode films on top of commercial P25 layers in dye-sensitized solar cells (DSSCs). Structural characterizations indicated that N@S@T mesoporous microspheres consisted of uniform β-$NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals, SiO_2 insulating middle shell and single-crystal-like anatase TiO_2 shell exposed with (101) facets. Studies revealed that introducing β-$NaYF_4$:Yb^{3+},Er^{3+}@SiO_2 into TiO_2 mesoporous microspheres would remarkably enhance the short-circuit current density (J_{sc}). The SiO_2 insulating middle shell played an role in packaging upconvertion nanoparticles (UCNPs) into TiO_2 mesoporous microspheres, which were constructed to effectively transfer photoinduced electrons and adsorb more dye molecules, benefitting from their high specific surface areas. DSSCs with the optimal doping amount of UCNPs exhibited the J_{sc} value of 14.95 mA cm^{-2} and conversion efficiency of 9.10%, which was a notable enhancement of 26.39% in efficiency compared with commercial P25 based DSSCs. Our work demonstrated that introducing N@S@T into photoanodes was an effective method of improving the overall performance of DSSCs.

1. Introduction

As one of the most promising photovoltaic devices, dye-sensitized solar cells (DSSCs) have drawn considerable attention in both academic and industrial fields owing to their high-efficiency and potentially low fabrication cost [1–9]. Since Grätzel et al. first fabricated DSSCs in 1991 [10], announcing the efficiencies (η) of 7.1 ~7.9%, the efficiencies of DSSCs have been greatly improved to ~13% in recently years [11,12].

A typical DSSC consists of four components: a photoanode with porous nanocrystalline TiO_2 film, dye molecules, redox electrolytes and a counter electrode (CE) [2]. For decades, no effort has been spared to develop new type of photoanodes [5–8], dye [12], electrolytes [11] and CEs [13–15] for higher-efficiency and lower-cost DSSCs, among which the development of photoanodes has played a critical role. Generally, DSSCs harvest sunlight by sensitizers adsorbed on photoanodes. As carriers of sensitizers, there are three main factors dominating the performance of photoanodes: the ability of adsorbing dye molecules, utilizing solar light and conducting electrons [3,4], for the purpose of assisting dye molecules generating more excitons and transferring electrons to out circuit rapidly, which would influence the performance of DSSCs to a great extent.

Benefitting from their wide band gap, high stability, low expense, nontoxicity and excellent power conversion ability, TiO_2 porous nanocrystalline films are typically used as photoanodes in DSSCs. Except the traditional TiO_2 nanoparticles [16–18], there have been many other structures reported as excellent TiO_2-based photoanodes for DSSCs, such as core-shell structures [19–21], one-dimensional nanowires [22,23] and nanotubes [24–26], three-dimensional branched nanowires and nanotubes [27]. Among these, three-dimensional nanostructures are supposed to harvest sunlight and transport charge more effectively, also owning large

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specific surface areas. Based on such preconceive, various submicron or micron-sized TiO_2 microspheres with different features have been used as photoanodes in DSSCs [28–31]. For instance, TiO_2 microspheres which were fabricated to be nano-acicular rutile single crystals owned large specific surface areas of 132 $m^2 g^{-1}$ and the corresponding DSSCs exhibited the η value of 8.41% [28]; DSSCs based on hierarchical yolk@shell TiO_2 microspheres which exposed nearly 90% (001) facets announced an entire efficiency of 6.01% [29]; micron-sized mesoporous TiO_2 single crystal showed long-range electronic connectivity and structural coherence and the corresponding all-solid-stated DSSCs owned an efficiency of 7.3% [30].

These state-of-the-art designs of TiO_2 architecture have almost solved the problems of adsorbing dye molecules, scattering sunlight and conducting electrons. But as we all know, the main absorption wavelength ranges of dye molecules (commonly N719 and N3) are only up to 700 nm, which means that near-infrared (NIR) light, occupying 43% of the sunlight, can hardly be used up [32]. As reported, an available method of harvesting NIR light is to utilize rare earth elements doped upconversion nanoparticles (UCNPs), which can transform NIR light (>900 nm) to shorter wavelength light (<750 nm) via multiphoton processes [33]. For instance, double-shell β-$NaYF_4$:Yb^{3+}, Er^{3+}/SiO_2/TiO_2 submicroplates used as scattering and upconverting layer for efficient DSSCs have been reported by Liang, et al., which implied the promising application of UCNPs and TiO_2 [34]. Despite the fact that there have been several works about coating UCNPs with TiO_2 nanocrystalline aimed at harvesting more NIR light through upconvertion process [35,36], it is still critically challenging to further optimize the architecture of the UCNPs and TiO_2 composites as photoanode films in DSSCs.

Herein, we presented a facile evaporation-driven oriented assembly method (EDOA) to integrate UCNPs (β-$NaYF_4$:Yb^{3+},Er^{3+}@SiO_2) with TiO_2 mesoporous microspheres as multifunctional photoanode films on top of P25 layers for DSSCs [37]. Compared with those thermal methods of fabricating TiO_2 mesoporous microspheres, EDOA was so moderate that the features of β-$NaYF_4$:Yb^{3+},Er^{3+} crystal could be completely preserved. In our work, the isolating silica layers coating β-$NaYF_4$:Yb^{3+},Er^{3+} were designed to prevent bare UCNPs from recombining electron-hole pairs on their surface [36]. Meanwhile, SiO_2 had three-dimensional network structure with many unsaturated bonds and hydroxyls at different state, which could interact with HO- and —C—O—C— of PEO-PPO-PEO (pore-forming templates) by covalent or hydrogen bond so as to package β-$NaYF_4$:Yb^{3+},Er^{3+} into TiO_2 mesoporous microspheres. As reported, due to the hydrophilicity and hydrophobicity distinction of PEO and PPO, uniform microspheres assembled by UCNPs@SiO_2/PEO-PPO-PEO/titania oligomer micelles after the first step evaporation at 40 °C [37]. The microspheres and nanocrystal building blocks grew up orientedly, driven by the second step evaporation at 80 °C [37]. After calcinating triblock copolymer templates, β-$NaYF_4$:Yb^{3+},Er^{3+}@SiO_2@TiO_2 (N@S@T) mesoporous microspheres with UCNPs inset and single-crystal-like anatase TiO_2 walls exposed (101) facets were finally fabricated. The schematic representation of the experimental process was shown in Fig. 1.

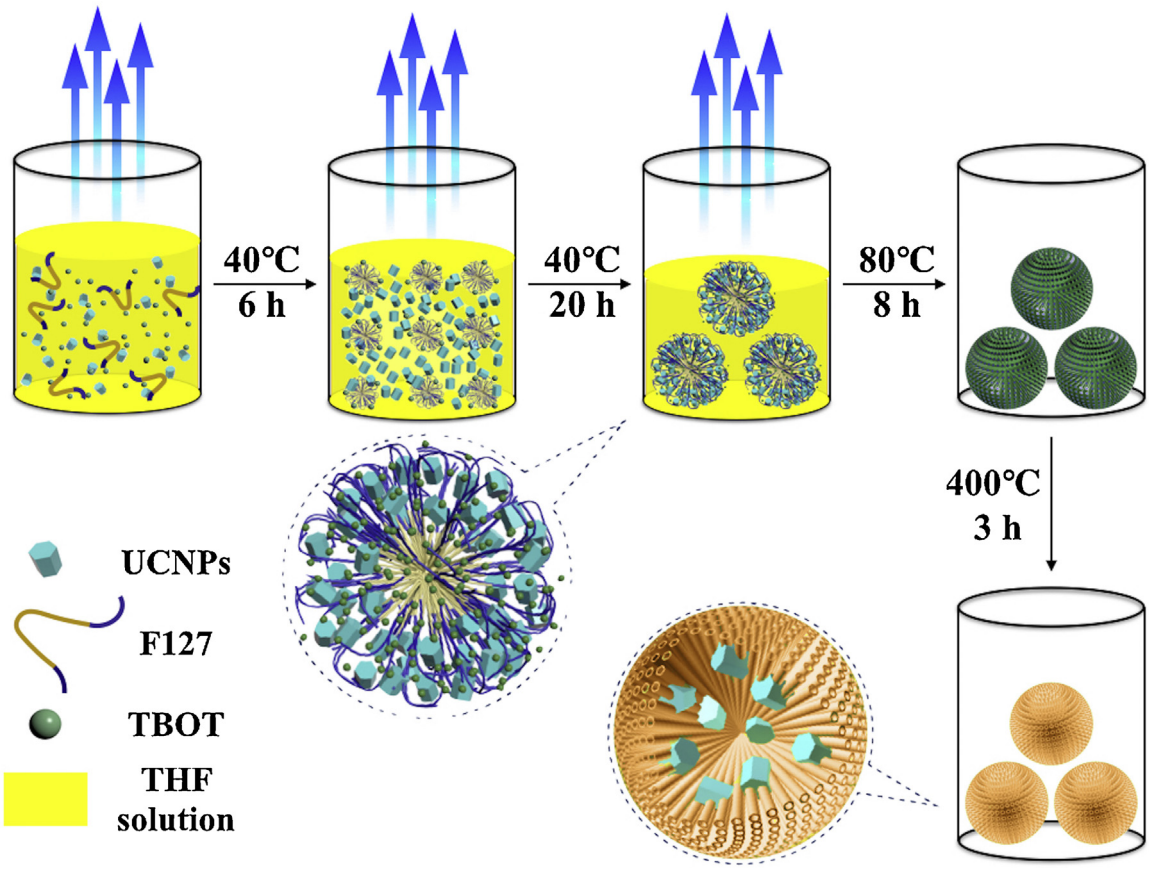

Fig. 1. Schematic representation of the experimental process for N@S@T mesoporous microspheres.