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Oxalate-assisted morphological effect of $NaYF_4:Yb^{3+},Er^{3+}$ on photoelectrochemical performance for dye-sensitized solar cells☆

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ABSTRACT

In this study, we have employed a facile oxalate-assisted hydrothermal approach to tailor the morphology of β-$NaYF_4:Er^{3+},Yb^{3+}$ (NYFEY) powders through the variation of the molar ratio of oxalate ions (Oxa^{2-}) and rare earth ions (RE^{3+}) in the range of 0.5:1, 1:1, 2:1, 5:1, and 10:1. The obtained results show that the crystallinity, particle size and upconversion luminescence intensity of the as-synthesized NYFEY particles are gradually decreased as the Oxa^{2-}:RE^{3+} molar ratio increases from 0.5:1 to 10:1. For the purpose of photoelectrochemical performance evaluation, the as-synthesized NYFEY particles with different morphologies are incorporated into the nanocrystalline TiO_2 films to form the multifunctional nano- and sub-micrometer composite photoanodes of dye-sensitized solar cells (DSSCs). A short-circuit current density (J_{SC}) of 14.26 mA/cm^2 and power conversion efficiency (PCE) of 7.31% are obtained for DSSCs prepared with hexagonal rod-like NYFEY crystals, evidencing an increase of 29.8% compared with DSSCs prepared with only TiO_2 nanoparticles. The demonstrated synthesis approach for tailoring the morphology and size of NYFEY particles and enhancing the performance of DSSCs can also be applied for other types of solar cells.

1. Introduction

Upconversion (UC), first proposed in 1959, is the conversion of two or more low energy photons into one high energy photon by certain materials.[1] Upconversion luminescence (UCL) is seen in the rare-earth elements or lanthanides when included in a suitable host material such as crystals, fibers and glass ceramics.[2–4] In recent years, UC materials are considered in application in biomedical imaging,[5] semiconductor quantum dots,[6] photovoltaic applications[7,8] and flat-panel displays.[9] In photovoltaics, the UC process has the potential to increase cell efficiency in a cost-effective way. Generally, dye-sensitized solar cells (DSSCs) with a TiO_2 photoelectrode have a maximum absorption in the visible region of the total incident solar irradiation,[10,11] which means that approximately 50% of solar irradiation energy in the ultraviolet and infrared regions is not utilized[12]; therefore, the solar energy conversion efficiency of DSSCs is limited in these cases.[13] Accordingly, extending the spectral response range of DSSCs to the infrared or ultraviolet region is extremely important to increase the efficiency of DSSCs. Upconversion lanthanide-based nanoparticles (NPs) have received considerable attention because they can convert near-infrared (NIR) photons to visible light by absorbing low-energy photons and then emitting high-energy photons.

Among the investigated UC materials so far, the β-$NaYF_4$ has been widely recognized as the most efficient host for UC phosphor (UCP) until now due to its low phonon energy and efficient multicolor emissions.[14] As known, Er^{3+} is one of the most efficient rare-earth ions[15,16] because of its versatile energy levels in the near infrared region. Yb^{3+}, which has a high and broad absorption band, is considered to be an excellent sensitizer for the Er^{3+}-activated optical materials.[17] Moreover, the Yb^{3+} lasers possess several advantages, such as no energy loss caused by excited state absorption, high quantum efficiency, and large accumulation power of optical energy. Subsequently, the Yb^{3+} and Er^{3+} co-doped β-$NaYF_4$ designated as β-$NaYF_4:Er^{3+},Yb^{3+}$ (NYFEY) has become the most

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promising visible light emitting UC phosphor with two main emission peaks at about 545 and 655 nm under the irradiation of 980 nm.[18–21] The UC process can be made more efficient by careful selection of lanthanide-dopant combinations, low vibrational host matrices, and nano-structural optimization.[2,4] A low phonon energy of the host material decreases the multi-phonon relaxation, thus reducing non-radiative losses[22–24] and leading to a stronger UCL. Recently, the studies enhancing the photoelectric conversion efficiency (PCE) of DSSCs via incorporating with such UC materials have been made. Liang et al.[25,26] once designed a highly uniform core/double-shell (CDS) structure consisting of β–$NaYF_4$:Er^{3+},Yb^{3+} (NYFEY) crystal as core, amorphous SiO_2 as inner shell, and interconnected anatase TiO_2 grains as outer shell. Guo et al.[27] synthesized highly uniform, monodisperse NYFEY upconversion phosphor submicron hexagonal prisms coated with a SiO_2 layer via a hydrothermal route with an aqueous solution of sodium citrate. Zhang et al.[28] prepared a multifunctional β-$NaYF_4$:Er^{3+},Yb^{3+}/TiO_2 core–shell structured nanocomposite and used as a photoelectrode of DSSCs to investigate the possibility of increasing the spectral response of DSSCs. $NaYF_4$:Er^{3+}/Yb^{3+}-graphene composites were successfully prepared by growing $NaYF_4$:Er^{3+}/Yb^{3+} nanoparticles in interlayers of expanded graphite, accompanied with the simultaneous exfoliation of expanded graphite under polyvinylpyrrolidone-assisted hydrothermal conditions.[29] Yuan et al.[30] fabricated colloidal $NaYF_4$:Er^{3+}/Yb^{3+} UC nanocrystals for energy relay solar cell light harvesting in the near-infrared region. Khan et al.[31] achieved core–shell nanophosphor ($NaYF_4$:Er,Yb/$NaYF_4$) with enhanced NIR-visible upconversion as spectrum modifier for enhancement of solar cell efficiency. The results of those experiments are interesting, but the pure $NaYF_4$:Er^{3+}/Yb^{3+} was synthesized by variation of frequently-used surfactants (citrate, PVP, CTAB and so forth) or the complex routes, and doping amounts of surfactant and rare earth ion were not adjusted, and consequently the morphology of the $NaYF_4$:Er^{3+}/Yb^{3+} changed unremarkablely. Recently, oxalate has been effectively employed in the hydrothermal process as a chelating ligand and structure-directing agent to produce nano-crystals with different morphologies.[32,33] A number of studies demonstrated that the morphology of the product has a strong dependence on oxalate. The oxalate-assisted hydrothermal synthesis has been speculated to apply to control the morphology and size of particles. However, the reports on the hydrothermal synthesis of $NaYF_4$:Er^{3+}/Yb^{3+} using oxalate as the surfactant are few.

Therefore, in this paper, we report a facile oxalate-assisted hydrothermal process to prepare nano- and micro-scaled β-$NaYF_4$:Er^{3+},Yb^{3+} powders with various morphologies through the variation of the molar ratio between oxalate ions (Oxa^{2-}) and of rare earth ions (RE^{3+}) in the range of 0.5:1, 1:1, 2:1, 5:1, and 10:1. For the purpose of matching well with nanocrystalline TiO_2 nanoparticles (TNPs) and light scattering demand, the different kinds of NYFEY were incorporated into TiO_2 nanocrystalline films to form the multifunctional nano-/sub-micrometer composite photoanodes network. To further investigate the influence and mechanism of such composite network on the performance of the photoanodes and the DSSCs, it is greatly expected that performance of DSSCs can be effectively enhanced by employing these multifunctional TNPs and NYFEY powder sin photoelectrodes.

2. Experimental

2.1. Preparation of TNPs

The TNPs were synthesized by hydrolysis technique[34,35] from tetrabutyl titanate (98 wt%, Shanghai Zhanyun Chemical Co., Ltd.). In the synthesis process, tetrabutyl titanate was hydrolyzed with ethanol aqueous solution (70%–75%, Xi'an Chemical Reagent Factory) under strong stirring at pH = 3 and then dried at 80 °C for 2 h.

2.2. Preparation of β-$NaYF_4$:Er^{3+},Yb^{3+} submicron-sized plates

Monodispersed β-$NaYF_4$:Er^{3+},Yb^{3+} submicron plates were prepared by a modified hydrothermal reduction technique.[36] In a typical synthesis, aqueous solution (20 mL) of $Y(NO_3)_3$ (99%, Sinopharm Chemical Reagent Co., Ltd.), $Yb(NO_3)_3$ (99.9%, Sinopharm Chemical Reagent Co., Ltd.) and $Er(NO_3)_3$ (99.9%, Sinopharm Chemical Reagent Co., Ltd.) with the Y/Yb/Er molar ratio of 78:20:2 was mixed with 10 mL aqueous solution of oxalate (99.5%, Tianjin Shengao Chemical Reagent Co., Ltd.) and NaOH (96%, Xi'an Chemical Reagent Factory) (Oxa^{2-}:RE^{3+} molar ratio of 0.5:1) under magnetic stirring for 30 min to form a homogeneous solution. Subsequently, aqueous solution (40 mL) of NaF (1.05 g) (99.99%, Tianjin Kermel Chemical Reagent Co., Ltd.) was added to the above solution and stirred for 0.5 h, resulting in a complex. Then, the pH of the solution was adjusted to 11 by adding dilute HNO_3 (65%, Tianjin Tianli Chemical Reagent Co., Ltd.). After being stirred for another 30 min, the as-obtained solution was transferred into a 100 mL autoclave, sealed, and hydrothermally treated at 200 °C for 3 h. After cooling to room temperature, the white precipitates obtained were separated by centrifugation and washed with deionized water and ethanol to remove the excess sodium citrate and then dried at 80 °C for 12 h. Parallel experiments with different molar ratios of Oxa^{2-}:RE^{3+} (1:1, 2:1, 5:1 and 10:1) were carried out under the identical experimental conditions.

2.3. Fabrication of composite photoanodes and DSSCs

TiO_2 (20–40 nm) paste for transparent layer was prepared by hydrolysis of titanium tetraisopropoxide (95 wt%, Shanghai Zhanyun Chemical Co., Ltd.) via the reported procedure. The TiO_2 pastes were prepared according to the mass ratio (NYFEY = 10%). These pastes were coated on FTO glasses by doctor blade method, then dried under ambient conditions and annealed at 500 °C for 30 min to obtain the photoanodes. All of the photoanodes described above were soaked in anhydrous ethanol (99.7%, Xi'an Chemical Reagent Factory) containing commercially available N719 dyes (0.3 mmol/L, *cis*-isothiocyanate-*bis* (2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium (II) bis(tetrabutylammonium); Solaronix Co.) for 24 h at room temperature. Pt counter electrodes were prepared by dropping 0.5 mmol/L H_2PtCl_6 (37.5%, Sigma–Aldrich) isopropanol solution on FTO glass, followed by heating at 450 °C for 20 min. The active area of the film (0.16 cm^2) was assembled together with the Pt-coated FTO glass by applying a 60 μm-thick hot-melt sealed film as the spacer (SX1170-60; Solaronix Co.). The liquid electrolyte used here was the solution containing the I^{3-}/I^- redox couple and commercially available (CJX-EH, CasJuxin Solar Technology Co., Ltd.). The electrolyte was injected between two electrodes and driven by a capillary force through the hole on the hot-melt sealed film.

2.4. Characterization

The X-ray diffraction (XRD) patterns were obtained using a PANalytical X'Pert PRO X-ray diffractometer with Cu Kα. The SEM observation was performed with a field emission-type HITACHI S-4800 scanning electron microscope. The photoluminescence (PL) spectra were measured by a SpectraPro 2500i spectrometer (Acton Research Corporation), and the excitation source was a CW Ti:sapphire laser (Mira 900, Coherent Inc.). The performance of the fabricated DSSCs was evaluated by measuring the photocurrent