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Regular Article

Eu^{3+} doped down shifting TiO_2 layer for efficient dye-sensitized solar cells

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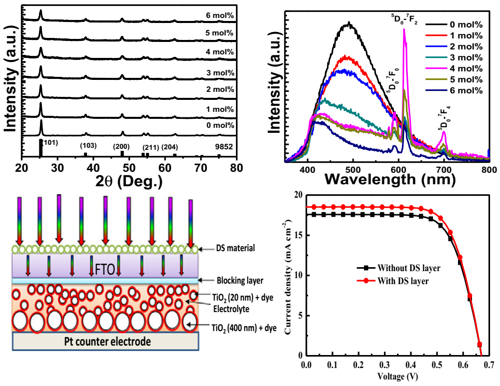
GRAPHICAL ABSTRACT



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ABSTRACT

Europium doped TiO_2 (TiO_2:Eu^{3+}) down-shifting (DS) nanophosphors (NPrs) were synthesized by the solution-combustion method with different concentrations of Eu^{3+}. The X-ray diffraction results confirmed the formation of a polycrystalline tetragonal structure of the TiO_2. The emission of colour of the TiO_2:Eu^{3+} DS NPr was tuned by varying the doping concentration of Eu^{3+}. The photoluminescence results confirmed that the TiO_2:Eu^{3+} DS NPrs converted the UV light into visible light by energy down-conversion process, i.e. down-shifting of high energy UV photons to low energy visible photons. These TiO_2:Eu^{3+} DS NPrs were used to enhance the efficiency of the Dye sensitized solar cell from 8.32% to 8.80.%

1. Introduction

Dye-sensitized solar cells (DSSCs) are considered to be one of the most promising photovoltaic technologies [1–3]. DSSCs are made from low-cost materials and can be significantly less expensive than conventional solid-state solar cells. These solar cells can also be designed on flexible and be mechanically robust sheets [4]. Although, a conversion efficiency of these innovative DSSC is less than the best known thin-film cells, its price/performance ratio should be low, make it a cost-effective source of electrical energy. There are many factors that limit the performance of a DSSC such as energy loss resulting from the spectral mismatch between the energy distribution of photons in the incident solar spectrum and excitation bands of the dye is very important. The other things is the degradation of dyes under UV light. Therefore, the development of photoluminescent materials for overcoming the poor

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spectral response to short wavelength is of a great interest to researchers, since the cell performance will be enhanced due to shifting the excitation spectrum to wavelengths that more closely match the excitation bands of the dye.

In solar cells fabricated using photoluminescent materials, the incident photons can be modified to an appropriate energy by up conversion (UC), down conversion (DC), down shifting (DS), or photoluminescence (PL) to provide a better overall performance [5]. Spectral modification is done to convert or shift the incident light towards the wavelength corresponding to the spectral responses before the incident light reaches the solar cells (in case of DC, DS and PL) or after it has passed through the devices (in case of UC). The DS process is primarily investigated for materials doped with rare-earth (RE) ions and happens either on a single ion or through energy transfer processes among various RE ions. Crystalline down-shifting phosphors, however, normally consist of grains in the sub-micrometer and micrometer sizes. These nanophosphors are too large to make the layers transparent as required for thin film solar cell applications.

Titanium dioxide (TiO_2) is one of the most important materials especially in the nano-scale, which have attracted attentions due to its unique properties. TiO_2 is a very interesting UV absorbing material not only from a scientific point of view but also due to its technological applications in dye sensitized solar cells, dielectric materials in capacitors, sensing [6–8]. TiO_2 has also demonstrated the possibility to be a good sensitizer to absorb primary excitation energy and transfer it to RE dopant ions. Studies of semiconductors doped with RE elements such as Eu, Er, Tm, and Eu have been intensively pursued because of their important applications in optoelectronics as emitters in visible region [9]. There are two main factors leading to the stable and sharp luminescence in RE elements: one is that the 4f orbital of RE ions is shielded by the outer 6 s, 5p and 5d orbitals, which weakens its coupling with the surrounding ligands; the other is that the f-f transitions are parity forbidden, resulting in small absorption cross sections [10]. The initial efforts of incorporating RE ions into Si and other narrow band gap semiconductors are hindered by the solubility constraints and the thermal quenching [11,12]. RE doped TiO_2 have been investigated most frequently for applications in sensors, light emitting materials and non-volatile memory devices, optoelectronics and photo catalysis [13–18].

In this paper, the effect of Eu concentration on the structure, morphology, chemical and luminescence properties of $TiO_2:Eu^{3+}$ DS nanophosphors (NPr) was investigated in detail. The optimized *Eu* doped TiO_2 DS NPr material was used to enhance the efficiency of the DSSC.

2. Experimental details

2.1. Synthesis of $TiO_2:Eu^{3+}$ down convertor nano-phosphor

$TiO_2:Eu^{3+}$ DS NPr with different doping concentration of Eu were synthesized using the solution combustion method. Titanium oxysulfate and urea were mixed and dissolved in distilled water. Europium nitrate pentahydrate was used as the Eu source in the solution. The concentration of Eu was varied from 0 to 6 mol%. A homogeneous solution was obtained after stirring for 1 h at 80 °C. The solution was transferred to a pre-heated muffle furnace maintained at a temperature of 600 ± 10 °C. All the liquid evaporated and a large amount of heat was released which resulted in a flame that decomposed the reagents further and released more gases. The flame lasted for ~60 s and the combustion process was completed within 5 min. The resulting $TiO_2:Eu^{3+}$ DS NPr powders were cooled down to room temperature and ground gently using a pestle and mortar. The down converter nanophosphor was annealed at 700 °C for 2 h in a microprocessor controlled furnace.

2.2. Fabrication of dye sensitized solar cell

The commercially available TiO_2 paste (DSL 18NR-T, Dyesol) as the transparent layer (9 mm) and DSL 18NR-AO, Dyesol as the scattering layer (5 mm) were used to prepare mesoporous nanocrystalline TiO_2 photo anodes on Fluorine-doped tin oxide (FTO) coated float glass substrates (TEC-7, Pilkington) pretreated twice with a 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min. The TiO_2 photo anodes were made by the doctor blend method. After this the TiO_2 photo anode was annealed with a ramping program on a hot plate [17]. TiO_2 photo anodes were further treated with a 40 mM $TiCl_4$ solution as described above, rinsed with water and annealed at 450 °C for 30 min. Thus prepared TiO_2 photo anodes were soaked in a N719 dye solution (Dyesol) for 20 h [2]. A Pt film was deposited on the FTO coated glass (TEC-7, Pilkington) by covering it with a drop of H_2PtCl_6 solution (2 mg/mL in ethanol) followed by annealing at 410 °C for 15 min. The Pt film thus deposited was used as the counter electrodes (CEs) in the DSSCs. The DSSC was assembled by making a sandwich structure of the photo anode and the CE, sealing it with 25 mm thick surlyn (Solaronix SA) which also acts as a spacer. The electrolyte consisting of 0.6 M 1,3-dimethylimadazolium iodide, 0.1 M lithium iodide, 0.05 M iodine, 0.5 M 4-*tert-butylpyridine* (TBP) and 0.6 M benzmethyl imidazolium iodide in acetonitrile: valeronitrile (85:15) was injected through a previously drilled hole in the CE. After the electrolyte injection the hole was sealed with a cover glass slide and surlyn. A mask of 0.25 cm^2 area was used on the photo electrode for specifying the solar cell area. The TiO2:Eu^{3+} DS NPr layer was fabricated on top of the glass of the DSSC by a spray pyrolysis method.

2.3. Characterization tools

The crystal structure was analysed using an X-ray diffractometer (XRD) (PAN analytical X'pert PRO). The undoped and doped TiO_2 DS NPr samples were performed using a Jeol JSM-7800F Field Emission Scanning Electron Microscope (FE-SEM). The X-ray photo electron (XPS) analysis was carried out with a PHI 5000 Versaprobe-Scanning XPS Microprobe before sputtering and after sputtering for 30 s with 2 kV 2 μm Ar^+ ions. The UV–vis reflectance spectra of undoped and Eu doped TiO_2 DS NPr at room temperature in the range of 300–800 nm were recorded using a Perkin Elmer Lambda 950 UV–vis. The PL data was recorded using a He-Cd laser at an excitation wavelength of 325 nm. The high resolution transmission electron microscopy (HRTEM) images were obtained by using FEI TecnaiTF20. The current-voltage (J-V) characteristics of the solar cells were measured under the irradiation source of a 450 W Xenon Light source (Osram XBO 450) fitted with a filter (Schott 113), whose power is regulated to the AM 1.5G (1000 W m^{-2}) solar standard by using a reference Si photo anode equipped with a colour matched filter (KG-3, Schott). This reduced the mismatch in the region of 350–750 nm between the simulated light and AM 1.5G to less than 4%. The measurement settling time between applying a voltage and measuring the current for the J-V characterizations of DSSCs was fixed to 80 ms. The device is mostly sensitive to UV and visible wavelengths of excitation.

3. Results and discussion

3.1. Structure and surface morphology

The XRD patterns of the $TiO_2:Eu^{3+}$ DS NPr with different concentrations of Eu are shown in Fig. 1. The peak positions and their