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Synthesis of $LaVO_4$: Dy^{3+} luminescent nanostructure and optimization of its performance as down-converter in dye-sensitized solar cells

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ABSTRACT

The effect of downconversion film of $LaVO_4$:Dy^{3+} nanocrystals, which could absorb UV light and downconvert it to visible light, for increasing the current density of DSSC has been studied. $La(CH_3CO_2)_3$ as a new source of La was used to synthesis of tetragonal $LaVO_4$:Dy^{3+} nanocrystals as down shifting material in dye sensitized solar cells by using hydrothermal method. Besides, the optimized Dy^{3+} concentration and annealing temperature which affect the morphology, particle size, photoluminescence and crystal structure of the produced nanostructures were found for the first time. The as-synthesized products were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution field-emission transmission electron microscopy (HRTEM), photoluminescence spectroscopy (PL), scanning electronic microscopy (SEM), spectra energy dispersive analysis of X-ray (EDAX) and ultraviolet–visible (UV–Vis) techniques. The photoluminescence studies of the $LaVO_4$:Dy^{3+} nanocrystals revealed strong enhancement in emission intensity, when Dy^{3+} concentration was increased from 0 to 0.08 mmol and annealed at 500 °C. The lattice structure transforms from tetragonal to monoclinic phase subsequent to annealing at 700 and 900 °C. Using this down-conversion material, the current density of solar cell increased by 6.7%, compared to the uncoated solar cell.

1. Introduction

In recent years, the main constraints for the efficiency improvement and practical use of solar cells is the spectral mismatch between the incident solar photon spectrum and the band gap of semiconductor and thermalization of charge carriers generated by absorption of high-energy photons and thermal degradation of dye-sensitized solar cell components. The incident high-energy photons, transform their extra energy to electron-hole pairs, and thereby convert it to heat. Low-energy photons cannot be absorbed by the solar cell, instead the sub band transmission loss occurs [1,2]. An effective way to reduce the energy losses is modifying the solar energy spectrum via luminescence phenomenon to the wavelength range in which the solar cells have high absorption probability [2]. The solar spectrum modification results in efficiency enhancement of solar cell through down shifting (DS), down conversion (DC) and up conversion (UC) [3–6].

Because of low cost fabrication, dye-sensitized solar cells (DSSCs) have attracted a great deal of interest [7,8]. For the practical use of DSSCs, the chemical stability is as important as its conversion efficiency. Irreversible electrochemical and thermal degradation of the dye or electrolyte components, originating from UV irradiation affect the chemical stability of DSSCs [9]. The common strategy to avoid the UV light is using a down conversion material to absorb UV rays and down convert it to visible light, which is reabsorbed by dye in DSSCs [10].

Because of very large surface to volume proportion and vital importance of surface states in improvement of optical and luminescence features, luminescent nanocrystals (NCs) have attracted great interest [11]. Due to their wide variety of applications, considerable efforts have been made to fabricate the rare earth doped luminescent nanostructures such as phosphors [12], laser host materials [13], catalysts [14] and up conversion materials [15]. Lanthanide orthovanadates such as $LaVO_4$ are an important rare earth luminescent family [16,17] due to their unique electronic structure and the numerous transition modes involving the 4f shell of rare earth ions [18].

$LaVO_4$ generally crystallize in two polymorphs, monoclinic (m-) phases with monazite structure and tetragonal (t-) phase with zircon structure. $LaVO_4$ chooses monazite type as the thermodynamically

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stable state. m-$LaVO_4$ can be obtained at ordinary pressures by conventional solid-state reaction [19]. t-$LaVO_4$ has a metastable phase and can only be prepared through solution process at high pressures such as hydrothermal method [20]. It has been found that m-$LaVO_4$ is not a suitable host for luminescent activators [21]. On the other hand, t-$LaVO_4$ is expected to have superior properties [19]. Also, studies have shown that the morphology and optical properties of the product are strongly dependent on the initial La sources [22].

In this work, $La(CH_3CO_2)_3$ as a new La source was used to produce the $LaVO_4$:Dy^{3+} nanocrystals by using hydrothermal method and the Dy^{3+} concentration and annealing temperature that crucially affect the optical properties of the synthesized nanoparticles were optimized for the first time. Besides the morphology, crystal structure and optical properties of the samples were investigated by changing the reaction conditions. Finally, the effect of produced nanostructures as downconversion layer in DSSC was investigated.

2. Experimental

2.1. Synthesis and characterization

All the chemicals reagents used in experiments were of analytical grade and used as received without further purification. $La_{1-x}VO_4$:Dy_x^{3+} (x=0, 0.02, 0.04, 0.06, 0.08, 0.1, 0.15) nanocrystals were prepared by hydrothermal method. First Na_3VO_4 aqueous solution was produced by dissolving 0.3 g NaOH and 0.03 g NH_4VO_3 in 2.5 ml DI water. Then, the mixture of 5 ml oleic acid and 5 ml ethanol, and a solution of $La(CH_3CO_2)_3 \cdot xH_2O$ and $Dy(NO_3)_3 \cdot 5H_2O$ (1 mmol total) were slowly added to the above solution at room temperature, while was stirred. After 30 min the resulting solution was transferred into 50 ml Teflon-Lined stainless-steel autoclave and sealed tightly, and the reaction was performed in a hydrothermal digestion system at the various conditions (Table 1). A dark brown solution was obtained. Finally, the system was left to cool to room temperature naturally. The obtained precipitate was collected by filtration, then, was washed with absolute cyclohexane and ethanol for several times. The product was dried in a vacuum oven at 70 °C for 4 h. Subsequently, the selected samples were heat-treated at temperatures 300, 500, 700 and 900 °C in air for 1 h. The resulting powders were $LaVO_4$:Dy^{3+} nanoparticles.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded by a Philips-X'pertpro, X-ray diffractometer using Ni-filtered Cu K_α radiation at scan range of 2θ (0–70). Scanning electron microscope (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. Transmission electron microscopy (TEM) was performed on a JEM-2100 transmission electron microscope with an accelerating voltage of 200 kV. Room temperature photoluminescence (PL) was studied on a Perkin-Elmer (LS 55) fluorescence spectrophotometer. UV–Vis diffuse reflectance spectroscopy analysis (UV–Vis) was carried out using Shimadzu UV–Vis scanning spectrometer. Energy dispersive analysis of X-ray (EDAX) spectrum was recorded on a XL30, Philips. Finally, the photovoltaic measurements were accomplished by solar simulator (Luzchem) and IVIUMSTAT (IVIUM) under AM 1.5 condition.

Table 1
Reaction conditions for $LaVO_4$:Dy^{3+}. Solvent values are relative to those of Section 2.1.

Sample no.	Time (h)	Temperature (°C)	Surfactant	Solvent value
1	4	140	Oleic acid	1
2	6	140	Oleic acid	1
3	8	140	Oleic acid	1
4	4	160	Oleic acid	1
5	4	140	Triphenylphosphine	1
6	4	140	Brig 35	1
7	4	140	CTAB	1
8	4	140	Oleic acid	0.5
9	4	140	Oleic acid	2

3. Results and discussion

Fig. 1((a)–(c)) shows the XRD patterns of $La_{1-x}VO_4$: Dy_x^{3+} NCs for different x values of 0, 0.02 and 0.08, respectively. The XRD pattern is consistent with the spectrum of $LaVO_4$:Dy^{3+}. Bragg's reflections from LaVO4 nanocrystals were observed in XRD pattern at 2θ values of 18, 24, 32, 47 and 55° representing [1 0 1], [2 0 0], [1 1 2], [3 1 2] and [4 2 0] planes of tetragonal phase with zircon structure and space group of $I41/amd$ (JCPDS card no. 32-0504) with the lattice constants of $a=b=7.49$ Å and $c=6.59$ Å. From XRD data the crystallite diameter (Dc) of 10–60 nm was obtained for the as-prepared $LaVO_4$:Dy^{3+} nanocrystal using the Scherer equation [23]:

$$D_c = \frac{K\lambda}{\beta \cos\theta}$$

where β is the width of the observed diffraction line at its half intensity maximum, K is the so-called shape factor, which usually takes a value of about 0.9, and λ is the wavelength of X-ray source used in XRD. As shown, the intensity of corresponding XRD peaks of $LaVO_4$:Dy^{3+} become stronger by increasing the amount of Dy^{3+} as an activator ion indicating improved crystalline structure. Also, the diffraction peak positions move slightly towards the higher angles which reveal a decrease in unit cell parameters due to the smaller ionic radius of Dy^{3+} compared to La^{3+}. Therefore, unit cell parameters reduce with replacing Dy^{3+} with

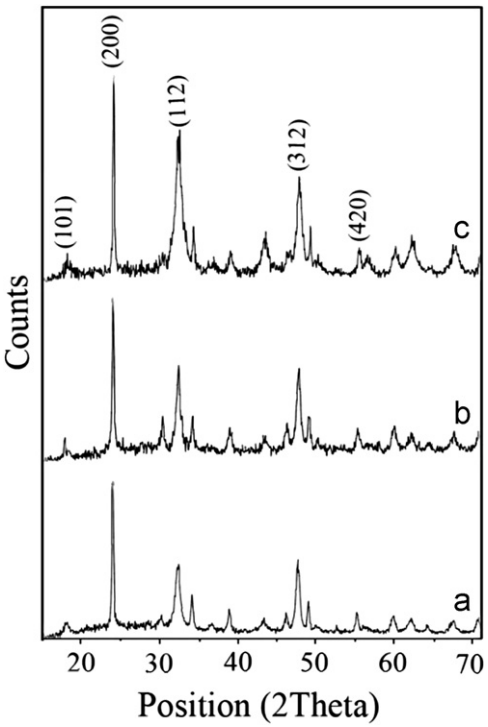

Fig. 1. XRD patterns of $La_{1-x}VO_4$:Dy_x^{3+} NCs: (a) x=0, (b) x=0.02, (c) x=0.08.