Preparation and Characterization of Downconversion Luminescent LaVO₄: Tm³⁺, Yb³⁺ and Tm³+/Yb³⁺ Nanosheets

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Abstract
Tm³⁺, Yb³⁺ and Tm³+/Yb³⁺ doped LaVO₄ nanostructures were synthesized for the first time by using the hydrothermal method with the aid of La(CH₃CO₂)₃ as lanthanum source in presence of oleic acid as surfactant. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence (PL) spectroscopy and UV–Vis diffuse reflectance spectroscopy. Besides, the effects of activator concentration and sensitizer on the emission intensity were investigated. The PL spectrum revealed that the emission intensity decreases with increase in the concentration of Tm³⁺, while adding Yb³⁺ as sensitizer causes the emission intensity to increase. The LaVO₄: Tm³⁺/Yb³⁺ may possibly have potential application in enhancing the conversion efficiency of dye-sensitized solar cells by increasing the absorption of dyes.

Keywords:
LaVO₄, Tm³⁺/Yb³⁺ Nanosheets, Downconversion Nanostructures, Hydrothermal

1. Introduction
Nanomaterials are of current interest owing to their unique properties and potential applications in catalysis, optoelectronic devices, and so on [1-9]. Luminescent nanocrystals (NCs) that are soluble in organic solvents and polymers attract a great deal of interest since these materials can easily be processed via spin-coating techniques to form a uniform film from an organic solution [10]. Rare-earth (RE) doped luminescent materials have been the focus of many scientists due to their widely use in many different fields, such as phosphor [11, 12], biomedical applications [13] and laser host materials [14]. Also, the luminescent materials are very useful for spectrum modification through down shifting (DS), down conversion (DC) and up conversion (UC) in order to solar spectra modification for the efficiency en-
hancement of solar cells, because one major energy loss in solar cells is the thermalization of charge carriers generated by the absorption of high energy photons or the spectral mismatch between the incident solar photon spectrum and the band gap of semiconductor [15-19]. For example the irreversible electrochemical and thermal degradation of the dye or electrolyte components, originating from UV irradiation affects the chemical stability of Dye-Sensitized Solar Cells (DSSCs) and 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 [20]. Lanthanide orthovanadates such as LaVO₄ are a significant rare earth luminescence family [21] due to their unique electronic structure and the numerous transition modes involving the 4f shell of rare earth ions [22]. Lanthanide orthovanadates generally crystallize in two polymorphs, monoclinic (m-) and tetragonal (t-). LaVO₄ has a monazite structure at ordinary pressures and a zircon structure at high pressures [23]. m-LaVO₄ is not a suitable host for luminescent activators [24] but t-LaVO₄ is expected to have superior properties. Sometimes, the efficiency that was observed or expected for photoluminescence emission in spectra conversion was low in singly doped media, because the direct excitation of the lanthanide ions is a relatively inefficient process, due to the forbidden character of the 4f transitions but it was quickly noticed that the mechanism could be made 1-2 orders of magnitude more efficient by use of ytterbium (Yb³⁺) as a sensitizer ion in addition to the active ion, namely, erbium, holmium, or thulium. Energy transfer from a host material or other ion with a higher absorption coefficient could lead to much more efficient materials [25-27]. In this work, the synthesis of lanthanide-doped LaVO₄ nanocrystals by using the hydrothermal method is presented. Tm³⁺ was used as an activator ion in LaVO₄ nanocrystals to create emission spectra. For increase the efficiency of emission spectra, Yb³⁺ also was added as a sensitizer. These nanocrystals provide the possibility to excite most of the lanthanide ions via the charge-transfer transition within the vanadate group, followed by energy transfer to the emissive Tm³⁺/Yb³⁺. The characterization of the as-synthesized LaVO₄ nanocrystals was performed by using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV–Vis diffuse reflectance spectroscopy analysis (UV–Vis) and photoluminescence (PL) spectroscopy.

2. Experimental

2.1. Synthesis

The La₁₋ₓₐVO₄: Tmₓ³⁺ (x= 0.005, 0.01, 0.02, 0.04) and La₀.₉₈VO₄: Yb₀.₀₂³⁺ and La₀.₈VO₄: Tm₀.₀₁³⁺/Yb₀.₁₉³⁺ nanocrystals were synthesized using a hydrothermal procedure. In a typical experimental procedure, 5 ml of oleic acid and 5 ml ethanol was added to a solution of 0.3 g NaOH and 0.03 g NH₄VO₃ dissolved in 2.5 ml DI water, while was stirring with vigorous magnetic stirrer. Then, a solution of La(CH₃CO₂)₃.x H₂O and Tm(NO₃).5H₂O (1 mmol total) was slowly added to the above solution at room temperature. After stirring for 30 min, the reactants were put into a 50 ml capacity teflon-lined autoclave. The autoclave was maintained at 140°C for 4 h and then cooled down to room temperature naturally. The NCs could be collected at the bottom of the vessels, and washed with cyclohexane and absolute ethanol for several times and dried in oven at 50°C for 10 h. Similarly, LaVO₄: Yb³⁺ were synthesized using La(CH₃CO₂)₃.x H₂O, YbCl₃.H₂O with a molar ratio of 0.98: 0.02 and Also, LaVO₄: Tm³⁺/Yb³⁺ were prepared by La(CH₃CO₂)₃.x H₂O, YbCl₃.H₂O and Tm(NO₃).5H₂O with a molar ratio of 0.8: 0.19: 0.01.
2.2. Characterization

X-ray diffraction (XRD) patterns were recorded by a Philips-X’pertpro, X-ray diffractometer using Ni-filtered CuKα radiation at scan range of 2θ (0-70). A LEO 1455VP scanning electron microscope (SEM) was used to investigate the morphology of the product. Transmission electron microscope (TEM) images and high-resolution TEM (HRTEM) image were obtained on a JEM-2100 transmission electron microscope with an accelerating voltage of 200 kV. Room temperature photoluminescence (PL) properties of the product were studied on a Perkin-Elmer (LS 55) fluorescence spectrophotometer. The electronic spectra of the complexes were taken on a Shimadzu Ultraviolet–visible (UV–vis) scanning spectrometer (Model 2101 PC).

3. Results and discussion

X-ray powder diffraction (XRD) patterns of LaVO₄ nanocrystals at room temperature are shown in Fig. 1. Fig. 1a, 1b, 1c, and 1d as the patterns of La₀.₉₉VO₄: Tm₀.₀₁³⁺, La₀.₉₆VO₄: Tm₀.₀₄³⁺, La₀.₉₈VO₄: Yb₀.₀₂³⁺, and La₀.₈VO₄: Yb₀.₁₉³⁺/Tm₀.₀₁³⁺ nanocrystals respectively. The result indicate that the as-prepared La₀.₉₉VO₄: Tm₀.₀₁³⁺, La₀.₉₆VO₄: Tm₀.₀₄³⁺, La₀.₉₈VO₄: Yb₀.₀₂³⁺, and La₀.₈VO₄: Tm₀.₀₁³⁺/Yb₀.₁₉³⁺ NCs (Fig. 1a, 1c, 1d) are well crystallized and all of the peaks can be well fitted with the tetragonal (t) phase of LaVO₄ with zircon structure (JCPDS Fill No. 32-0504) and the space group of I₄₁/amd and lattice constants a = b = 7.49 Å and c = 6.59 Å. Additionally, no other peak can be found in the patterns, revealing that a pure phase t-LaVO₄ can be obtained. From XRD data, the crystalite diameter (Dc) of La₀.₉₉VO₄: Tm₀.₀₁³⁺ nanocrystals were calculated to be 9-100 nm using the Scherer equation; $D_c = K\lambda /\beta \cos \theta$ [28] where β is the width of the observed diffraction line at its half intensity maximum (200), K is the so-called shape factor, which usually takes the value of about 0.9, and λ is the wavelength of X-ray source used in XRD. The XRD pattern of La₁₋ₓVO₄: Tmₓ³⁺ with different x (x = 0.005, 0.02) is similar to Fig. 1a, but increasing the amount of Tm³⁺ to x = 0.04 mmol leads to traces of tetragonal phase, which indicates that some of the Tm³⁺ ions crystallized as TmVO₃ and they cannot enter the lattice of LaVO₄, as shown in Fig. 1b which is in accordance with JCPDS (32-0504) and (25-0899).

![Fig. 1. XRD patterns of: (a) La₀.₉₉VO₄: Tm₀.₀₁³⁺ (b) La₀.₉₆VO₄: Tm₀.₀₄³⁺ (c) La₀.₉₈VO₄: Yb₀.₀₂³⁺ and (d) La₀.₈VO₄: Tm₀.₀₁³⁺/Yb₀.₁₉³⁺ nanocrystal.](image-url)
microscopy (SEM). SEM images of LaVO₄: Tm³⁺ nanocrystals are shown in Fig. 2.

![SEM images of LaVO₄: Tm³⁺ nanocrystals](image)

**Fig. 2.** SEM images of LaVO₄: Tm³⁺ nanocrystals

From the micrograph, it was observed that the as-prepared samples mainly composed of sheet-like morphology with an average length and diameter of 70 and 10 nm, respectively. These nanocrystals with irregular shapes were easily aggregated together. To further investigate the details of the morphology, TEM images were taken and shown in Fig. 3a, 3b and 3c. The size of nanosheets are about 50-150 nm, almost consistent with that observed from SEM image. The HRTEM image of the nanocrystals is shown in Fig. 3d, where the lattice fringe is measured to be 0.32 nm corresponding to the (2 0 0) lattice plane of tetragonal LaVO₄. It could be easily inferred from this image that these LaVO₄: Tm³⁺ nanosheets are single crystalline, uniform structure and free from defects in the examined area. Fig. 4 is the UV–Vis spectrum of the as-synthesized La₀.₉₉VO₄: Tm₀.₀₁³⁺ nanosheets dispersed in cyclohexane.

The UV–Vis diffuse reflectance spectra of sample show an absorption band in UV region with a maximum at 280 nm. This absorption peak of VO₄³⁻ groups is caused by a charge-transfer transition from the oxygen legends to the central vanadium atom in the V-O bond [10].

![TEM (a, b, c) and HRTEM (d) images of as-synthesized LaVO₄: Tm³⁺ nanosheets](image)

**Fig. 3.** TEM (a, b, c) and HRTEM (d) images of as-synthesized LaVO₄: Tm³⁺ nanosheets.

![UV-Vis diffuse reflectance spectra of La₀.₉₉VO₄: Tm₀.₀₁³⁺ nanosheets](image)

**Fig. 4.** UV-Vis diffuse reflectance spectra of La₀.₉₉VO₄: Tm₀.₀₁³⁺ nanosheets.

Also, the UV-Vis spectra of LaVO₄: Yb³⁺ and LaVO₄: Tm³⁺/Yb³⁺ NCs are similar to La₀.₉₉VO₄: Tm₀.₀₁³⁺. Therefore, the absorption spectrum is not dependent on the type of activator or sensitizer ion and it is related to the host lattice of LaVO₄ NCs. The downconversion luminescence of La₁₋ₓ(Tmₓ)VO₄: Tmₓ³⁺ (x= 0.005, 0.01, 0.02, 0.04) and La₀.₉₈VO₄: Yb₀.₀₂³⁺ and La₀.₉₈VO₄: Tm₀.₀₁³⁺/Yb₀.₁₉³⁺ nanocrystals were investigated. The room temperature PL spectra of the La₁₋ₓ(Tmₓ)VO₄: Tmₓ³⁺ NCs recorded in cyclohexane are shown in Fig. 5. These La₁₋ₓ(Tmₓ)VO₄: Tmₓ³⁺ NCs can emit spectral peaks in region 400-500 nm. The downconversion emission bands centered at 437 nm.
and 480 nm correspond to \(^{1}\text{D}_2 \to ^{3}\text{F}_4\) and \(^{1}\text{G}_4 \to ^{3}\text{H}_6\) transitions of Tm\(^{3+}\) ions, respectively. The PL intensity of LaVO\(_4\): Tm\(^{3+}\) NCs as a function of the activator ion concentration are shown in Fig. 6. It can be deduced that the relative emission of La\(_{1-x}\)VO\(_4\): Tm\(_x\)\(^{3+}\) NCs with lower Tm concentrations (x= 0.01 and 0.005) is much more intense and almost constant, but the emission intensity of La\(_{1-x}\)VO\(_4\): Tm\(_x\)\(^{3+}\) NCs is decreased with increasing Tm\(^{3+}\) concentration.

This behavior results from concentration quenching of Tm\(^{3+}\). The excess of Tm\(^{3+}\) ions causes the self interaction between adjoining Tm\(^{3+}\) ions and results in lower transitions from \(^{1}\text{G}_4\) and \(^{1}\text{D}_2\) levels. Eventually, the emission intensities of \(^{1}\text{G}_4 \to ^{3}\text{H}_6\) and \(^{1}\text{D}_2 \to ^{3}\text{F}_4\) transitions are diminished [30]. The emission spectra of La\(_{0.98}\)VO\(_4\): Yb\(_{0.02}\)\(^{3+}\) nanocrystals are shown in Fig. 7.

This sample with Yb\(^{3+}\) as activator emits spectra peak in region 700-800 nm, which can be ascribed to the transition of Yb\(^{3+}\) energy level from \(^2\text{F}_{5/2} \to ^2\text{F}_{7/2}\). Yb\(^{3+}\) ion has a single excited state \(^2\text{F}_{5/2}\) above the ground state \(^2\text{F}_{7/2}\), so it can emit photons at near infrared (NIR). Generally, Yb\(^{3+}\) has been used as sensitizer ion and according to the literature 17-20% Yb\(^{3+}\) is optimal doping [31,32]. So we chose 19% doping of Yb\(^{3+}\) and 1% Tm\(^{3+}\) as optimum value of Tm\(^{3+}\) according to Fig. 6, co-doped in La\(_{0.8}\)VO\(_4\): Tm\(_{0.01}\)\(^{3+}\)/Yb\(_{0.19}\)\(^{3+}\) nanocrystals.

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neighbor Tm$^{3+}$ ions and also cause the active excited state $^1G_4$ and $^3F_3$ of Tm$^{3+}$. As can be seen, more emission peaks are present in La$_{0.8}$VO$_4$: Tm$_{0.01}^{3+}$/Yb$_{0.19}^{3+}$ nanocrystals and the emission peak is intense comparing with LaVO$_4$: Tm$^{3+}$ and LaVO$_4$: Yb$^{3+}$.

Fig. 8. The emission spectra of La$_{0.8}$VO$_4$: Tm$_{0.01}^{3+}$/Yb$_{0.19}^{3+}$ nanocrystals.

Fig. 9 shows the absorption spectra of a Ru phenanthroline complex (Ru(dcphen)$_2$ (NCS)$_2$), as photosensitizer in the dye-sensitized solar cells, with a broad absorption band in region 400-700 nm [33]. Therefore, it may have potential to reabsorb the emitted light by LaVO$_4$: Tm$^{3+}$/Yb$^{3+}$ and regenerate excitons and enhance the photovoltaic conversion of dye solar cells.

In comparison with other methods, this process is simple, low cost, scale-up route and uses nontoxic precursor and solvent. Also for the first time, the hydrothermal method was used to synthesis of LaVO$_4$: Tm$^{3+}$ NCs. In this route, Yb$^{3+}$ was utilized as sensitizer for improvement of photoluminescence properties and the effect of activator materials on the photoluminescence characteristics was investigated.

Fig. 9. The absorption spectra of a Ru phenanthroline complex (Ru (dcphen)$_2$ (NCS)$_2$) [34].

4. Conclusion

In summary, LaVO$_4$: Tm$^{3+}$, Yb$^{3+}$ and Tm$^{3+}$/Yb$^{3+}$ nanocrystals were successfully synthesized through a hydrothermal method. As-synthesized nanocrystals show LaVO$_4$: Tm$^{3+}$, Yb$^{3+}$ and Tm$^{3+}$/Yb$^{3+}$ phase with tetragonal structure without any other impurities. The luminescent properties of LaVO$_4$: Tm$^{3+}$ has been improved with decreasing the molar concentration of Tm$^{3+}$ ions. The PL measurements showed that LaVO$_4$: Tm$^{3+}$/Yb$^{3+}$ nanocrystals could emit much more intense luminescence downconversion than LaVO$_4$: Tm$^{3+}$ nanocrystals. Therefore, LaVO$_4$: Tm$^{3+}$/Yb$^{3+}$ nanocrystals can be potentially used as downconversion material for enhancing the dye-sensitized solar cell efficiency.

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References