

Additive assisted hydrothermal synthesis, characterization and optical properties of one dimensional $\text{DyPO}_4:\text{Ce}^{3+}$ nanostructures

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ABSTRACT

One dimensional nanostructures of cerium doped dysprosium phosphate ($\text{DyPO}_4:\text{Ce}^{3+}$) were synthesized via hydrothermal route in the presence of different surfactants [sodium dodecyl sulfate (SDS), dodecyl sulfosuccinate (DSS), polyvinyl pyrrolidone (PVP)] and solvent [ethylene glycol and water]. The prepared nanostructures were characterized by Powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), Field emission scanning electron microscopy (FE-SEM), Transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), UV-VIS-NIR absorption spectrophotometer and photoluminescence (PL) studies. The PXRD and FTIR results indicate purity, good crystallinity and effective doping of Ce^{3+} in nanostructures. SEM and TEM micrographs display nanorods, nanowires and nanobundles like morphology of $\text{DyPO}_4:\text{Ce}^{3+}$. Energy-dispersive X-ray spectra (EDS) of $\text{DyPO}_4:\text{Ce}^{3+}$ nanostructures confirm the presence of dopant. UV-VIS-NIR absorption spectra of prepared compounds are used to calculate band gap and explore their optical properties. Luminescent properties of $\text{DyPO}_4:\text{Ce}^{3+}$ was studied by using PL emission spectra. The effect of additives and solvents on the uniformity, morphology and optical properties of the nanostructures were studied in detail.

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1. Introduction

Uniform inorganic nanostructures which have desirable phases and morphologies are quite important in modern chemistry and material science. They exhibit many interesting size- and shape-dependent properties which are both scientifically and technically important [1–4]. Uniform nanostructures of diverse morphologies, sizes, crystal structures and properties can be produced by the assistance of surfactants, polymers, solvent and capping ligands [5,6]. Now a day, one dimensional (1D) nanostructures such as nanorods, nanowires, nanotubes and nanobundles are the focus of attention in material science research because of their unique optical, thermal, electric and mechanical properties, which are different from those of their corresponding bulk material [7–10]. A remarkable progress has been made in exploring applications of one dimensional (1D) luminescent lanthanide ion based nanomaterials in telecommunication components, solid state lasers, displays, LEDs, catalysis, and biological fluorescence labelling [11–16]. In particular, much attention have been focussed on the

synthesis and optical properties of 1D rare earth metal ion doped lanthanide phosphate materials for their promising applications in the field of optoelectronic devices [17,18]. Among lanthanide orthophosphates, dysprosium orthophosphate (DyPO_4) has gained intensive interest due to its distinctive optical structural and magnetic properties [19–21]. Dysprosium orthophosphate is known to exist in the boundary positions between the hexagonal and the tetragonal phase and show polymorph transformation. So, its phase controlled synthesis has gained much attention. H. Lai et al. reported the influence of temperature and pH on phase specific synthesis of DyPO_4 and the polymorph transformation from tetragonal DyPO_4 to hexagonal $\text{DyPO}_4 \cdot 1.5\text{H}_2\text{O}$ in the presence of organic additives (EDTA). Thus, controlled synthesis of DyPO_4 is an interesting field and has attracted the attention of researchers. Besides this, although a series of DyPO_4 nanocrystals have been successfully synthesized by several researchers but their optical properties are not widely explored. The luminescent properties of $\text{DyPO}_4:\text{Eu}^{3+}$ with different crystal structures and morphologies were investigated by H. Lai et al. [22]. To the best of author's knowledge, there is no previous report regarding surfactant and ethylene glycol assisted hydrothermal synthesis and optical properties of Ce doped DyPO_4 .

Various techniques and methodologies have been used to prepare nanomaterials such as thermal decomposition [23],

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co-precipitation [24], hydrothermal [25], solvothermal synthesis [26] and sonochemical assisted [27] etc. Among these methods, hydrothermal synthesis is most efficient as it permits exceptional control over morphology, particle size and crystallinity of material [28,29]. In this method, the synthesis is carried out in a Teflon lined autoclave using water as a solvent. The nanoparticles synthesis takes place under high autogenous pressure at a temperature above the boiling point of the solution which ensures solubility of even sparingly soluble salts. In addition to this, conditions (temperature and pH) and organic additives (polymers, surfactants and capping ligands) are very important in determining the crystal structures and morphology of final products [30–32]. Yong Zhong et al. have reported a surfactant mediated micelle encapsulation method to produce porphyrin nanocrystals using the optically active precursor zinc porphyrin (ZnTPP) [33]. Yanshen Li et al. have synthesized uniform and well-dispersed one-dimensional $\text{Zn}_2\text{GeO}_4\text{:Mn}^{2+}$ phosphors via a facile solvothermal process with $\text{H}_2\text{O/EG}$ as solvent [34]. Yunzhi Dai et al. synthesized needle-like $\text{CaCO}_3\text{:Eu}^{3+}$ calcite phosphors by a simple carbonization method in an ethylene glycol– H_2O system and reported that needle-like $\text{CaCO}_3\text{:Eu}^{3+}$ calcite nanoparticles exhibit much stronger red emission under UV light excitation than cubic and spindle-like $\text{CaCO}_3\text{:Eu}^{3+}$ calcite nanoparticles [35].

Here, in this work, one dimensional $\text{DyPO}_4\text{:Ce}^{3+}$ nanostructures were successfully synthesized via hydrothermal method in the presence of surfactants [Sodium dodecyl sulfate (SDS), Dodecyl sulfosuccinate (DSS) and Polyvinyl pyrrolidone (PVP)] and solvent [ethylene glycol and water]. The effects of nature of additive and solvent on the preparation and optical properties of $\text{DyPO}_4\text{:Ce}^{3+}$ have been systematically investigated.

2. Experimental section

2.1. Materials

Dysprosium (III) nitrate monohydrate $\text{Dy}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (99.9%) and cerium nitrate hexahydrate $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%) were purchased from Alfa Aesar and used as received without further purification. Sodium dodecyl sulfate (SDS), dodecyl sulfosuccinate (DSS), polyvinyl pyrrolidone (PVP) and ethylene glycol was purchased from Sigma Aldrich. Phosphoric acid (H_3PO_4) was supplied by Himedia Chemical Reagent Company. Deionized water was used throughout the experiment.

2.2. Synthesis of $\text{DyPO}_4\text{:Ce}^{3+}$ nanostructures

In a typical synthesis, 0.45 mmol of $\text{Dy}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ and 0.05 mmol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were added to 10 ml of an aqueous solution containing 0.5 mmol additive (SDS/DSS/PVP). The mixture was vigorously stirred for 10 min 10 mL aqueous solution of 0.5 mmol H_3PO_4 was added dropwise to the above mentioned mixture. The obtained mixture was agitated for 30 min and then transferred into autoclave, sealed and maintained at 180°C for 18 h. After cooling of autoclave to room temperature naturally, the precipitates were collected and washed with deionized water and ethanol and then dried at 70°C for 12 h in air. $\text{DyPO}_4\text{:Ce}^{3+}$ nanostructures were also synthesized in water and ethylene glycol without any surfactant to study the effect of solvent on the properties of the products.

For reference undoped DyPO_4 was also prepared in aqueous solution using same reaction conditions without any additive. The prepared samples such as undoped DyPO_4 and $\text{DyPO}_4\text{:Ce}^{3+}$

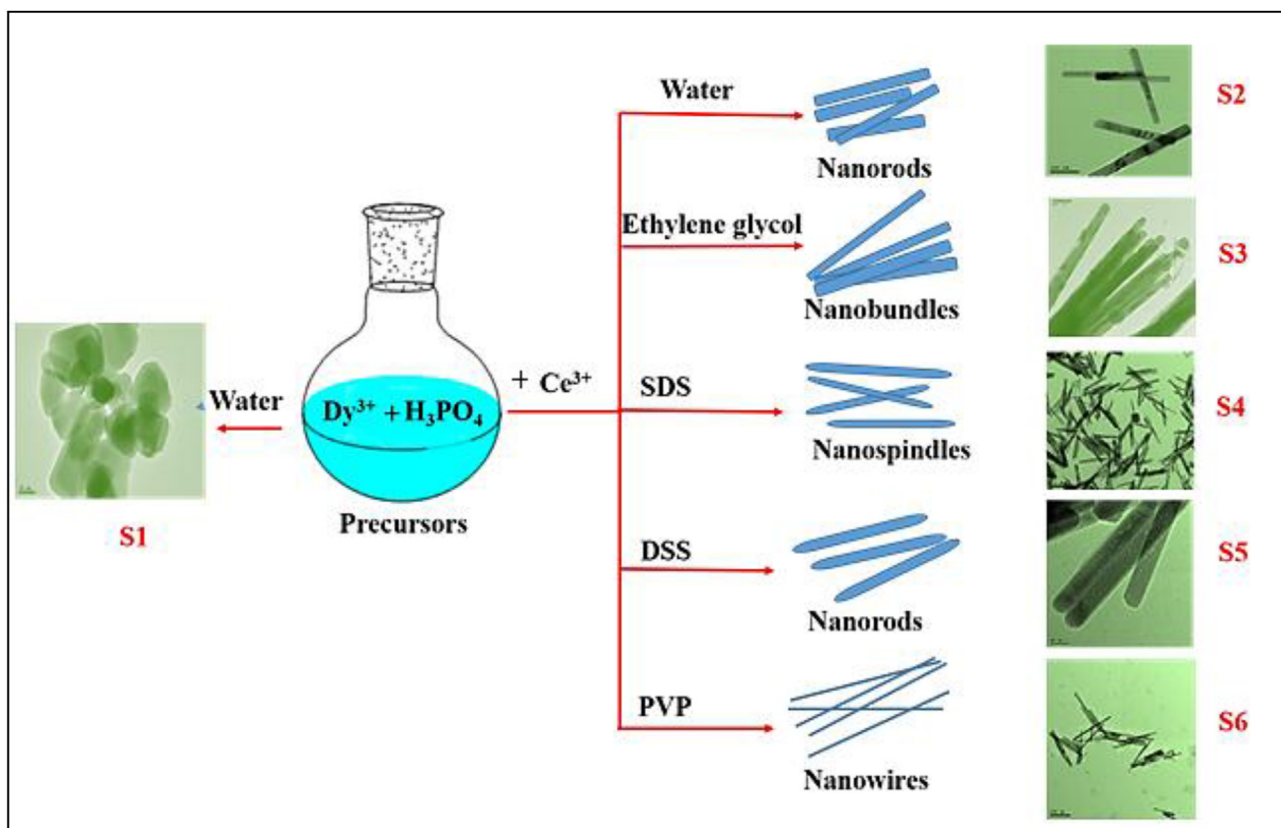


Fig. 1. Schematic diagram of the one dimensional $\text{DyPO}_4\text{:Ce}^{3+}$ nanostructures.

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