Effect of surface coating on structural and photophysical properties of CePO$_4$:Tb, nanorods

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A B S T R A C T

A facile and efficient method was established for the more productive synthesis of highly fluorescent CePO$_4$:Tb (core) and CePO$_4$:Tb@LaPO$_4$ (core/shell) nanorods (NRs) at low temperature. Subsequently, the surface of the core/shell NRs was functionalized by silica layer (CePO$_4$:Tb@LaPO$_4$@SiO$_2$, core/shell/Si) to enhance the solubility and colloidal stability character in an aqueous and non-aqueous solvent. XRD pattern shows the phase purity, crystallinity and single-crystalline nature of the hexagonal-rhabdophane type structure of NRs, which was further verified from FETEM images. TEM image shows a thin silica layer around the seed core/shell NRs. After coating of silica shell the resulting core/shell NRs have a mean diameter of about 20 nm and length up to 100 nm. The core/shell NRs demonstrate highest excitation and emission intensity, which was suppressed after silica layer coating due to enhancement in the multiphoton-relaxation process. However, core/shell/Si NRs represent high solubility in an aqueous environment on that basis it could find potential applications in photonic and photonic based biomedical sciences.

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1. Introduction

Since the unique luminescence properties of lanthanide nanomaterials (NMs) such as sharp absorption and emission lines, long decay time, large stock shift, low photobleaching, high thermally and photochemically stable, excellent biocompatibility and low toxicity [1–7]. Moreover, it is easy to achieved multicolor emission under a single excitation by changing the doped lanthanide ions or matrices [8–10]. Due to these novel luminescence properties, lanthanide NMs have been successfully applied in the different field of applied material sciences as well as biomedical sciences [11–14]. For luminescent nanoscale lanthanide materials, the decreasing size presents particular photophysical properties [13,15,16], which are different from bulk materials, and find the potential for use in optoelectronic devices and fluorescent bio-labeling. It is known that the luminescent properties of NMs are highly sensitive to their shape and dimensionally [17–19]. Therefore, synthesis of NMs in different shapes is a major challenge before employing these materials for developing functional structures for various applications. Presently, different solution based chemical routes have been developed to fabricate and assembled 1D nanostructures including, microwave [20], micro-emulsion [21], sonochemical, hydrothermal/solvothermal [22–25], sol–gel, thermally decomposition and

polyol-mediated process [26–29]. Most of these synthesis methods suffer from the requirements of high temperature, tedious procedures, special conditions, the yielding product is very low and weak solubility in normal media. Therefore, the development of practical methods for fabricating a large number of 1D nanostructure at low cost, at ambient conditions and aqueous soluble is still a great challenge for further study. Among these synthesis processes, co-precipitation method is cost effective, eco-friendly and operated at low temperature and generate novel materials with unusual properties such as large scale production, good dispersibility and particular shape and dimensional nanostructure [30–33]. Due to these lanthanide, NMs synthesized in an aqueous environment, they are hydrophilic in nature and can be easily functionalized for conjugation with biomolecules. However, in most of the cases, luminescence efficiency plays a key role because the sensitivity of labeling and efficacy of therapy are dependent on the luminescence of nanocrystals [34–36]. The core/shell structure is one of the most effective and practical strategies via coating a similar refractive index crystalline material on the surface of luminescent seed core NRs for enhancement the luminescence efficiency [37]. However, hydrophobic nature of these core/shell NMs was increase after core/shell structure formation, so that these NMs can post surface modified to render them aqueous soluble. Silica surface coating is most popular and effective strategy to enhance the solubility and colloidal stability, biocompatibility of the as

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prepared luminescent NMs [38,39]. Silica layer protects the core nanocrystals from the surrounding environment, inexpensive, and optically active, biocompatible, nontoxic and easy to functionalize with proteins and biomolecules.

Here, we proposed a facile and effective simple synthesis method for preparation of terbium doped cerium phosphate NRs for large scale production. Subsequently, an undoped LaPO$_4$ and silica layer were assembled around the surface of luminescent seed CePO$_4$:Tb (core) NRs. An undoped LaPO$_4$ layer protects the luminescent core from the oxidation of Ce^{3+} ion and surrounding surface trapping center, which plays as nonradiative centers. Amorphous silica surface coating provides the stability of colloid formed solution, resistance to high temperature and oxidation and prevents from damaging impact of aggressive agents. Furthermore, silica shell improves the solubility, colloidal stability, and biocompatibility in various aqueous and non-aqueous solvents. X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive-X-ray(EDX) analysis, Fourier transformed infrared (FTIR) and UV/Vis spectral techniques were used to investigated the crystal structure, morphology and surface properties of the as-prepared samples. The Tb^{3+} ion in core/shell nanostructure showed strongest emission intensity when excited by ultraviolet light. We observed that the surface chemistry remarkably altered the optical and photoluminescence properties of the luminescent NMs without changing the crystal structure because of formation of some tapping centers over the luminescent seed core NRs. The main motivation of this research is to develop a cost-effective, large scale productive and highly fluorescent with good solubility core/shell/Si NRs. These core/shell NRs not only have intense luminescence but also have high solubility and colloidal stability in aqueous media, which make them suitable for fluorescent biolabeling applications.

2. Experimental section

2.1. Materials

Cerium nitrate hexahydrate (BDH, UK), Terbium oxide (99.9%, Alfa Aesar, Germany), lanthanum oxide (BDH, UK), Na$_2$HPO$_4$, urea, ethanol, ammonia and tetraethyl-orthosilicate (TEOS) were analytical grade. Lanthanum nitrate and terbium nitrate were prepared by dissolving corresponding oxides into diluted nitric acid. Milli-Q water was used for the synthesis of the material.

2.2. Synthesis of terbium doped cerium phosphate NRs

Nanostructured CePO$_4$:Tb was synthesized at low temperature by a simple aqueous rout using urea hydrolysis. Briefly, 0.156 g (0.9 mmol) Ce(NO$_3$)$_3$6H$_2$O and 0.018 g(0.1 mmol) Tb(NO$_3$)$_3$6H$_2$O were dissolved in a 50 ml distilled water to make the clear solution at room temperature with normal pH. An aqueous solution of urea (9.79 g) was mixed in lanthanide solution and the whole solution was kept on a hot plate for constant stirring with heating at 80 °C. Then 20 ml of an aqueous Na$_2$HPO$_4$ (0.147 g) solution was prepared and injected into the above mixed solution drop by drop. The resulting mixed system was stirred on a hot plate at 80 °C for 3 h. The obtained precipitate was separated by centrifugation, washed several times with Milli-Q water and then dried overnight at 60 °C.

2.3. Synthesis of CePO$_4$:Tb@LaPO$_4$ core/shell NRs

Above synthesis method was followed for preparation of CePO$_4$:Tb@LaPO$_4$ (core/shell) sample. 0.143 g CePO$_4$:Tb NRs was dispersed in minimum amount Milli-Q water and then 20 ml aqueous dissolved La(NO$_3$)$_3$6H$_2$O (0.186 g) solution was added, and the mixed solution was sonicated and later vigorously stirred for 1 h. Then aqueous dissolved Na$_2$HPO$_4$ (0.137 g) solution was added dropwise to the above suspension under magnetic stirring for 3 h. the resulting precipitate was centrifuged, washed several times with distilled water to remove unreacted reactant, then dried overnight at 60 °C.

2.4. Synthesis of CePO$_4$:Tb@LaPO$_4$@SiO$_2$ core/shell/Si NRs

For designing CePO$_4$:Tb@LaPO$_4$@SiO$_2$ nanostructured, the as prepared CePO$_4$:Tb@LaPO$_4$ sample (0.056 g) was treated with ethanol by ultrasonication for 30 min, which was then separated by centrifugation and dispersed in a mixture of ethanol (100 ml), MilliQ water (25 ml) and concentrated NH$_4$OH (500 µml). This suspension was vigorously stirred for 30 min at room temperature, then 300 µml TEOS was added dropwise into the reaction mixture. After stirring for 4–6 h, the product was separated by centrifugation and washed several times with Milli-Q water and ethanol and then dried overnight at 60 °C.

2.5. Characterization

Powder X-ray diffraction data were collected using a PANalytical X'-ray diffractometer equipped with Ni filter (Cu K$_\alpha$, λ = 1.5405 Å). Transmission electron microscopy (TEM) images were recorded using a Field emission transmission electron microscopy (JEOL, JEM-2100F, Japan) operating at 200 kV, which is equipped with energy dispersive X-ray diffraction analysis. Infrared spectra were recorded using a Fourier transmission infrared (FTIR) Vertex 80 (Bruker, USA) using KBr pellet technique. Optical absorption spectra were measured by Cary 60 UV–Vis (Agilent Technologies, USA) spectrophotometer. The photoluminescence spectra were measured on Fluorolog 3 spectrophotometer (Model, FL3-11, Horiba JobinYvon Edison, MJ, USA). All measurements were performed at room temperature.

3. Results and discussion

X-ray diffraction pattern was used for determination of crystal phase and crystallinity of the as-prepared nano-products. Fig. 1 illustrates the X-ray diffraction pattern of CePO$_4$:Tb(core), core/shell and silica modified core/shell/Si NRs. The results of XRD clearly indicate that all diffraction peaks are well indexed to the hexagonal rhabdophane type CePO$_4$ and lattice constant highly comparable to the values of (JCPDS card No. 35-0614) [40–43]. No impurity peak is detected from the XRD pattern, indicating the phase purity and homogeneously distribution of terbium ion into the single phase CePO$_4$ NRs. The broadening in diffraction planes widths should be due to the nanocrystalline nature of the as-prepared product. The observed lattice parameters are a = 6.7908 Å, b = 6.895 Å, and c = 6.457 Å with β = 103.5°. The values are comparable with bulk counterpart CePO$_4$ [34,35]. Notably, it is observed that the reflection lines are a little bit sharper in core/shell samples in respect to core sample, it could be due to enhancement in grain size after surface growth of crystalline passivated LaPO$_4$ shell [30,31]. It is worth noticing that, the reflection peak width in core/shell/Si NRs in slightly increase compared to the bare core and core/shell NRs, it suggested that silica framework expanded the nanopores structure over the core/shell NRs and rearranged the Si-O-Si network structure without any impurities. The strongest XRD peak was used for estimation of average particle size of the as-prepared core, core/shell and core/shell/Si NRs. According to the Scherrer formulae and the full-width-half-maxima of the main diffraction peak at 2θ = 30°, the average grain