Journal of Luminescence 157 (2015) 257–263

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Optical and structural studies of $CaMoO_4$:Sm, $CaMoO_4$:Sm@$CaMoO_4$ and $CaMoO_4$:Sm@$CaMoO_4$@SiO_2 core–shell nanoparticles

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A R T I C L E I N F O

Article history:
Received 16 August 2013
Received in revised form
28 August 2014
Accepted 1 September 2014
Available online 8 September 2014

Keywords:
Calcium molybdate nanoparticles
Band gap energy
Photoluminescence

A B S T R A C T

A simple polyol and Stober surface coating process was introduced to synthesize $CaMoO_4$:Sm and their silica-coated $CaMoO_4$:Sm nanoparticles. Powder X-ray diffraction (XRD) and different spectroscopic techniques were employed to investigate the structural and optical properties of as-prepared nanoparticles. The surface of $CaMoO_4$:Sm nanoparticles was modified to alter the solubility of the nanoparticles and to study the influence of surface coating on emission spectra of samarium ions. Optical properties of these nanoparticles showed a strong dependence on the surface modification of nanoparticles, indicating the influence of coating in the enhancement of luminescent intensity. These results were attributed to the formation of chemical bonds between $CaMoO_4$:Sm@ $CaMoO_4$ core and non-crystalline SiO_2 shell via Mo–O–Si bridges, which activate the 'dormant' Sm^{3+} ion on the surfaces of nanoparticles. It is, therefore, concluded that good hydrophilicity resulting from active functional groups in solutions and more intense luminescence enable doped core–shell nanoparticles to have great potential to be used as fluorescence biolabels in the future.

1. Introduction

In recent years, nanostructured and nanocrystalline materials, typically defined as polycrystalline solids with particle diameter less than 100 nm, offer new possibilities for advanced phosphor applications [1,2]. In fact, the bulk properties of those materials depend on a high percentage of grain boundaries, although atomic structure at interfaces is not completely understood. In particular, lanthanide ions in insulating hosts find uses in a variety of applications such as phosphors for fluorescent lighting, display monitors, X-ray imaging, scintillators and amplifiers for fiber-optics communication [3–6]. Besides their intrinsic interest, nanostructured materials also provide model systems for studying the effect of surfaces on bulk properties. However, the luminescence efficiency of these materials is often limited by dynamics of the lanthanide ion, which depends on interactions with insulating host and therefore lanthanide dopant can be used as a sensitive probe of chemistry and structure of its host [1,2]. Moreover, it has been shown that quantum efficiency of luminescent ion-doped nanocrystals increases as the size of crystals increases. This quantum efficiency of these nanomaterials further can be improved by surface coating of a crystalline shell around the nanocrystals [7–10]. The crystalline materials coating reduces defects on the surface and minimizes quenching of the excited states of lanthanide ions. To reduce these defects, the growth of crystalline shell of a suitable inorganic material around each nanocrystal to form the core–shell structures has been regarded as an effective strategy to improve luminescent efficiency. Previously, some investigators applied this strategy to enhance the luminescent efficiency of lanthanide ion-doped nanomaterials through growth of a crystalline shell on the surface of nanocrystals [7–10]. These systems doped with lanthanide ions are based on two materials with similar lattice constants to avoid the formation of defects at the core–shell interface. In this structure, the distance between luminescent lanthanide ions and surface quenchers is increased, thus reducing the nonradiative pathways and increasing the quantum yield of nanomaterials.

Herein, $CaMoO_4$:Sm nanoparticles were selected as a target material to study for the following reasons: (i) $CaMoO_4$ belongs to the family of ABO_4 metal oxides that have been extensively applied as phosphors, laser hosts, and catalysts; (ii) $CaMoO_4$ is an excellent luminescent host, owing to the efficient energy transfer (ET) from MoO_4 absorption to the excited states of the activators (lanthanide-ions) [5,11]. In addition, luminescence is highly sensitive to variations of lattice parameters. Therefore, Sm^{3+} could be taken to act as a structural probe and a luminescence center to study

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http://dx.doi.org/10.1016/j.jlumin.2014.09.001
0022-2313/© 2014 Published by Elsevier B.V.

local environments pertinent to the lattice structural changes and energy transfer; (iii) such as all other alkali-earth metal molybdate and tungstate nanoparticles, $CaMoO_4$ nanoparticles may have surfaces perturbed by molybdate groups $[MoO_4]^{2-}$, in which it is highly possible to tune lattice structure and electron interactions, and moreover to change from lattice expansion to lattice contraction; in particular; (iv) many researchers have reported on the luminescent properties of lanthanide ion-doped $CaMoO_4$ nanoparticles prepared by various synthetic methods, which may provide a strong basis for studying the particle size dependences of lattice parameters and properties.

In this work, we report the synthesis of $CaMoO_4$:Sm, $CaMoO_4$:Sm@$CaMoO_4$ and $CaMoO_4$:Sm@$CaMoO_4$@SiO_2 core–shell nanoparticles using a polyol process under urea thermal decomposition. Comparative powder X-ray diffraction, optical absorption spectra, optical band gap energy, FT-IR, FT-Raman and photoluminescent properties were discussed to investigate the alteration in structural and optical properties after core–shell formation. The formation of crystalline shell around the surface of core-nanoparticles enhanced the luminescent intensity due to reduced surface defects by minimizing nonradiative decay. The $CaMoO_4$:Sm@$CaMoO_4$ core–shell nanoparticles would be toxic, and have weak biocompatibility and poor solubility. To overcome these problems, an amorphous silica shell was encapsulated around the core nanoparticles, which is optically transparent, cheap, chemically inert, non-toxic, biocompatible, photochemically stable even under laser photolysis and easily transferred into a wide range of solvents. The introduced silica shell could be used for further bioanalysis applications.

2. Experimental section

2.1. Materials

Samarium oxide (99.99%, Alfa Aesar, Germany), calcium carbonate ($CaCO_3$, 99.99%, E-Merck, Germany), ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$,99.3%, Acros Organics), tetraethylorthosilicate (TEOS, 99 wt% analytical reagent A.R.), ethylene glycol (EG; E-Merck, Germany), Urea $(NH_2)_2CO$; E-Merck, Germany), C_2H_5OH, HNO_3 and NH_4OH were used as starting materials without any further purification. Nanopure water was used for the preparation of solutions. The ultrapure de-ionized water was prepared using a Milli-Q system (Millipore, Bedford, MA, USA). All other chemicals used were of reagent grade.

2.2. Preparation of $CaMoO_4$:Sm nanoparticles

For typical preparation of Sm^{3+}-doped $CaMoO_4$ nanoparticles, $CaMoO_4$:Sm^{3+} was prepared at a low temperature 150 °C using urea hydrolysis in ethylene glycol as a chelating agent. 1.0 g of $CaCO_3$ and 0.5 g of Sm_2O_3 were dissolved together in concentrated nitric acid (HNO_3) and heated up to 80 °C to remove excess acid and neutralized by the addition of de-ionized water. 0.1436 g ammonium molybdate dissolved in methanol (50 ml) was mixed up in this forgoing reaction and kept for constant stirring with heating (80 °C) on a hot plate for 1 h. 2.0 g urea dissolved in 50 ml EG was introduced into this reaction. The reaction mixture was heated up to 150 °C for 3 h under reflux conditions until the white precipitate appeared. The synthesized product precipitate was then collected by centrifugation, washed with de-ionized water and absolute ethanol several times, and dried in an oven at 200 °C for 6 h for further characterization.

2.3. Preparation of $CaMoO_4$:Sm@$CaMoO_4$ core–shell nanoparticles

For the preparation of $CaMoO_4$: Sm@$CaMoO_4$ core–shell nanoparticles, similar polyol process was used as discussed above. 1.00 g of $CaMoO_4$:Sm was dispersed in 4 ml of de-ionized water containing 1 g of EG and 2 g urea with constant stirring for 30 min. Typically 0.72 g $CaCO_3$ was dissolved in HNO_3 acid and excess amount of HNO_3 was evaporated on a hot plate by adding de-ionized water. Then a solution of calcium carbonate and 1.27 g ammonium molybdate dissolved in methanol was injected into the foregoing mixed system, and the suspension was refluxed at 150 °C for 3 h until precipitation occurred. This white precipitate was centrifuged and washed many times with methanol to remove excess un-reacted reactants [7]. The core–shell nanoparticles were collected after centrifugation and allowed to dry at ambient temperature for further characterization.

2.4. Preparation of silica-coated $CaMoO_4$:Sm@$CaMoO_4$@SiO_2 core–shell nanoparticles

The $CaMoO_4$:Sm@$CaMoO_4$@SiO_2 core–shell nanoparticles were prepared through a versatile solution sol–gel method as follows [12–14]. The synthesized $CaMoO_4$:Sm@$CaMoO_4$ nanoparticles (50 mg) were well dispersed in a mixed solution of deionized water (50 ml), ethanol (70 ml) and concentrated aqueous ammonia (1.0 ml) in a three-neck round-bottomed flask. Afterward, 2.0 ml of tetraethyl orthosilicate (TEOS) was added drop-wise in 2 min, and the reaction was allowed to proceed for 6 h under continuous mechanical stirring. After 6 h continuous stirring the silica-coated $CaMoO_4$:Sm@$CaMoO_4$ core–shell nanoparticles were separated by centrifugation and then washed several times with ethanol and dried at room temperature.

2.5. Characterization

The X-ray diffraction (XRD) of powder samples was examined at room temperature with the use of PANalytical X'Pert X-ray diffractometer equipped with a Ni filtered using Cu Kα ($\lambda = 1.54056$ Å) radiations as X-ray source. Raman spectra were recorded on a Jobin Yvon Horiba HR800 UV Raman microscope using a HeNe laser emitting at 632.8 nm. The UV/vis absorption spectra were measured using a Perkin-Elmer Lambda-40 spectrophotometer, with the sample contained in 1 cm^3 stoppered quartz cell of 1 cm path length, in the range 190–600 nm. Thermogravimetric analysis (TGA) was performed with TGA/DTA, Mettler Toledo AG, Analytical CH-8603, Schwerzenbach, Switzerland. The FTIR spectra were recorded on a Perkin-Elmer 580B IR spectrometer using a KBr pellet technique in the range 4000–400 cm^{-1}. The photoluminescence (PL) spectra were recorded on Horiba Synapse 1024 × 256 pixels, size of the pixel 26 μm, detection range: 300 (efficiency 30%) to 1000 nm (efficiency:35%). A slit width of 100 μm was employed, ensuring a spectral resolution better than 1 cm^{-1}. All measurements were performed at room temperature.

3. Results and discussion

3.1. XRD study

Powder X-ray diffraction (XRD) pattern of $CaMoO_4$:Sm, $CaMoO_4$:Sm@$CaMoO_4$ and $CaMoO_4$:Sm@$CaMoO_4$@SiO_2 core–shell nanoparticles was recorded to examine the crystalline nature of as-synthesized products. It is found that the diffraction peak positions and intensity are well-defined matches, indicating high crystallinity of the synthesized nanoparticles [3–7]. They show