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Novel EGCG assisted ultrasound synthesis of self-assembled Ca_2SiO_4:Eu^{3+} hierarchical superstructures: Photometric characteristics and LED applications

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ABSTRACT

This paper reports for the first time ultrasound, EGCG assisted synthesis of pure and Eu^{3+} (1–5 mol%) activated Ca_2SiO_4 nanophosphors having self-assembled superstructures with high purity. The shape, size and morphology of the product were tuned by controlling influential parameters. It was found that morphology was highly dependent on EGCG concentration, sonication time, pH and sonication power. The probable formation mechanism for various hierarchical superstructures was proposed. The PL studies of Ca_2SiO_4:Eu^{3+} phosphors can be effectively excited by the near ultraviolet (UV) (396 nm) light and exhibited strong red emission around 613 nm, which was attributed to the Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$) transition. The concentration quenching phenomenon was explained based on energy transfer between defect and Eu^{3+} ions, electron–phonon coupling and Eu^{3+}–Eu^{3+} interaction. The Judd–Ofelt intensity parameters and radiative properties were estimated by using PL emission spectra. The photometric studies indicate that the obtained phosphors could be a promising red component for possible applications in the field of white light emitting diodes.

1. Introduction

Advances in nano/bulk superstructures have been led by the improvement of novel synthesis routes which offer the control of size, morphology, surface area of the product for selective applications. Recently, it has been reported that various nanostructures have been prepared by sonochemical process with several advantages over other methods namely uniform size distribution, higher surface area and high purity. In this method, consumption of high intensity ultrasound offers a novel and versatile approach for obtaining self assembled nanomaterials. The chemical reaction which occurs at high temperature and pressure in a short duration of time provides the necessary environment for the nucleation and to self oriented hierarchical superstructures [1,2]. The molecules in the solution undergo chemical reaction followed by acoustic cavitation and formation (nucleation) of bubbles. Further, when it was subjected to ultrasonic radiation (20 kHz–10 MHz) there will be a growth by diffusion of solute atoms into the bubbles and mechanical collapse of critical-sized bubbles in the liquid solutions. During collapsing (<1 ns), the temperature and cooling rate was extremely high (5000–25,000 K and 10^{11} K/s), causing the broken of chemical bonds. Further, in ultrasonic irradiation faster hydrolysis rate was achieved as a result crystallinity of material greatly enhanced [2].

Nanophosphors may have more advantages over traditional micronsized phosphors as a result, electrical and optical properties greatly enhanced. Further, nano sized particles exhibit quantum size effect, as well as high surface to volume ratio, band gap can reduce, enhance the luminescence and improves the surface and interfacial effects [3,4]. Therefore, phosphors are significant materials for the potential applications, like fluorescent lamps, light emitting diodes (LEDs), field emission display (FEDs), plasma

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display panels (PDPs) and high energy detectors [5,6]. Among these applications phosphor converted white light emitting diodes (pc-WLEDs) are important candidates for solid state lighting because of their excellent properties such as long operational lifetime, energy saving, high brightness, higher luminescent efficiency, compactness, and environment friendliness [7].

Silicates are highly chemical resistance and visible light transparency and hence they are attractive class of inorganic materials used for wide range of applications [8]. Further, they have been extensively studied due to their high thermal, chemical stabilities, low cost, excellent water resistance and strong absorption in the near-UV region [9]. RE activated silicate phosphors have considerable practical applications such as display devices, detector systems, immunoassays, scintillators, LEDs etc. Table.1 shows the various Eu^{3+} activated silicate hosts prepared by different chemical methods [10–16].

Herein, for the first time we report controlled fabrication of several hierarchical superstructures of Ca_2SiO_4:Eu^{3+} nanophosphor with high yield and good uniformity using EGCG ultrasound assisted synthesis. In addition, various novel self-oriented superstructures were also obtained by varying the experimental conditions. Effect of morphology on sonochemical time, power and the pH of the precursor solution were discussed in detail. The possible formation mechanism of different hierarchical superstructures was put forward on the basis of time-dependent experiments. To evaluate the potential applications of the product, the photometric properties (PL, CIE, CCT and color purity) of Ca_2SiO_4:Eu^{3+} nano/micro superstructures were studied in detail.

2. Synthesis

Undoped and Eu^{3+} doped Ca_2SiO_4 nano/microstructures with varying Eu^{3+} ions concentrations were synthesized by EGCG assisted ultrasound method. The chemicals used for the synthesis were tabulated in Table 2. The stoichiometric quantities of precursors were considered for the preparation of Eu^{3+} doped Ca_2SiO_4. 11.099 g of $Ca(NO_3)_2$ as a source of calcium dissolved in 50 ml of distilled water and 11.18 ml of tetra ethyl orthosilicate (TEOS) as a source of silicate into distilled water which make up the solution to 50 ml. These aqueous solutions were thoroughly mixed in a magnetic stirrer to get a uniform solution. The different concentrations of Eu^{3+} ions (1–5 mol%) was also added in the above solution. 5 g of EGCG ($C_{22}H_{18}O_{11}$; 458.372 g/mol) extract was dissolved in 100 ml double distilled water and added to the resultant mixture slowly (5, 10, 15, 20 and 25 ml). Then, the solution mixture was stirred ultrasonically (ultrasonic frequency 20 kHz, power 300 W) at a fixed temperature of 60 ± 3 °C and by varying sonication time (1–6 h). The solution was kept undisturbed until a white precipitate was formed. The precipitate was filtered and washed several times by distilled water and ethanol to remove any unreacted material in the centrifuge instrument. The precipitated powder was dried at 60 ± 3 °C for 3 h in a vacuum oven and calcined at 950 ± 10 °C used for further characterizations. The schematic diagram for the synthesis of Eu^{3+} doped Ca_2SiO_4 nanophosphor was shown in Fig. 1.

Table 2
Chemicals used in the present study.

Material	Assay
Tetra ethyl orthosilicate	99.9% Sigma Aldrich (India)
Calcium nitrate	99.9% Sigma Aldrich (India)
Europium nitrate	99.9% Sigma Aldrich (India)
Anhydrous sodium hydroxide	99% S D fine-chem. Limited (India)
Ethanol	99% S D fine-chem. Limited (India)
EGCG	99.9% Phyto Biotech Pvt. Ltd. (India)

2.1. Characterization

Phase purity and crystallinity of nanophosphors were measured using a powder X-ray diffractometer (PXRD, Shimadzu 7000). Cuk_α (1.541 Å) radiation with nickel filter was used. Scanning electron microscopy (SEM) measurements were performed on a Hitachi table top, Model TM 3000. Transmission electron microscopy (TEM) was performed on a Hitachi H-8100 accelerating voltage up to 200 kV, LaB_6 filament equipped with EDS (Kevex sigma TM Quasar, USA). The prepared samples were dispersed on a sticky carbon pad. The thin layer of gold (Au) was deposited on the sample to get better image quality. The diffuse reflectance spectroscopy of the samples was recorded on spectrometer Perkin Elmer (Lambda-35). The Jobin-Yvon spectroflourimeterfluorolog-3 operational with 450 W xenon lamp as an excitation source was used for photoluminescence (PL) measurement.

3. Results and discussion

The SEM images of the optimized Eu^{3+} (4 mol%) doped Ca_2SiO_4 phosphors without EGCG at different sonication times (1, 2, 3, 4, 5 and 6 h) was shown in Fig. 2. By comparing the micrographs of the phosphors with various sonication times, it was evident that ultrasound duration time significantly changes the morphological features. The SEM micrographs of Ca_2SiO_4:Eu^{3+} (4 mol%) nanophosphor obtained for1 h sonication exhibit an agglomerated particles (Fig. 2(a)). When the ultra-sonication time was increased to 2 h, the needle-like shape morphology was dominated (Fig. 2 (b)). However, when the sonication time was increased to 3 h, flower like morphology was obtained (Fig. 2(c)). When increase the reaction time to 4 h showed the formation of large number of long needle-like shaped with well-defined morphology with typical widths of (30–50) μm and lengths in the range of (80–140) μm respectively. Normally in sonochemical synthesis two types' of reactions occur; (i) interaction between cavitation bubble with the surrounding bulk solution leads to crystalline nature and (ii) inside the collapsing bubbles leads to amorphous material. In the present case, crystalline powders with needle like morphology was obtained, hence the formation of the Ca_2SiO_4 was in the interfacial region. The formation mechanism of the needle-like

Table 1
Method of preparation, formation temperature and morphology of the product obtained in various silicate phosphors.

Material	Method of preparation	Formation temperature	Morphology of the product	References
Sr_2SiO_4:Eu^{3+}	Spray-drying process	1150 °C	Microspheres	Hao Feng et al. [10]
Sr_2SiO_4:Eu^{3+}	Solution combustion method	900 °C	Porous and irregular shaped particles	Nagabhushana et al. [11]
$CaSrSiO_4$:Eu^{3+}	Co-precipitating solvo-thermal	1200 °C	Pop-corn like structure	Sakthivel Gandhi et al. [12]
Zn_2SiO_4:xEu^{3+}	Solid state method	800 °C	Irregular shaped particles	Nur Alia Sheh Omar et al. [13]
Ca_2SiO_4:Eu^{3+}	Solution combustion process	950 °C	Highly porous and agglomerated particles	Sunitha et al. [14]
Mg_2SiO_4:Eu^{3+}	Solution combustion process	350 °C	Highly porous and irregular morphology	Ramachandra Naik et al. [15]
Mg_2SiO_4:Eu^{3+}	Polyacrylamide gel method	900 °C	Irregular shaped particles	Tabrizi et al. [16]
Ca_2SiO_4:Eu^{3+}	Sonochemical synthesis	900 °C	Hierarchical superstructures	Present work