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An overview of morphological studies of various dopants on Strontium titanate

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Abstract: SiO_2@$SrTiO_3$:Eu^{3+} (1 mol%), Li (1 wt%) core–shell nanopowders (NPs) were prepared by using combustion process and its morphology was studied. SiO_2@$SrTiO_3$: Dy^{3+} (5 mol %) nanopowders fabricated via the low temperature sonochemical route by utilizing bio-surfactant Aloe Vera gel extract. SEM analysis was done. Broom-like hierarchical structures of $SrTiO_3$:Nd^{3+} (1–11 mol %) nanophosphors (NPs) were fabricated via CTAB assisted hydrothermal route. Controlled experiments namely, reaction temperature, surfactant concentration, pH and time duration were performed and its influences on morphology of the product was investigated. These conditions may tune the simple structures to broom-like hierarchical structures.

Keywords: Bio- surfactant, Core-shell, Alkali – halide fluxes, Nanophosphor

1. INTRODUCTION

Nano research created many advantages in the field of surface based science due to its quantum size effects and increased surface to volume ratio [1–3]. The surface modified nanopowders (NPs) with fine-tuned morphology create numerous interest for the researchers due to its many scientific and industrial applications [4]. Generally, the surface defects may hindrance the various properties of the NPs. To overcome from such a problem, the core-shell materials with nano/micron size were extensively used owing to its tunable sizes and inexpensive than other materials [5–8]. As a consequence, silica was extensively used as a surface modifier due to its outstanding chemical stability, optical transparency, certainly thickness controllable shell, low cytotoxicity and biocompatibility [9]. Hence, silica modified NPs acts as a luminescent probe and offers many possible applications in the fields, namely immunoassaying, DNA sequencing and clinical diagnosing. In addition, silica modified NPs can avoid renal filtration, results for long habitation time in the bloodstream, which gives sufficient information of diseased tissues [10].

Till date, many host materials were reported in the literature. Among, strontium titanate ($SrTiO_3$) was considered to be novel host for low-voltage electron-excitation displays and white LEDs applications because of its wide energy band gap (3.3–4.5 eV) nature and chemical and compositional stability at harsh environment [11]. In addition, SrTiO3 based materials offers many potential applications, namely dynamic random access memory, tunable microwave gadgets, photo-electrodes for hydrogen production, hydrogen storage etc. [12,13].

2. EXPERIMENTAL METHODS OR METHODOLOGY

2.1 Synthesis of SiO_2@$SrTiO_3$:Eu^{3+}: Li^+ nanoparticle using solution combustion method

The micrometer sized uniform SiO_2 spheres were synthesized via well-known Stöber method [14]. In a typical synthesis tetraethyl orthosilicate (TEOS, 99 wt%) was added into 42.4 ml ethanol solution, 5.4 ml double distilled H_2O and 29.4 ml $NH_3.H_2O$ (25–28 wt%) to synthesize SiO_2 particles. The silica particles were centrifuged and washed several times with absolute ethanol and double distilled water. The obtained product was dried at 80 ^oC for 20 h.

The core–shell structured $SrTiO_3$:Eu^{3+} (1 mol%), Li (1 wt%) NPs was synthesized by a solution combustion method. The stoichiometric quantities of Strontium nitrate: $Sr(NO_3)_2$ (Sigma Aldrich 99 %), Europium nitrate: $Eu(NO_3)_3$ (Sigma Aldrich 99 %), Lithium nitrate: $LiNO_3$ (AR), Titanium (IV) isopropoxide: $Ti[OCH(CH_3)_2]_4$ (Sigma Aldrich 97 %), Citric acid: $[C_6H_8O_7]$ (Sigma Aldrich 99 %) and Polyethylene glycol: $C_{2n}H_{4n+2}O_{n+1}$ were dissolved in double distilled water. The SiO_2 particles obtained from Stöber route was added to the above solution and introduced into a pre-heated muffle furnace maintained at 500 ^oC. Due to the addition of citric acid into the reaction mixture, combustion took place instantaneously and forms NPs. Step by step reaction mechanism for the formation of $SrTiO_3$:Eu^{3+}: Li^+ NPs on the surface of SiO_2 core shells was shown in Fig.1.

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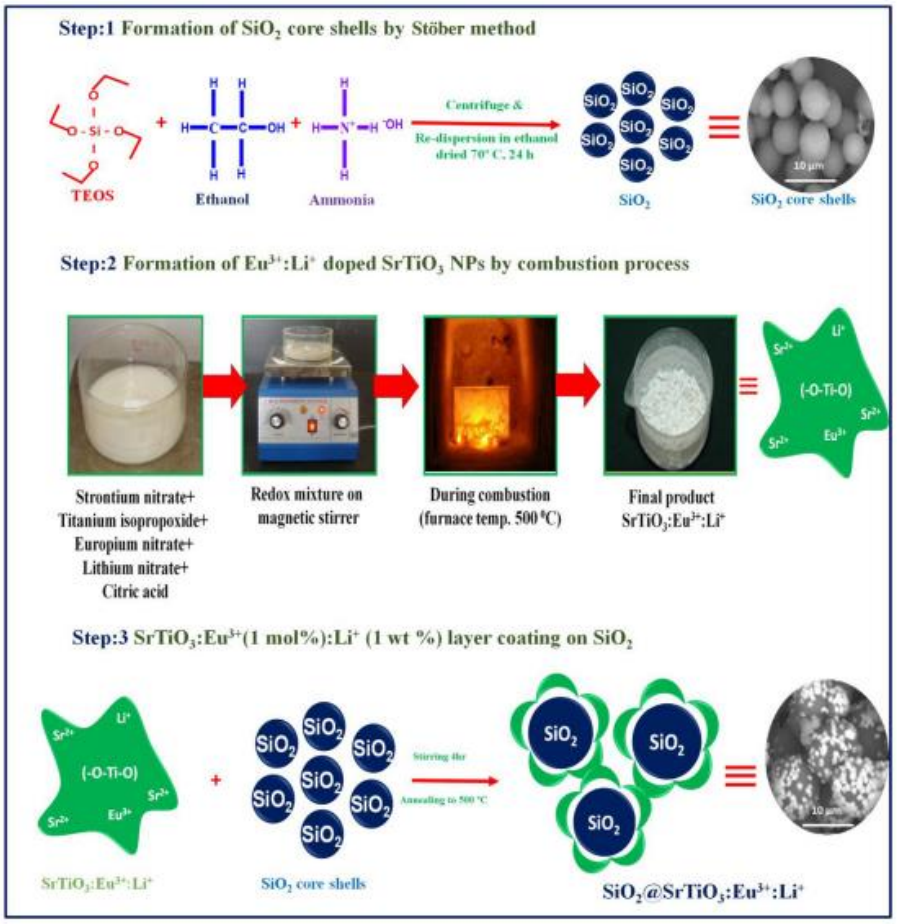

2.2. Synthesis of SiO_2@$SrTiO_3$:Dy^{3+} nanopowders using ultrasound method

The STD NPs was prepared by using stoichiometric quantities of Strontium chloride [$SrCl_2$, (Sigma Aldrich 99.9%)], Titanium (IV) chloride [$TiCl_4$, (Sigma Aldrich 97%)] and Dysprosium (III) chloride hexahydrate [$DyCl_3.6H_2O$, (Sigma Aldrich, 99.9%)] and Aloe Vera gel extract (as a bio-surfactant) was thoroughly dissolved in double distilled (DD) water (~100 ml) using a magnetic stirrer. The resultant reaction solution was treated with ultrasound using titanium made horn probe sonicator by adjusting ultrasonic frequency ~20 kHz and power ~ 300 W. After a certain time, the reaction mixture undergoes precipitation and obtained product was washed and filtered many times using DD water and alcohol. The resultant powder was dried at the ~ 80 °C for 1 h and further calcined at ~ 800 °C for 3 h. Thereafter standard Stöber method was followed for coating [15]. The stoichiometric amounts of fabricated STD NPs were thoroughly mixed in 50 ml of absolute ethanol by using an ultrasonic probe sonicator for ~ 1 h.

The 30 ml of ammonium hydroxide solution and 1 ml of TEOS were added slowly in a dropwise to the above resultant solution. The final reaction mixture was thoroughly mixed using a probe sonicator for ~ 3 h in an ice bath. The precipitate obtained at the end of the reaction was centrifuged, washed several times and dried in a hot oven at the ~ 80 °C for 8 h. The obtained product was calcined at ~ 600 °C for 4 h. Further, in order to produce thin layers of SiO_2, the same coating protocol was used in varying TEOS concentration (2 ml and 3 ml). Schematic diagram to demonstrate synthesis of SO@STD NPs was depicted in Fig.2.

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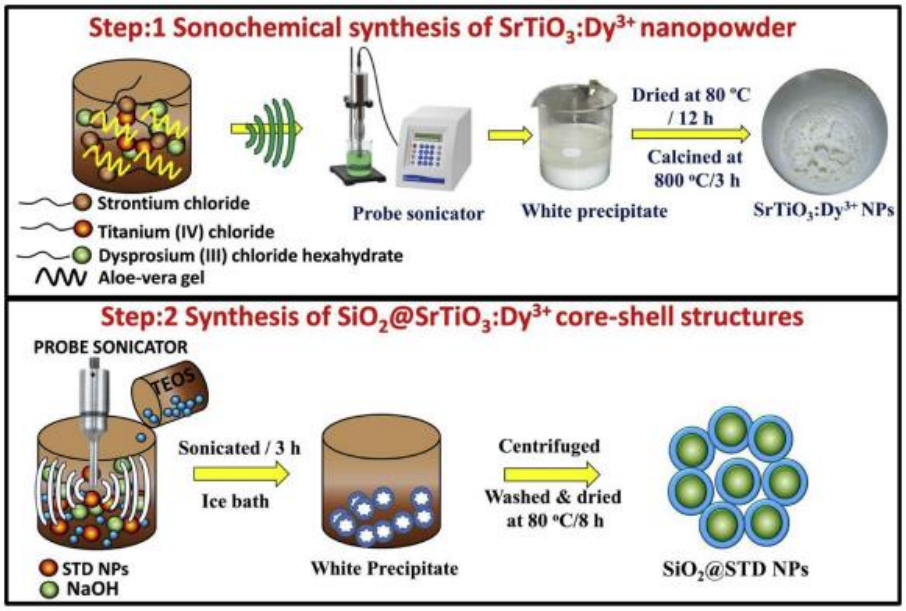

Fig.2. Schematic illustration for the synthesis of STD NPs by ultrasonication route and its surface modification by SiO_2 by Stöber method

2.3. Synthesis of $SrTiO_3:Nd^{3+}$ nanopowders using hydrothermal method

The chemicals used in the present communication were purchased from Sigma Aldrich Co. and used further purification. The AR grade Strontoum nitrate [$Sr(NO_3)_2$ (99.9 %)], Titanium (IV) isopropoxide [$Ti[OCH(CH_3)_2]_4$ (99.9 %)] and Neodymium nitrate [$Nd(NO_3)_3.5H_2O$ (99.9 %)] were used as oxidizers and EGCG as a bio-surfactant. In a typical procedure, stoichiometric quantity of titanium isopropoxide, strontium nitrate, neodymium nitrate and prepared EGCG was dissolved in ~ 100 ml of distilled water under constant stirring in magnetic stirrer. Then, 1M NaOH (40 ml) was added drop-wise to the precursor solution with continuous stirring up to ~ 1 h. Subsequently, the colloidal solution was obtained and was transferred to a Teflon lined stainless steel autoclave maintained at ~ 100 °C for 24 h. Finally, white precipitation was achieved after cooling the autoclave to room temperature. The obtained precipitate was washed many times with distilled water and dried at ~ 50 °C for 24 h. The dried powder was calcined at ~ 900 °C for 6 h to eliminate the impurities. The same experimental procedure was followed by varying dopant Nd^{3+} ion concentration (1-11 mol %), temperature (100, 120, 140, 160 and 180 °C), EGCG concentration (10-35 ml), reaction time (12, 18, 24 and 30 h) and pH level of the precursor solution.

3. CHARACTERIZATION

Powdered X-ray diffraction (PXRD) profiles of the prepared samples were obtained via Shimadzu 7000 X-ray diffractometer with 0.028/s scanning rate using Cu kα (1.541 Å) radiation. Morphologies of the prepared NPs was observed through scanning electron microscopy (SEM, Hitachi table top, Model TM 3000).

4. RESULTS AND DISCUSSION

4.1 Morphological study of $SiO_2@SrTiO_3:Eu^{3+}$: Li^+ nanoparticle

Fig.3 shows the SEM and TEM images of SiO_2 particles and $SiO_2@SrTiO_3:Eu^{3+}$ (1 mol%), Li^+ (1 wt%) NPs. The SiO_2 particles had a uniform spherical shape with smooth surface and average particles size of 130 nm. The pure $SrTiO_3:Eu^{3+}$, Li^+ particles were cubic shape. After coating with $SrTiO_3:Eu^{3+}$, Li^+, the silica particles still retained the spherical shape, however even after four cycles of coating the surface become smooth. The average particle size was somewhat increased to 150 nm when silica nanoparticles were subjected to four cycles of coating. TEM images prove that the silica nanoparticles were covered with cubic shaped particles (Fig. 5(D)). Therefore, the coated particles had a core–shell structure.

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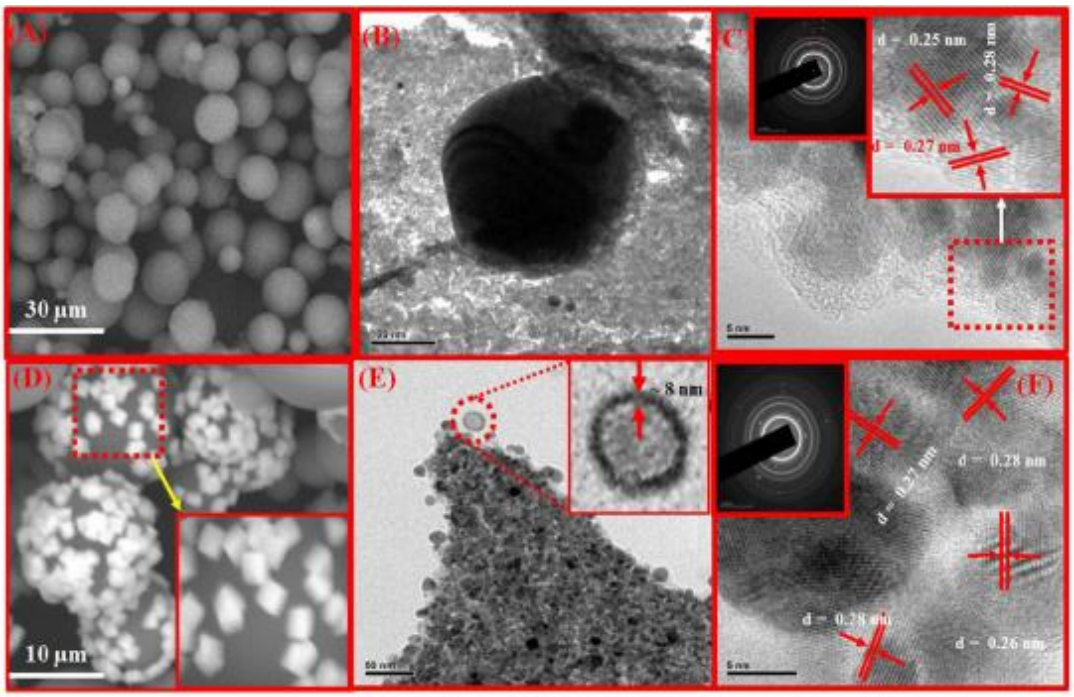

Fig. 3. SEM & TEM images of (A–C) SiO_2 and (D–F) SiO_2@$SrTiO_3$:Eu^{3+} (1 mol%): Li^+ (1 wt%) NPs.

4.2 Morphological study of SiO_2@$SrTiO_3$:Dy^{3+} nanoparticle

SEM micrographs of STD and SO@STD NPs was shown in Fig.4. It was evident that the dumbbell shaped particles were observed for STD samples (Fig. 4 (a)). However, agglomerated and fused particles were observed in the thick SiO_2 coated samples (Fig. 4 (b–d)).

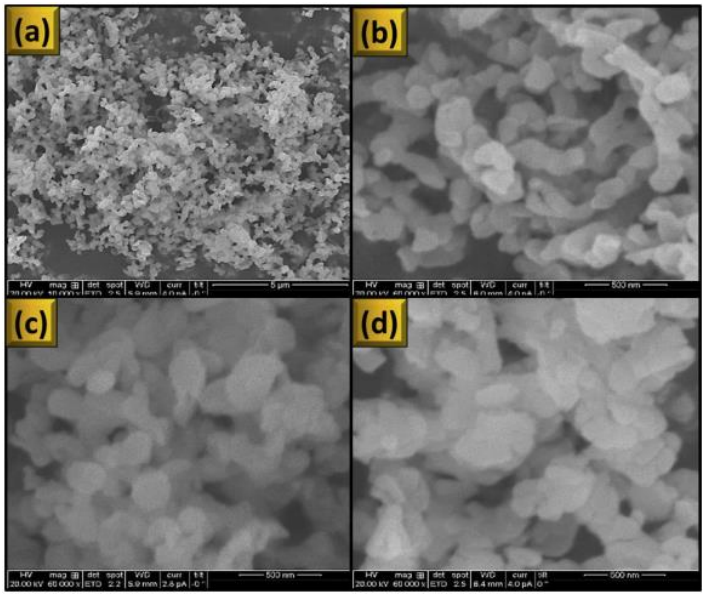

Fig. 4. SEM micrographs of (a) STD NPs, (b–d) SO@STD NPs with coat I-III

4.3 Morphological study of $SrTiO_3$:Nd^{3+} nanoparticle

The role of hydrothermal temperature on morphology was studied and depicted in Fig. 5. As can be evident from the microstructures, the reaction temperature significantly alters the morphology of the prepared product. When the hydrothermal temperature was maintained at 100 °C, irregular shapes with different orientations were clearly observed (Fig. 5(a)). This can be ascribed to reduced energy induced in a hydrothermal media by the temperature. By prolonged hydrothermal temperature to 120 °C, generates high energy in the reaction media results in the pyramidal shaped structures (Fig. 5(b)). When hydrothermal temperature was increased to 140 °C and 160 °C, well developed pyramidal

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shapes with sharp edges were clearly noticed (Fig. 5(c & d)). Furthermore, by extended increase of temperature to 180 °C, sufficient energy was created in the reaction solution that could separate the pyramidal particles from each other (Fig. 5(e)). At this temperature, the surface of the pyramidal particles completely smoothened with sharp edges were clearly identified.

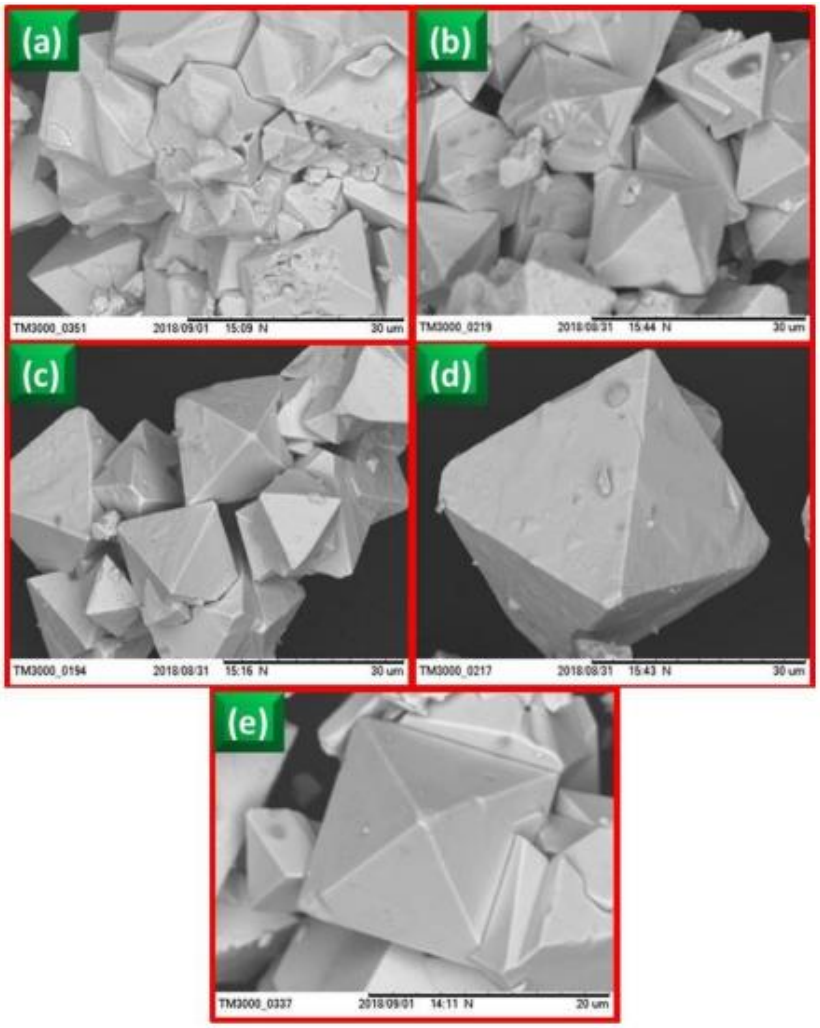

Fig.5. SEM images of $SrTiO_3:Nd^{3+}$ (5 mol%) NPs prepared with various hydrothermal temp (100 – 180 °C)

CONCLUSIONS

SiO_2@$SrTiO_3:Eu^{3+}$ (1 mol%), Li (1 wt%) phosphors with a core– shell structures have been effectively fabricated by a solution based combustion route. The obtained core–shell particles display a uniform size with spherical shape morphology; all are with narrow size distribution as well as good dispersion. From SEM and TEM analysis, $SrTiO_3:Eu^{3+}$, Li^+ NPs were successfully coated on SiO_2 core shell particles.

SiO_2 coated STD NPs were successfully synthesized and its morphology was studied. Hierarchical pyramidal shaped intense blue light emissive $SrTiO_3:Nd^{3+}$ (1-11 mol %) NPs were successfully synthesized by hydrothermal route using EGCG as a capping agent and its morphology was studied.

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