

Morphology Control and Photochemical Properties of Rare Earth Oxides Particles by Solvothermal Reactions

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Chapter 1. General introduction

The present human society is very well practiced with the use of excellent technological materials. In certain case, the performance of the functional materials decreases with time since the properties depends on many factors including the morphology, preparation method and physico-chemical properties. The requirement of technological materials has been increasing day-by-day. However, the researchers should look for environmentally benign materials and techniques for the preparation of advanced materials in order to make sure the safety of human kind. Moreover, once should take care about the negative impact of the process or the functional materials. In order to save energy, time and money we need to develop facile methods for the preparation of functional materials and materials for environmental applications. Moreover recent research developments on rare earth oxides shows that the morphology and size control can improve the photochemical properties. Many methods were used to control the morphology and size of functionally important rare earth oxides. However an easy, cost effective and rapid method has not been realized yet. The present work proposes a solvothermal refluxing route and subcritical and supercritical solvothermal/hydrothermal method to control the morphology and improve the photochemical properties.

Chapter 2. Refluxing solvothermal synthesis and photoluminescence properties of RE³⁺ (RE³⁺= Eu, Tm and Tb) doped Y₂O₃ nanocrystals

Two different synthesis routes were adopted in order to prepare dispersed RE³⁺ (RE³⁺= Eu, Tm and Tb) doped Y₂O nanocrystals. Route-1 is co-precipitation refluxing calcinations where in a co-precipitated gel powder was refluxed in different organic solvents i.e. propylene glycol, 1, 3-butanediol and polyethylene glycol and the reaction temperature was near to the boiling point of respective organic solvents. Each solvent showed difference on the particle size and morphology before and after calcinations.

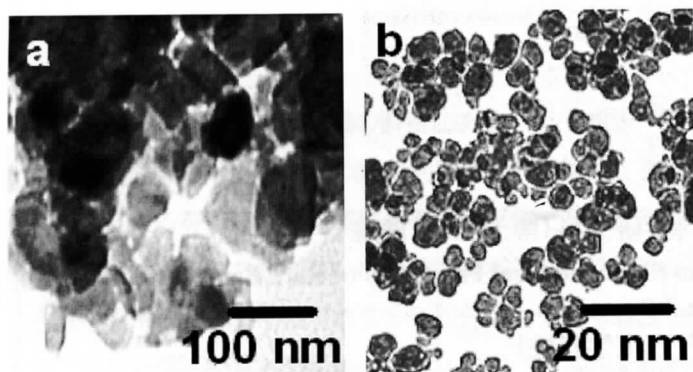


Fig. 2. As prepared sample via route-1(a) and route-2 (b).

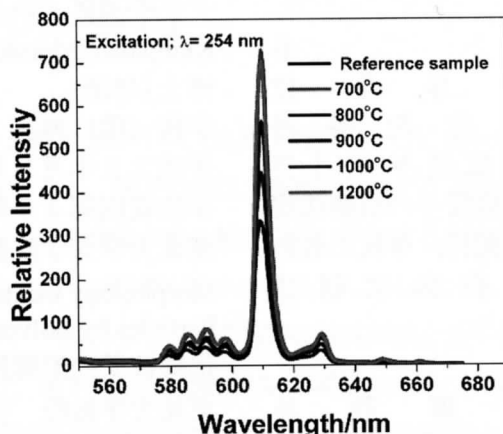


Fig. 3. Photoluminescence spectra of calcined samples at Various calcinations temperature

However, the as-prepared sample in polyethylene glycol showed good dispersion with 60-80 nm in diameter and improved photoluminescence property over conventional product. Route-2 is refluxing calcinations where the preparation was carried out by taking desired amount of rare earth aqueous solution in mixed solution containing methanol-ethylene glycol and hexane-ethylene glycol followed by refluxing at 70 and 170 °C for 2h. The particle prepared by route-2 showed great particles dispersion before and after calcinations when compared to the particles prepared via route-1 (Fig.2). The calcined samples after prepared via route-2 showed excellent room temperature photoluminescence property as shown in Fig 3.

Chapter 3. Hydrothermal synthesis of RE³⁺ (RE³⁺= Eu, Tm and Tb) doped Y₂O₃ nanospheres, rods, bundles of rods and nanotubes

Until know a rapid method for morphology and size controlled synthesis of RE³⁺ (RE³⁺= Eu, Tm and Tb) doped Y₂O₃ materials without using any surfactant or template is not reported. Herein, we prepared these materials with various morphology and size in the absence of surfactant and template. Aqueous solution of 20 ml of 0.25 M YCl₃ aqueous solution and 0.25 mmol of rare earth chloride (Tm³⁺, Tb³⁺ and Eu³⁺) powder corresponding to

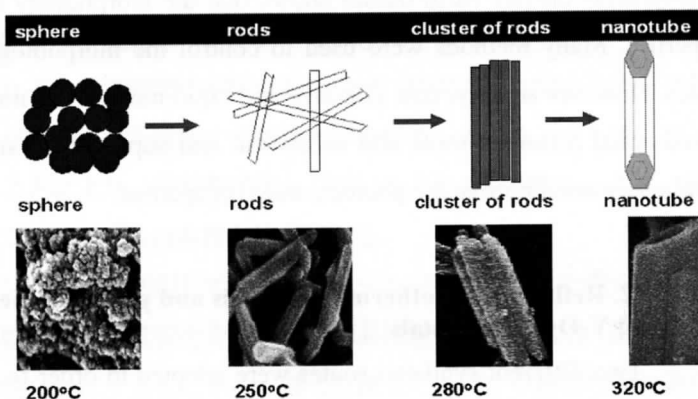


Fig. 4. Formation mechanism of rare earth oxide doped nanotube

5 mol% rare earth ion doping were used as starting materials. The experiments were carried out at 200-320 °C for about 5 min. The as prepared materials were identified as hexagonal Y(OH)₃ and rare earth ion doped Y₂O₃ nanotubes were prepared by calcination of the as-prepared product in air at 500 °C for 4 h. The as-prepared materials at 200 °C, 250 °C and 280 °C exhibited sphere, rods and bundles of rods shaped morphology (Fig. 4)

with 20-150 nm before and after calcinations. Where as the sample prepared at 320 °C exhibited beautiful nanotubes (Fig. 4) like morphology and optical properties of RE^{3+} ($RE^{3+} = Eu, Tm$ and Tb) doped Y_2O_3 nanotubes were discussed.

Chapter 4. Supercritical solvothermal synthesis and characterization of RE^{3+} ($RE^{3+} = Eu$ and Tb) doped Y_2O_3 microspheres, microcubes and hollow microspheres

Micron sized rare earth oxide particles are necessary for the operation of low voltage systems such as FED and CRT's. Herein, we prepared rare earth RE^{3+} ($RE^{3+} = Eu$ and Tb) doped Y_2O_3 microspheres, microcubes and hollow microspheres (Fig. 5) at supercritical conditions. Metal salts and mixed solution of water/ethanol, water/methanol and water/1-propanol were used to control the morphology. The synthesis was carried out for short period of reaction time (5-10 min), the formation mechanism was illustrated and effect of reaction temperature, pH and reaction time was investigated. The morphology does not change even after calcinations at very high temperature (900 °C). The effect of morphology on the photoluminescence property was discussed. As a result, the highest emission is obtained for the hollow microspheres due to its unique morphology.

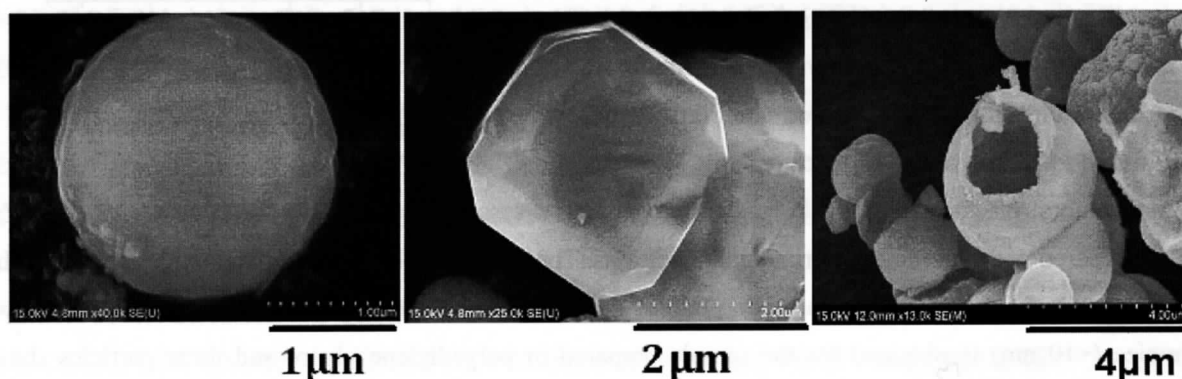


Fig. 5. FESEM of as prepared microsphere, microcubes and hollow microspheres

5. Subcritical and supercritical solvothermal synthesis and characterization of CeO_2 nanorods, nanosphere, hollow nanospheres and 3D micro/nanostructure

CeO_2 nanorods and nanospheres were prepared by just changing the source of starting materials at supercritical conditions. CeO_2 nanorods were obtained using $CeCl_3 \cdot 7H_2O$ as starting material. Where as CeO_2 nanospheres were obtained when $Ce(NO_3)_3 \cdot 6H_2O$ was used as starting material. Ethanol and methanol were used as solvothermal reacting solvents. The as-prepared nanorod and nanosphere exhibited 300-500 nm in diameter and exhibit excellent UV shielding property and catalytic activity by CO oxidation. Surfactant assisted solvothermal synthesis at subcritical conditions were carried out for the preparation of CeO_2 hollow nanospheres with 500-150 nm in diameter. The cheap and non-toxic

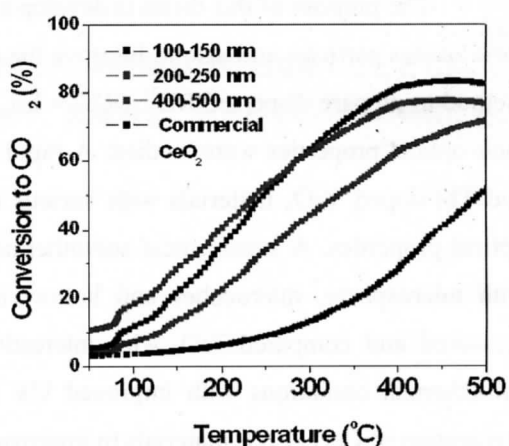


Fig. 6. Catalytic activity for CO oxidation

PVA500# was used as surfactant with varying amount. The excellent UV shielding activity and size dependent catalytic activity by CO oxidation (Fig.6) after calcinations was investigated. Using ethylene glycol as solvent, CeO₂ 3D micro/nanostructures were also synthesized with improved catalytic activity. The formation mechanism of hollow nanospheres and CeO₂ 3D micro/nanostructures was illustrated.

Chapter 6. Supercritical synthesis and characterization of CeO₂-ZrO₂ mixed oxides for catalytic applications

Until now, several methods were used for the preparation of CeO₂-ZrO₂ mixed oxides either need high calcinations temperature or long experimental duration. Herein, we propose a direct and rapid method to prepare CeO₂-ZrO₂ mixed oxides with different Zr content. In a typical preparation, 36 ml of mixed aqueous solutions of Ce(NH₄)₂(NO₃)₆ and ZrO(NO₃)₂·2H₂O (Ce + Zr = 1 M) were taken in a beaker containing 4 ml of ethanol, ethylene glycol and polyethylene glycol, followed by stirring for 15 min and the resulted blood red colored solution (10 ml) was transferred to 20 ml volume of batch reactors (4 reactors).

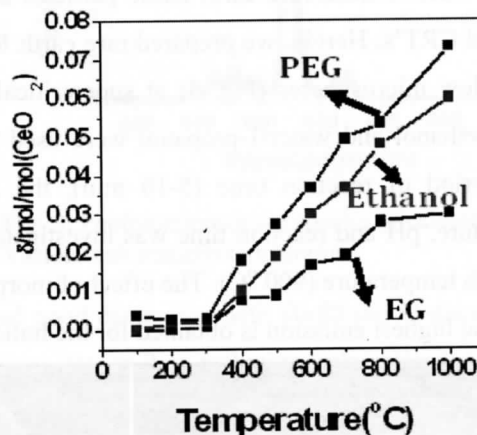


Fig. 7. Oxygen storage capacity at various temperatures

Then, the reactors were heated at 400 °C under autogeneous pressure of ca. 40 MPa for 10 min. CeO₂ and ZrO₂ were also prepared with the same experimental conditions. The prepared CeO₂-ZrO₂ mixed oxides showed sphere morphology with different diameter size depending upon organic solvents used in the synthesis. The lowest particle size (<10 nm) is obtained for the sample prepared in polyethylene glycol and these particles showed excellent oxygen storage capacity (Fig.7) and CO oxidation ability.

Chapter 7. Conclusions

The purpose of this thesis is develop a low cost, rapid and easy methods to control the morphology of rare earth oxides particles and also to improve the photochemical properties. For that, we have proposed solvothermal method to prepare dispersed RE³⁺ (RE³⁺= Eu, Tm and Tb) doped Y₂O₃ materials with 20-80 nm in diameter and their optical properties were studied. A rapid hydrothermal synthesis was used to prepare RE³⁺ (RE³⁺= Eu, Tm and Tb) doped Y₂O₃ materials with various morphology and size. The obtained nanotubes showed interesting optical properties. A supercritical solvothermal method was successfully used to prepare micron sized particles with microsphere, microcubes and hollow microspheres morphology and photoluminescence property was measured and compared. CeO₂ with interesting morphologies were prepared via subcritical and supercritical solvothermal conditions with improved UV shielding ability and catalytic activity. A direct method for the preparation of CeO₂-ZrO₂ materials to improve the catalytic property was proposed.

論文審査結果の要旨

希土類酸化物は多様な分野で利用されており、それらの機能性の高度発現のためには原料粉末の形態の精密制御が必要である。本研究は、水や有機化合物を反応溶媒とするソルボサーマル反応により希土類酸化物の形態をナノからマクロまで階層的に制御する手法を開発し、蛍光特性、紫外線吸収特性、環境浄化触媒特性等の光化学特性に及ぼす形態や結晶化度の影響について系統的に調べた研究であり、全編7章よりなる。

第1章は緒論であり、希土類酸化物の合成法、光化学特性などに関する過去の研究を網羅し、その特徴を述べ、また、重要ながら未解明な事項を列挙し、その上で、本研究の目指す方向とその概要を述べている。

第2章は、有機化合物を溶媒として用いるソルボサーマル還元反応により、 Eu^{3+} 、 Tm^{3+} 、 Tb^{3+} ドーピング Y_2O_3 前駆体ナノ粒子を合成した後、空气中仮焼により前駆体の形態を転写した Eu^{3+} 、 Tm^{3+} 、 Tb^{3+} ドーピング Y_2O_3 ナノ粒子を合成する手法を開発するとともに、生成物の蛍光特性に及ぼす形態や結晶化度の影響について明らかにした。

第3章は、水熱反応により Eu^{3+} 、 Tm^{3+} 、 Tb^{3+} ドーピング Y_2O_3 前駆体ナノ粒子を合成した後、空气中仮焼により前駆体の形態を転写した Eu^{3+} 、 Tm^{3+} 、 Tb^{3+} ドーピング Y_2O_3 ナノ粒子を合成する手法を開発するとともに、生成物の蛍光特性に及ぼす形態や結晶化度の影響について明らかにした。

第4章は、有機溶媒を用いる超臨界ソルボサーマル反応により Eu^{3+} 、 Tb^{3+} ドーピング Y_2O_3 前駆体立方体粒子や中空球状粒子を合成した後、空气中仮焼により前駆体の形態を転写した Eu^{3+} 、 Tb^{3+} ドーピング Y_2O_3 立方体粒子や中空球状粒子を合成する手法を開発するとともに、生成物の蛍光特性に及ぼす形態や結晶化度の影響について明らかにした。

第5章は、有機溶媒を用いる超臨界ソルボサーマル反応により CeO_2 ナノロッドやナノ粒子を合成する手法を開発するとともに、生成物の紫外線吸収特性やCO浄化触媒特性に及ぼす形態や結晶化度の影響について明らかにした。

第6章は、有機溶媒を用いる超臨界ソルボサーマル反応により CeO_2 - ZrO_2 ナノ粒子を合成する手法を開発するとともに、生成物の酸素吸蔵能やCO浄化触媒特性に及ぼす形態や化学組成の影響について明らかにした。

第7章は結論であり、各章の結言を要約している。

以上、本論文は、多様な分野において工業的に重要な希土類酸化物粒子の形態制御技術を開発するとともに、光化学特性に及ぼす諸因子の影響について系統的に調べた研究であり、環境科学、物質科学の分野の発展に寄与するところ少なくない。

よって、本論文は博士(学術)の学位論文として合格と認める。