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Unprecedented rapid synthesis of $REPO_4$ monospheres (RE = La-Lu lanthanide and Y) and investigation of multi-color photoluminescence

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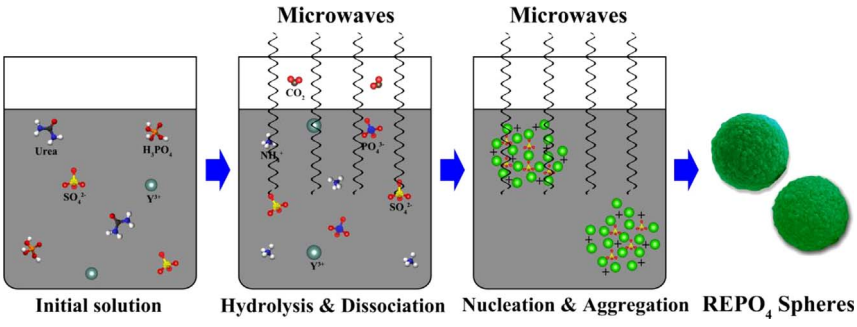
HIGHLIGHTS

- $REPO_4$ monospheres were originally, facilely and rapidly synthesized.
- The microwave heating method promoted burst nucleation of $REPO_4$.
- SO_4^{2-} anions efficiently aggregated the nuclei/subunits into monospheres.
- The photoluminescence of RE^{3+} was comprehensively elaborated in YPO_4.

GRAPHICAL ABSTRACT



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ABSTRACT

Monodispersed spheres (monospheres) of the rare-earth orthophosphate ($REPO_4$, RE = La-Lu in the lanthanide family and Y, excluding radioactive Pm) have been originally synthesized *via* fast microwave irradiation of mixed solutions containing RE^{3+}, phosphoric acid, urea and sulfate anions. Through systematic and in-depth investigations into the influences of heating method (microwave and water-bath), SO_4^{2-}/RE^{3+} molar ratio, sulfate source, $PO_4^{3-}:Y^{3+}$ molar ratio and solution pH, the mechanisms of morphology evolution were unveiled. The effects of lanthanide contraction and post calcination on the phase structure and particle morphology of the products were also clarified. The key feature of this technique is utilizing microwave heating to promote burst nucleation of $REPO_4$ and SO_4^{2-} anions to efficiently aggregate the nuclei/subunits into monospheres. The photoluminescence of various RE^{3+} activators (RE = Ce, Pr, Sm, Eu, Tb, Dy, Er and Tm) was comprehensively elaborated with YPO_4 as a representative host lattice, and the thermal quenching of Eu^{3+} emission was also investigated. The microwave assisted homogeneous precipitation technique established in this work for $REPO_4$ may have wide implications to the generation of other types of inorganic monospheres.

1. Introduction

Monodispersed spheres (monospheres) are being studied in broad areas and were verified to have important applications in the fields of drug delivery, biolabeling, combinatorial synthesis, and so forth [1–4]. The most prominent and frequently used techniques to produce monospheres seem to be emulsion polymerization for polymer latexes and silica and urea-based homogeneous precipitation (UBHP) for

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amorphous basic-carbonates of the rare-earth (RE) elements [5–7]. Mechanistic investigation further demonstrated that the inorganic monospheres of ≥100 nm in diameter are mostly formed through aggregation of subunits [8–10], and the process of which is significantly more complicated than the burst nucleation followed by diffusional growth model initially suggested by LaMer and Dinegar [11,12]. The UBHP methodology, which utilizes the *in situ* and homogeneous hydrolysis of urea to provide the precipitating OH^- and/or CO_3^{2-} anions, has also been modified and/or improved to fabricate the inorganic spheres of other constituents. For example, Chen et al. operated UBHP under hydrothermal conditions and in the presence of sodium dodecyl sulfate (SDS), through which transition-metal phosphate colloidal spheres (TMPCS) with diameters of ~250–300 nm were successfully obtained [13]. During the past years, a number of other techniques have also been developed to fabricate monospheres of various compositions, typically including templated synthesis, hydro-/solvo-thermal reaction, and coprecipitation. For example, the generation of urchin-shaped RE phosphate ($REPO_4$) and vanadate ($REVO_4$) hollow spheres via consuming $RE(OH)CO_3$ monospheres under hydrothermal conditions [14–17], the synthesis of YVO_4:Eu, YBO_3:Eu/Tb, and Gd_2O_2S:Eu/Tb solid monospheres *via* ethylene glycol (EG) mediated solvothermal reaction [18–20], and the production of REF_3 monospheres through low-temperature precipitation in the absence of any surfactant [21]. $REPO_4$ are well known to be a series of excellent hosts for visual and biological applications. Though $REPO_4$ crystals have been obtained in various forms (nanowires, nanorods, nano-spindles, submicron-sized hexagonal prisms, submicron-sized hexagonal prisms with concave center, prism-like hexagonal nanoparticles, and hexagonal nanoplates) [22–25], the fabrication of $REPO_4$ monospheres, however, has never been achieved through the UBHP technique, to the best of our knowledge, primarily owing to the fact that $REPO_4$ is readily crystallized to undergo anisotropy growth either at an elevated temperature or during lengthy precipitation reaction [24,25].

To prepare $REPO_4$ monospheres, a low enough solution pH of the initial reaction system is needed to prevent any premature precipitation that is rooted from the extremely low solubility product of $REPO_4$ (10^{-25}–10^{-27}) [26] and meanwhile complete precipitation must be fulfilled at a sufficiently low temperature within a short period of time to prevent significant crystallization/anisotropic growth of the $REPO_4$ crystallites. Accordingly, microwave heating is taken into account since the material under microwave irradiation is heated through absorbing electromagnetic energy rather than thermal transmission from the surroundings and can be substantially faster [27]. Urea, as an organic compound, better absorbs microwave energy than water molecules do, thus leading to targeted and preferential heating of the former. This would allow rapid hydrolysis of urea to take place before the whole reaction system reaches the ~83 °C needed in conventional heating, and would in turn allow $REPO_4$ to be formed without substantial occurrence of the aforementioned crystallization and anisotropic growth. On the other hand, aggregation of the nuclei/subunits in an aqueous solution can be interpreted in terms of pair potentials involving a summation of van der Waals attraction and electrostatic repulsion [28]. Suitably adjusting the repulsive interaction may therefore make it possible to control over the aggregation process. SO_4^{2-} was previously found in several works to be able to adjust the surface charge of newly formed nuclei through absorption [29,30]. Considering that the $REPO_4$ nuclei/subunits would be generated under highly acidic conditions in our system, SO_4^{2-} was thus expected to be capable of minimizing the electrostatic repulsion through neutralizing surface adsorbed protons.

With the above conception and through careful experimental design, we achieved in this work unprecedented rapid (within minutes) generation of $REPO_4$ monospheres for the whole spectrum of lanthanides (RE = La-Lu, excluding Pm) and Y *via* microwave irradiating mixed aqueous solutions of RE^{3+}, phosphoric acid, urea, and SO_4^{2-}. Taking $LaPO_4$ and YPO_4 as representatives, the formation mechanisms of $REPO_4$ monospheres were lucubrated, and the effects of lanthanide contraction and subsequent calcination on the phase structure and particle morphology were also investigated. Furthermore, adjusting the SO_4^{2-}:Y^{3+} molar ratio has led to size-tunable synthesis of YPO_4 monospheres, and the influences of heating method (microwave against water-bath), sulfate source, PO_4^{3-}:Y^{3+} molar ratio and solution pH on the properties of the products were systematically explored. The photoluminescent properties of various RE^{3+} activators (RE = Ce, Pr, Sm, Eu, Td, Dy, Er, Tm) in YPO_4 were also expatiated, and multicolor luminescence was achieved. We believe that the facile, rapid and highly reproducible synthesis strategy developed in this work may arouse broad interest and have wide implications to the generation of other types of inorganic monospheres *via* homogeneous precipitation.

2. Experimental section

2.1. Materials

The starting rare-earth sources are $Ce(NO_3)_3{\cdot}6H_2O$ (99.96% pure), Pr_6O_{11} (99.96% pure), Tb_4O_7 (99.99% pure), and RE_2O_3 (99.99% pure, RE = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, and Y), all purchased from Huizhou Ruier Rare-Chem. Hi-Tech. Co. Ltd (Huizhou, China). Analytical grade nitric acid (HNO_3, 63 wt%), phosphoric acid (H_3PO_4, 85 wt%), ammonium sulfate ($(NH_4)_2SO_4$, 99% pure), urea ($CO(NH_2)_2$, 99% pure), ammonium hydroxide ($NH_3{\cdot}H_2O$, 25–28 wt%), and sulfuric acid (H_2SO_4, 98 wt%) were obtained from Shenyang Chemical Reagent Factory (Shenyang, China). The nitrate solution of RE^{3+} was prepared by dissolving the corresponding oxide with a slightly excessive amount of nitric acid, followed by evaporation at ~90 °C to dryness to remove the superfluous acid. The $Y_2(SO_4)_3$ solution was prepared by titrating $Y(NO_3)_3$ solution with an excessive amount of $NH_3{\cdot}H_2O$ to form a white precipitate, followed by dissolving the precipitate with a stoichiometric amount of dilute sulfuric acid after centrifugation collection and repeated washing with distilled water.

2.2. Sample preparation

For each run of the synthesis, certain amounts of H_3PO_4 and $(NH_4)_2SO_4$ were added into an aqueous solution (500 mL) containing $CO(NH_2)_2$ (0.25 mol) to get a transparent solution, to which $RE(NO_3)_3$ (5 mmol) was then added after magnetic stirring for 10 min. The pH of the mixture was adjusted to a certain value with HNO_3 before being transferred into a microwave oven (output power: 700 W). With a heating rate of ~8 °C·min^{-1}, a suspension was obtained after ~8 min of microwave irradiation. The resultant suspension was left to cool naturally to room temperature and the precipitate was collected *via* centrifugation, followed by washing with water three times and ethanol once and air drying at 70 °C for 24 h. The reaction parameters studied for YPO_4 synthesis are summarized in Table 1. Calcination of the

Table 1
Experimental parameters for sample synthesis.

Sample	PO_4^{3-}:SO_4^{2-}:Y^{3+}	Solution pH	Sulfur source
P1	10:0:1	1.0	$(NH_4)_2SO_4$
P2	10:0.2:1	1.0	$(NH_4)_2SO_4$
P3	10:0.5:1	1.0	$(NH_4)_2SO_4$
P4	10:1:1	1.0	$(NH_4)_2SO_4$
P5	10:1.5:1	1.0	$(NH_4)_2SO_4$
P6	10:2:1	1.0	$(NH_4)_2SO_4$
P7	10:1.5:1	1.0	$Y_2(SO_4)_3$
P8	10:0.5:1	1.0	H_2SO_4
P9	2:0.5:1	1.0	$(NH_4)_2SO_4$
P10	5:0.5:1	1.0	$(NH_4)_2SO_4$
P11	20:0.5:1	1.0	$(NH_4)_2SO_4$
P12	10:0.5:1	1.2	$(NH_4)_2SO_4$
P13	10:0.5:1	0.8	$(NH_4)_2SO_4$
P14	10:0.5:1	0.6	$(NH_4)_2SO_4$