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# SrF<sub>2</sub> hierarchical flowerlike structures: Solvothermal synthesis, formation mechanism, and optical properties

Zewei Quan <sup>a,b</sup>, Dongmei Yang <sup>a,b</sup>, Chunxia Li <sup>a</sup>, Piaoping Yang <sup>a</sup>, Ziyong Cheng <sup>a</sup>, Jun Yang <sup>a,b</sup>, Deyan Kong <sup>a,b</sup>, Jun Lin <sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China <sup>b</sup> Graduate University of the Chinese Academy of Sciences, Beijing 100049, PR China

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#### 1. Introduction

The synthesis of inorganic nano- and micromaterials with welldefined and controllable morphologies has stimulated considerable attention, because it is well known that the properties of the materials closely interrelate with geometrical factors such as morphology, dimensionality, and size [1-5]. Recently, there are increasing effort devoted to the preparation of organized extended structures (superstructures) based on the assembly of nanostructured building blocks due to their potential applications in catalysis, medicine, electronics, ceramics, pigments and cosmetics [6,7]. Such a hierarchical superstructure with the cooperation of microstructure and nanostructure provides a novel approach to bring forth new properties [8]. Because of the distinct size, shape, and chemical functionality, these hierarchical superstructures possess the advantages from microstructure and nanostructure and can be promising candidates for many applications [9]. Therefore, a number of strategies have been developed to spatially pattern and control higher-order organization [10-12]. Among them, solvothermal method has been proven as an effective and convenient process in preparing various inorganic materials with diverse controllable morphologies and hierarchical architectures in terms of cost and potential for large-scale production [13–15].

#### ABSTRACT

We present a solvothermal route to the synthesis of SrF<sub>2</sub> hierarchical flowerlike structures based on thermal decomposition of single source precursor (SSP) of strontium trifluoroacetate in benzylamine solvent. These flowerlike superstructures are actually composed of numerous aggregated nanoplates, and the growth process involves the initial formation of spherical nanoparticles and subsequent transformation into nanoplates, which aggregated together to form microdisks and finally flowerlike superstructures. The results demonstrate the important role of benzylamine in the formation of well-defined SrF<sub>2</sub> superstructures, not only providing size and shape control to form nanoplates but also contributing to the self-assembly behavior of nanoplates to build into flower-like superstructures. Additionally, the photoluminescence properties of the obtained SrF<sub>2</sub> superstructures are studied.

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Solid inorganic fluorides have attracted vast attention due to their uncommon properties, such as electron-acceptor behavior, high resistivity, and anionic conductivity [16]. In particular, due to their low energy phonons and high ionicity, inorganic fluorides have a wide range of potential optical applications such as windows, lenses, scintillation crystals and as host crystals for rare earth ions exhibiting interesting properties in optoelectronics such as lasing, light amplification and up conversion [17]. As an important kind of alkaline earth metal fluorides, strontium fluoride (SrF<sub>2</sub>) are dielectric and thus has great applications in microelectric and optoelectric devices [18]. However, to the best of our knowledge, there are few reports on the controlled synthesis of well-defined SrF<sub>2</sub> nano/microstructures [19]. The major reason rests with the rapid precipitation reaction between soluble strontium salts and NaF/NH4F in aqueous solutions, making it difficult to achieve controlled nucleation and growth process that is prerequisite to obtain uniform and well-defined nano/microcrystals. Recently, Yan and co-workers has reported the synthesis of a series of high-quality rare earth fluoride nanocrystals based on the thermal decomposition of corresponding rare earth trifluoroacetates in high-boiling point solvents [20-22]. In these complex trifluoroacetates, both metal and fluorine elements are integrated in the same compound, which may provide a much better controlled-synthesis of fluoride nanocrystals than the direct liquid precipitation methods. Based on these results, it is natural to come up with such imagination: the adoption of  $Sr(CF_3COO)_2$  as single source precursor (SSP) could be applied to obtain well-defined SrF<sub>2</sub> nano/microstructures.

<sup>\*</sup> Corresponding author. Tel.: +86 431 85262031; fax: +86 431 85698041. *E-mail address:* jlin@ciac.jl.cn (J. Lin).

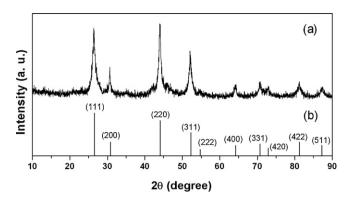
<sup>0025-5408/\$ –</sup> see front matter © 2008 Elsevier Ltd. All rights reserved. doi:10.1016/j.materresbull.2008.11.011

In this paper, we for the first time prepare well-defined  $SrF_2$  hierarchical structures through a simple one-pot solvothermal process with  $Sr(CF_3COO)_2$  as precursor. A phenomenological growth process for these flowerlike superstructures has been proposed, that is, from spherical nanoparticles to microdisks as intermediate products, and finally to flowerlike superstructures composed of numerous nanoplates. The adoption of benzylamine as solvent plays important roles in the formation of the subunits, nanoplates, and the subsequent self-assembly into flower-like superstructures. The resultant  $SrF_2$  superstructures can emit purple light under UV irradiation.

#### 2. Experimental

#### 2.1. Materials

Strontium carbonates (SrCO<sub>3</sub>), trifluoroacetic acid (CF<sub>3</sub>COOH), benzylamine, absolute ethanol and cyclohexane were all analytical grade (A.R.) and purchased from Beijing Beihua Chemicals Co., Ltd. All of the materials were used without further purification.



**Fig. 1.** XRD pattern (a) of  $SrF_2$  superstructures, as well as the standard data (b) for  $SrF_2$  crystal (ICDD 06-0262).

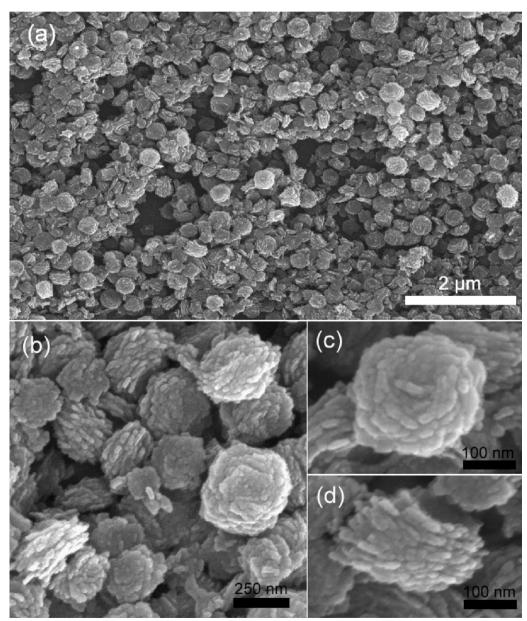


Fig. 2. SEM images of SrF<sub>2</sub> superstructures at various magnifications.

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