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超声化学法制备 SrF_2 纳米片自组装微球

许 可[1,2] 徐 朗[1] 朱俊杰*,[1]

([1]南京大学化学化工学院,生命分析化学教育部重点实验室,南京 210093)

([2]皖西学院化学与生命科学系,六安 237006)

摘要:通过简单的超声化学方法制备了 SrF_2 纳米片自组装微球。合成的产物通过粉末 X 射线衍射仪、场发射扫描电子显微镜、透射电子显微镜进行了表征和分析,结果表明这些微球是由规则、有序的纳米片组成。而这些纳米片互相垂直连接组装成微球。研究还发现反应物的浓度,配位剂和 pH 值对产物的形貌和尺寸有着重要的作用。

关键词:超声化学; SrF_2; 自组装; 分级结构; 微球

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Sonochemical Route to SrF_2 Microspheres by Nanoplates Self-assembly

XU Ke[1,2] XU Lang[1] ZHU Jun-Jie*,[1]

([1]*The Key Laboratory of Analytical Chemistry for Life Science (MOE), School of Chemistry and Chemical Engineering, Nanjing University, Nanjing* 210093)

([2]*Department of Chemistry and Biology Science, West Anhui University, Lu'an, Anhui* 237006)

Abstract: The SrF_2 microspheres by the self-assembly of nanoplates are fabricated via a facile sonochemical route. The products were characterized by the X-ray diffraction (XRD), field emission scanning electron microscopy(FE-SEM), and transmission electron microscopy(TEM). The results showed that the microspheres with a hierarchical structure are composed of regularly ordered nanoplates. These nanoplates are connected with each other to form sphere with vertical orientation. The concentrations of the reactants, capping agent and pH value have important effects on the morphologies and sizes of the products.

Key words: sonochemical; SrF_2; self-Assembly; hierarchical structure; microsphere

Fluoride materials have received much attention in recent years owing to their various applications in many areas, such as energy storage and conversion[1], laser[2], superconductors[3], and optics[4]. As an important fluoride material, SrF_2 has been widely used in ion conductors[5], optics[6], and catalysis[7]. To date, various methods have been reported for the synthesis of SrF_2 nanostructures, such as solvothermal[4], hydrothermal[8], flame[9], and microwave[10]. Different morphologies of SrF_2 have been prepared by these methods, such as nanospheres[8] and nanoparticles[4,9,10]. The hierarchical structure, ranging from the microscopic to the macroscopic scale, is the result of the self-organizing processes in inorganic-organic hybrid systems[11], which are common in nature. Therefore, the fabrication of the hierarchical structure is important to science and engineering. However, to the best of our knowledge, there are very few reports on the synthesis of SrF_2 hierarchical structures.

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*通讯联系人。E-mail:jjzhu@nju.edu.cn,Tel&Fax:025-83594976

第一作者:许 可,男,46 岁,副教授;研究方向:纳米材料化学。

Recently, sonochemical method has become an important tool for the synthesis of nanomaterial [12 ~16]. When liquids are irradiated with ultrasonic irradiation, acoustic cavitation produces a variety of physical and chemical effects, such as high temperature(>5 000 K), pressure(>20 MPa), and cooling rate($>10^{10}$ K·s^{-1}), which could provide a unique environment for chemical reactions under extreme conditions[17].

Herein, we report a sonochemical route for the synthesis of the SrF_2 nanoplates-composed microspheres is presented. The effects of concentrations of the reactants and capping agent, and pH value on the morphology and size of the products are investigated. To the best of our knowledge, this is the first paper concerning the sonochemical synthesis of the SrF_2 hierarchical structure.

1 Experimental

1.1 Synthesis of the SrF_2 microspheres

All chemicals were of analytical grade and were used without further purification. In a typical synthesis, an aqueous solution of $Sr(NO_3)_2$ (60 mL, 0.021 mol·L^{-1}) was mixed with an aqueous solution of NH_4F (20 mL, 0.128 mol·L^{-1}). Then, the reaction system was exposed to high-intensity ultrasound irradiation under ambient air for 20 min. Ultrasound irradiation was generated with a high-intensity ultrasonic probe(Xinzhi Co., China, JY 92-2D, 0.6 cm diameter; Ti-horn, 20 kHz, 60 W·cm^{-2}) immersed in the reaction system. The white precipitate was centrifuged, washed with distilled water and absolute ethanol in sequence, and finally dried in air.

1.2 Characterization

The X-ray diffraction(XRD) patterns were recorded on a Shimadzu XD-3A X-ray diffractometer at a 35 kV and 15 mA and scanning rate of 4°·min^{-1} in the 2θ range from 20° to 90° equipped with a graphite monochromatized Cu $K\alpha$ radiation source(λ=0.154 18 nm). X ray intensities were determined by X celerator detection system. The scanning electron microscopy (SEM) analyses were performed on a LEO-1530 VP with 5 kV accelerating voltage. The transmission electron microscopy(TEM) analyses were obtained with a JEOL JEM-200CX using an accelerating voltage of 200 kV.

2 Results and discussion

Fig.1 exhibits the XRD pattern of the as-prepared SrF_2 nanoplates-composed microspheres. All the diffraction peaks of the XRD pattern could be assigned to the pure cubic phase of SrF_2 (PDF No. 06-0262). Fig.2 shows the representative SEM images of the SrF_2 microspheres. These microspheres are uniform in size

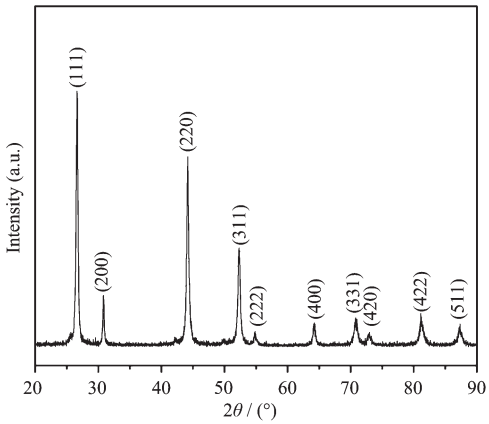


Fig.1　XRD pattern of the SrF_2 nanoplates-composed microspheres

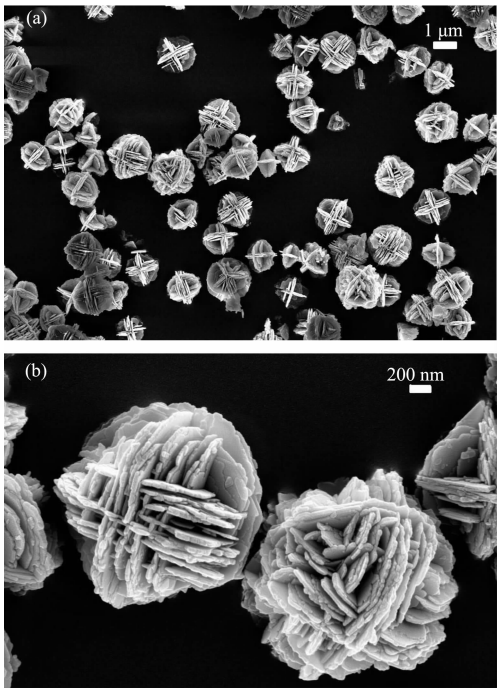


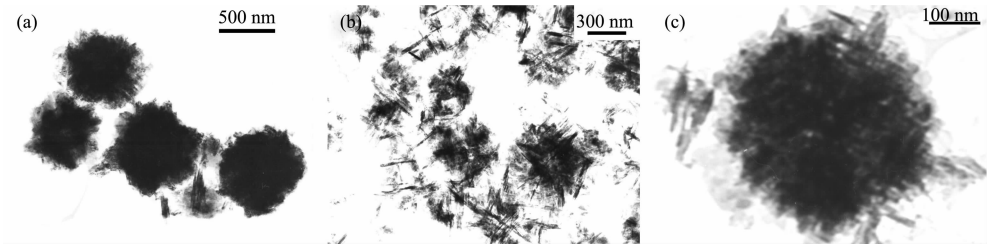
Fig.2　(a) typical and (b) higher-magnifications SEM images of the SrF_2 nanoplates-composed microspheres

(about 1.5 μm). It could be observed that the SrF_2 microspheres were composed of nanoplates with a thickness of 40 nm. It is worth mentioning that the nanoplates with different extention directions are vertical whereas those with the same extention direction are parallel.

To study the effect of the reactant concentration on the size of the SrF_2 microspheres, three samples were synthesized with different concentrations of $Sr(NO_3)_2$ and NH_4F (the molar ratio of Sr source to F remains 1∶2), as listed in table 1. Fig.3 exhibits the relevant TEM images of the products. It could be observed that the higher concentrations of the reactants lead to the products with smaller sizes.

Table 1 Size of the product as a function of reactant concentration

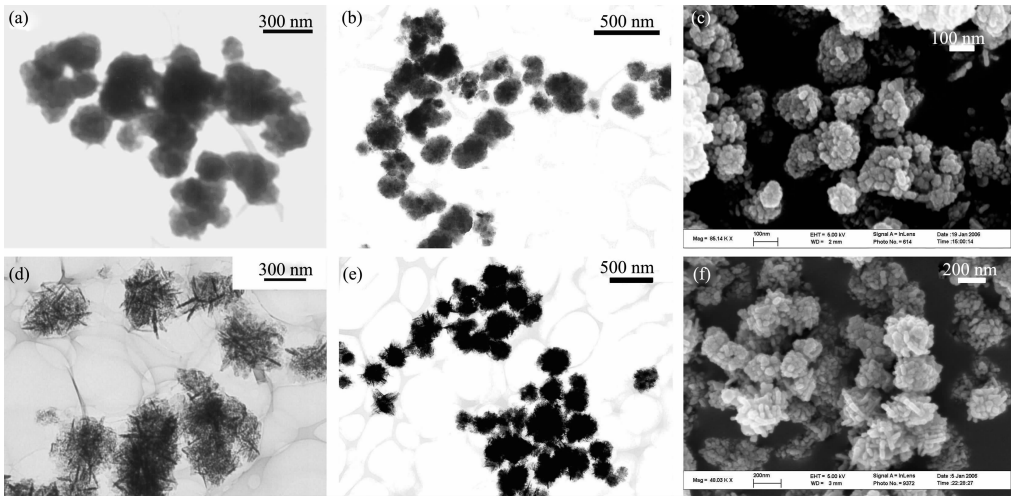
$c_{Sr(NO_3)_2}$ / (mol·L^{-1})	c_{NH_4F} / (mol·L^{-1})	Size / nm
0.025	0.050	800
0.032	0.064	500
0.064	0.128	300



(a) 0.025 mol·L^{-1}, (b) 0.032 mol·L^{-1}, (c) 0.064 mol·L^{-1}

Fig.3 TEM images of the products synthesized with different concentrations of $Sr(NO_3)_2$

When the capping agent nitrilotriacetic acid(NTA) is added into the reaction system, changes are observed in the morphology and size of the products. Owing to the addition of NTA, the reaction solution becomes acidic; thus ammonia water is added to adjust the pH value in the reaction system. To investigate the effect of NTA and pH value, six samples were prepared in the same concentration of $Sr(NO_3)_2$ and NH_4F but with different concentrations of NTA and pH values. The relative electron microscopy images are shown in Fig.4. As list-



(a) 0.032 mol·L^{-1}, pH=4; (b) 0.048 mol·L^{-1}, pH=4; (c) 0.064 mol·L^{-1}, pH=4; (d) 0.032 mol·L^{-1}, pH=2; (e) 0.048 mol·L^{-1}, pH=2; (f) 0.064 mol·L^{-1}, pH=2

Fig.4 TEM and SEM images of the products prepared in 0.016 mol·L^{-1} $Sr(NO_3)_2$ and 0.032 mol·L^{-1} NH_4F with different concentrations of NTA and pH values

Table 2　Size of the products as a function of nitrilotriacetic acid(NTA) concentration and pH value of the reaction system

c_{NTA} / (mol·L^{-1})	pH value	Size / nm
0.032	4	150~200
0.048	4	180~200
0.064	4	150~200
0.032	2	300~400
0.048	2	300~380
0.064	2	300~350

ed in table 2, it could be concluded: firstly, the original hierarchical morphology is replaced by the nanoparticles-composed sub-microstructures; secondly, the concentration of NTA has little effect on the size of the products when the pH value is constant, while the pH value has a significant effect on the size of the products when the concentration of NTA keeps identical.

3　Conclusions

In summary, SrF_2 nanoplates-composed microspheres were successfully synthesized via a convenient and fast sonochemical route. The as-prepared hierarchical microspheres are composed of regularly ordered nanoplates. These nanoplates are connected with each other to form sphere with vertical orientation, whereas those with the same extention direction are parallel. It is observed that the concentrations of the reactants have an important influence on the size of the products. Furthermore, the capping agent NTA could change the morphology of the products. In the reaction system with NTA, the pH value has a significant effect on the size of the products.

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