Front. Optoelectron. China 2011, 4(2): 150–155
DOI 10.1007/s12200-011-0167-4

RESEARCH ARTICLE

Room temperature synthesis of flower-like CuS nanostructures under assistance of ionic liquid

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Abstract Flower-like CuS nanostructures have been synthesized via a liquid precipitation route by the reaction between $CuCl_2 \cdot 2H_2O$ and thioacetamide (CH_3CSNH_2, TAA) in the ionic liquid 1-butyl-3-methyl imidazole six hexafluorophosphoric acid salts ([BMIM][PF_6]) aqueous solution at room temperature. The products were characterized by X-ray powder diffraction (XRD), field emission scanning electronic microscopy (FESEM), Brunauer-Emmett-Teller (BET), Ultraviolet-Visible Spectrophotometer (UV-Vis) and Photoluminescence (PL) techniques. The as-prepared CuS nanostructures have a mean diameter of about 1 μm. A plausible mechanism was proposed to explain the formation of CuS nanostructures. The effects of experimental parameters on the formation of the products were also explored. With BET theory, it is found that the as-prepared CuS nanostructures have a specific area of 39 m^2/g. The Barrett-Joyner-Halenda (BJH) pore size distribution of the as-prepared CuS nanostructures presents smaller pores centers about 60 nm. The UV-Vis and PL curves indicate that the as-prepared CuS nanostructures are promising candidates for the development of photoelectric devices.

Keywords nanostructures, liquid precipitation method, ionic liquid

1 Introduction

CuS, as an important member of the semiconductor family, exhibits many unique properties and has a great potential in a versatile range of applications such as cathode material of lithium batteries [1], solar radiation absorber [2], nonlinear optical material [3] and catalyst [4]. The traditional methods to fabricate CuS nanostructures are solvothermal route [5], vapor-liquid-solid [6] and template method [7–9]. So far, CuS crystals with tubular structure [10], hollow sphere [11,12], flower-like morphologies [13], urchin-like architecture and snowflake-like pattern [14], rod-like [15,16], and sphere-like morphologies [17] have been successfully synthesized. However, it is still a challenge to get special structures CuS with a facile, green and environmentally friendly route.

Recently, room temperature ionic liquids (RTILs) that are organic salts with low melting points, have aroused increasing interest worldwide as green solvents because of their unique properties such as high fluidity, nonflammability, high chemical and thermal stability, low vapor pressure, high ionic conductivity, low toxicity, and ability to dissolve a variety of materials [18]. Especially, as a new reaction medium, RTILs have many advantages in the synthesis of inorganic nanostructures. For example, by selecting suitable RTILs reaction systems, Au nanoshe-ets [19] and dendritic nanostructures [20], CoPt nanorods [21], nanocrystals of elemental chalcogens [22], flower-like ZnO [23], Bi_2S_3 nanostructures [24], Te nanowires [25], nanosized metal fluorides [26], and $InVO_4$ nanorods [27] were successfully prepared. Nevertheless, the potential of RTILs in the controlled synthesis of inorganic nanomaterials remains to be fully explored.

Liquid precipitation is one of the most popular methods of synthesis of nanometer crystals and is still regarded as a convenient, economical, environmentally friendly method [28]. In this paper, by combing the advantages of both RTILs and liquid precipitation, we report for the first time the synthesis of flower-like spheres CuS nanostructures in ionic liquid 1-butyl-3-methyl imidazole six hexafluorophosphoric acid salts ([BMIM][PF_6]) aqueous solution at room temperature.

Received November 15, 2010; accepted November 30, 2010

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2 Experiments

2.1 Materials and synthesis procedure

$[BMIM][PF_6]$ was purchased from Henan Lihua Pharmaceutical Co., Ltd. (China), and the chemical structure is shown in Fig. 1. Other chemicals were obtained from Shanghai Chemical Co., Ltd. These chemicals were of analytical grade and were used as received without further purification. The experimental procedure was designed as follows: 4.8 mmol $CuCl_2 \cdot 2H_2O$ and 4 mL $[BMIM][PF_6]$ were dissolved in 40 mL de-ionized water to form a homogeneous blue solution in a glass beaker under constant stirring. 4.8 mmol thioacetamide (CH_3CSNH_2, TAA) was dissolved in 40 mL de-ionized water. Then TAA solution was slowly added into the $CuCl_2$ solution without stirring. Such reaction mixture solution was maintained at room temperature for 48 h. The resulting black precipitate was separated by centrifugation, washed with de-ionized water and ethanol for several times, and dried in a vacuum at 50°C for 8 h.

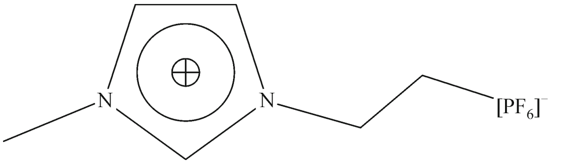

Fig. 1 Chemical structure of $[BMIM][PF_6]$

2.2 Characterization

The X-ray powder diffraction (XRD) patterns were recorded by a X-ray diffractometer (XD-3 system, Beijing Purkinje general instrument Co., Ltd.) with Cu Kα (λ = 1.54056 Å) radiation with a scanning rate of $0.02° \cdot s^{-1}$ in the 2θ range from 20° to 80°. The field emission scanning electronic microscopy (FESEM) was performed with a FEI Nova 400 scanning electron microanalyzer. Nitrogen absorb-desorbs and pore size distribution were recorded with an AS1-MP-9 Automatic surface area and pore size analyzer (Quantachrome Instruments). The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. Pore size distributions were estimated from desorption branch of the isotherm by the Barrett-Joyner-Halenda (BJH) method. The UV-Vis absorption spectra were recorded with a U-3310 spectrophotometer. Photoluminescence (PL) spectra were measured on an F-7000 Fluorescence spectrophotometer using a Xe lamp with an excitation wavelength of 350 nm at room temperature.

3 Results and discussion

Figure 2 shows the XRD pattern of the as-prepared CuS powder. All the peaks can be indexed to the hexagonal phase CuS with lattice constants of $a = b = 0.3792$ nm, and $c = 1.634$ nm (JCPDS Card 06-0464). No diffraction peaks from other species could be detected, indicating that the sample is composed of a single phase hexagonal CuS.

The morphology and structure of the as-prepared CuS nanostructures were examined by electron microscopy techniques. Figure 3(a) is a representative FESEM image of the collected products with the reaction time lasting for 48 h. It reveals that the sample is flower-like porous spheres with the diameters ranging from 600 nm to 1 μm. The enlarged picture (Fig. 3(b)) exhibits that the flower-like CuS was constructed by nanoflakes with a thickness of 10 nm standing perpendicularly to the surfaces of the microspheres to form many small pores.

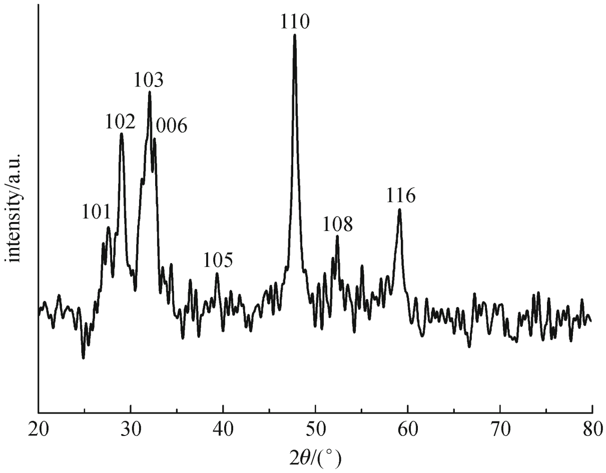

Fig. 2 XRD patterns of sample prepared in $[BMIM][PF_6]$-water solution at room temperature for 48 h

In our method, the chemical reactions can be described as follows:

$$CH_3CSNH_2 + 2H_2O \rightarrow S^{2-} + CH_3COO^- + NH_4^+ + 2H^+ \tag{1}$$

$$Cu^{2+} + S^{2-} \rightarrow CuS \tag{2}$$

In order to investigate the formation mechanism, time-dependent experiments and parallel experiments were carried out. The synthetic procedure was similar to the typical process described in experimental section, except for some changes in the reaction conditions. At the initial stage, tiny black precipitates can be obtained when the reaction lasts for 24 h. The corresponding SEM image (Fig. 4(a)) shows that the sample possesses a spheroidic morphology with diameters ranging from 100 to 200 nm. Meanwhile, it is found that the spheroidic CuS is constructed by numerous nanoflakes. With the reaction

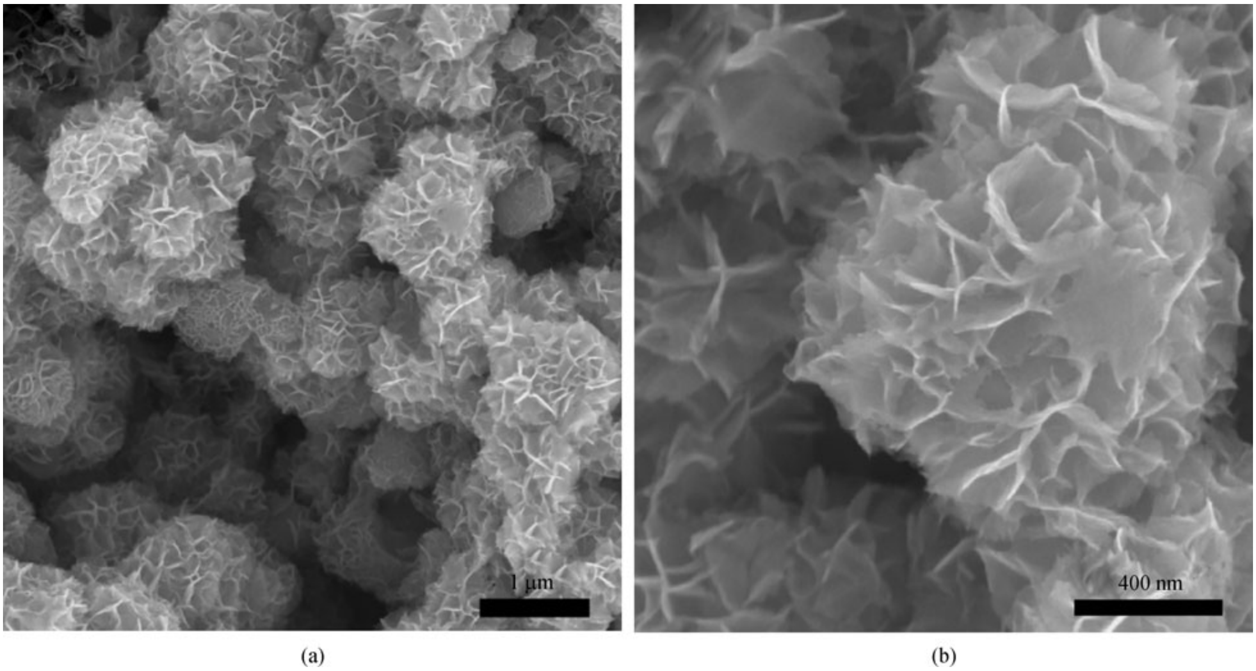

Fig. 3 FESEM images of flower-like CuS nanostructures. (a) Low magnification; (b) high magnification

time prolonged to 48 h (Fig. 3(a)), microspheres were formed and spheroidic morphology particles disappeared, suggesting that the microspheres grew at the expense of the spheroidic morphology particles. With the reaction time prolonged to 60 h (Fig. 4(b)), it is found that the diameter of the CuS microsphere is more than 2 μm. The results indicate that CuS microspheres grow larger with the prolonging of the reaction time.

On the basis of the above analyses and the experiment results, we propose the following mechanism for the growth of CuS nanostructures: a) at the initial stage, nuclei were formal through the reaction of Cu^{2+} and S^{2-}. After that, these nuclei preferentially turned to form nanoflakes due to the intrinsic anisotropic characteristics of the CuS hexagonal crystal structure [29,30]; b) as an ionic liquid has polarity, their low interfacial tension enables the inorganic species a high nucleation ratio, which propelled the formation of the nanocrystal. In addition, the ionic liquid also facilitates the polar reactions for inorganic syntheses in the water-rich system; c) to minimize the interfacial free energy, these nanoflakes self-assemble steadily into flower-like microspheres by reducing the surface areas [31].

This mechanism is confirmed by the following experiments. If de-ionized water was used as a sole solvent without using [BMIM][PF_6], no uniform CuS microspheres were observed (Fig. 4(c)). If reducing the [BMIM][PF_6] volume to 2 mL, we obtained no uniform CuS microspheres (Fig. 4(d)), either. It is undoubted that an ionic liquid played a crucial role in the formation of CuS microspheres. [BMIM][PF_6] shows many unique solvent properties, which are directly related to the chemical reaction processes in solution. Especially, its viscosity at 298 K is much larger than that of water (0.8937 mPa·s), although the reported values varied in a relatively large range (196–250 mPa·s), possibly due to the difficulty in experimental measurements and the purity of the ionic liquid (IL) [32]. Such a high viscosity would significantly slow down the diffusion of reaction ions in the solution. As a consequence, CuS nanostructures were formed due to a much slower rate of diffusion-controlled reaction in our present IL-water system. Thus, in this method, IL [BMIM][PF_6] performed both as a diffusion controller and an anisotropic growth director.

The nitrogen adsorption-desorption isotherm and corresponding pore size distribution of the CuS nanostructures are shown in Fig. 5. It is a typical type IV adsorption-desorption isotherm with a hysteresis loop characteristic of mesoporous materials. The BET surface area of the as-prepared CuS nanostructures is 39 m^2/g. The corresponding pore volume is 0.2 cm^3/g. As shown by BJH analyses, the as-prepared CuS nanostructures have a pore size distribution at around 60 nm (Fig. 5, inset).

The UV-Vis absorption spectrum (Fig. 6) of the CuS nanostructures re-dispersed in ethanol shows an absorption peak at about 268 nm. Similar absorption feature was also reported by Zhang et al. [33]. Compared with bulk CuS [34], the absorption peaks of CuS nanostructures obtained

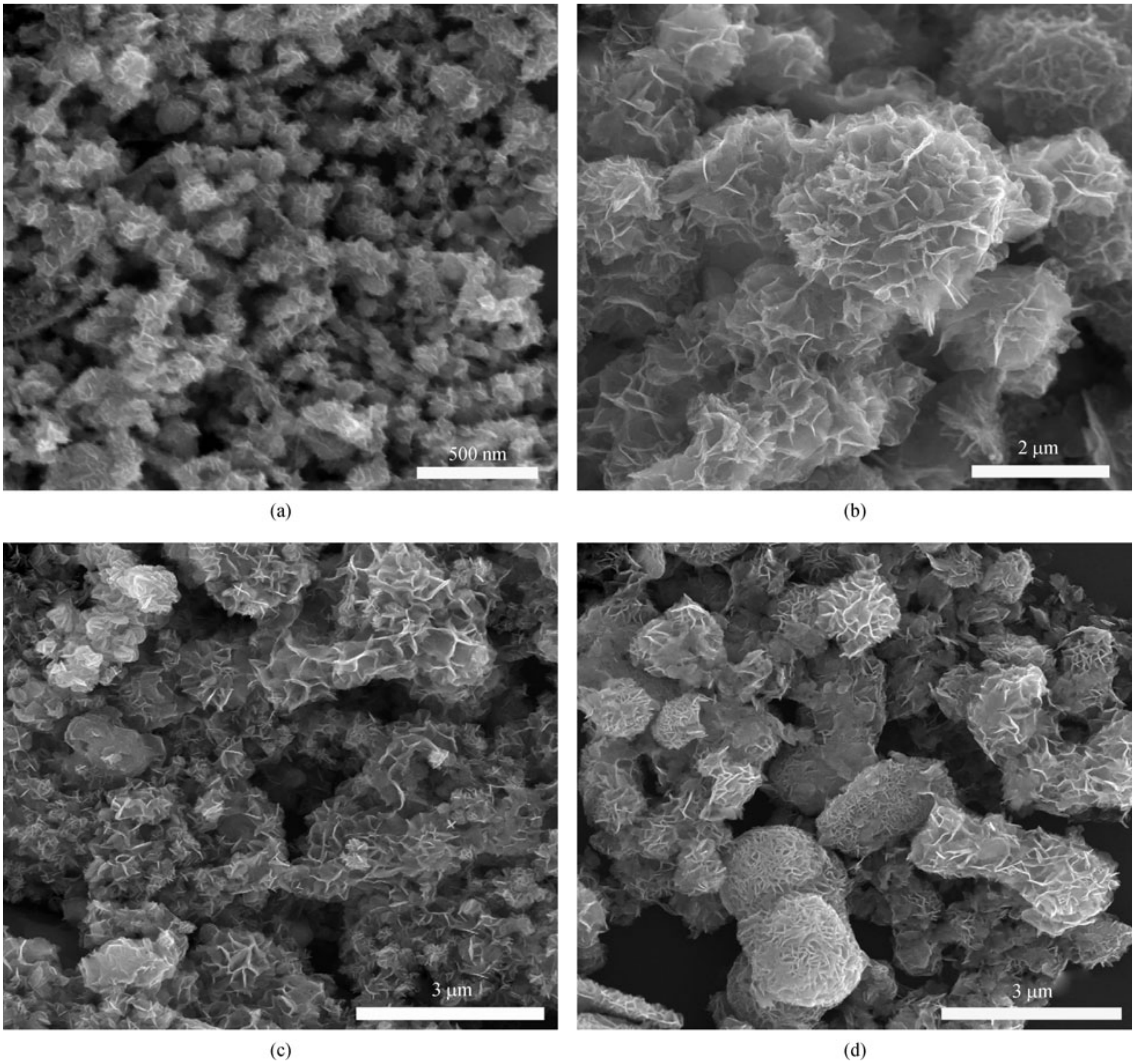

Fig. 4 FESEM images of CuS nanostructures in different conditions. (a) Reaction time for 24 h; (b) reaction time for 60 h; (c) in absence of [BMIM][PF_6]; (d) 2 mL [BMIM][PF_6]

in our work exhibit a large and distinct blue-shift, which is possibly attributed to the quantum confinement effects of the flower-like CuS nanostructures [35].

Figure 7 shows a typical room-temperature PL spectrum of the as-prepared CuS microspheres. The emission spectrum was obtained in the excitation wavelength of 350 nm. The spectrum exhibited two emission peaks. One is a weak blue emission peak centered at 432 nm. The other is a strong green emission with the peak maximum centered at 570 nm. The results are in accordance with the emission peaks of Ref. [36]. The emissions are influenced by several parameters such as shapes, size, and crystallinity, which were controlled by the synthesis conditions.

4 Conclusions

In summary, we have developed a simple and environment-friendly methods for the synthesis of flower-like CuS nanostructures in the ionic liquid 1-butyl-3-methyl imidazole six hexafluorophosphoric acid salts ([BMIM][PF_6]) at room temperature. It was found that the IL performed both as a diffusion controller and an anisotropic growth director. The as-obtained CuS nanostructures contained pores with a diameter of 60 nm and a specific surface area of 39 m^2/g. The optical properties of the as-prepared flower-like CuS nanostructures were also discussed, which indicated that the as-prepared CuS nanostructures are promising candidates in the development of photoelectric devices. This

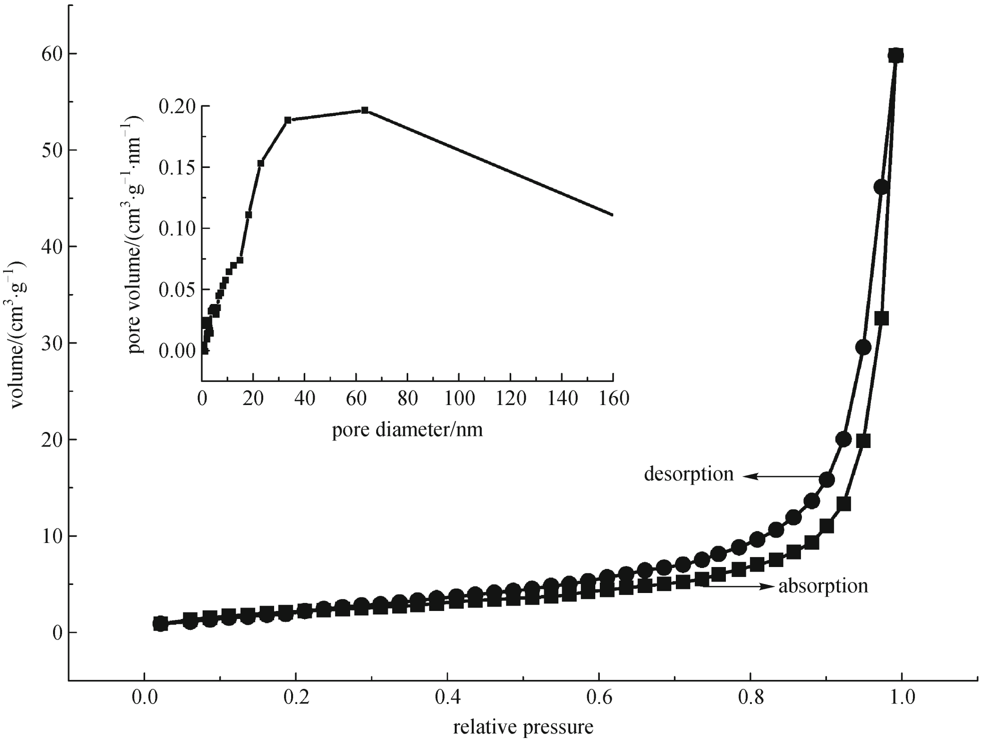

Fig. 5 Nitrogen adsorption-desorption isotherm and pore size distributions (inset) of CuS nanostructures

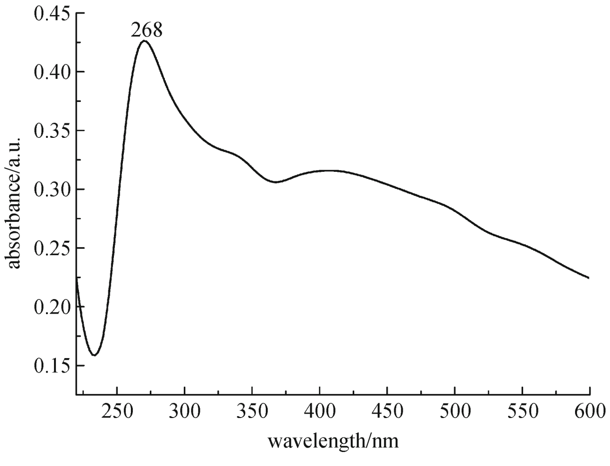

Fig. 6 UV-Vis absorption spectrum of CuS nanostructures

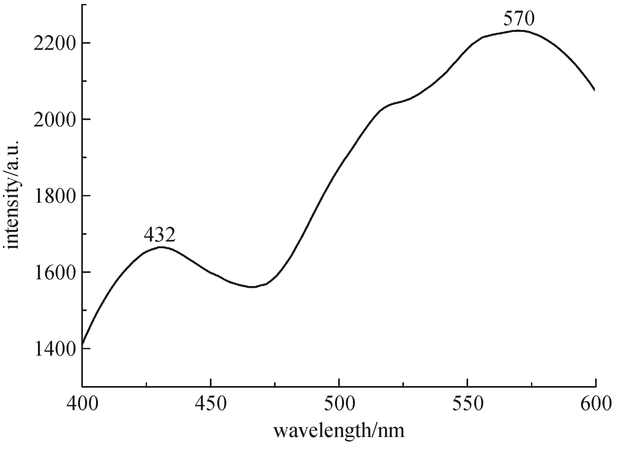

Fig. 7 Photoluminescence spectrum (excited at 350 nm) of CuS nanostructures

synthetic strategy may open new route to the synthesis of inorganic nanostructures as well as functional devices.

Acknowledgements This work was supported by the Scientific Research Foundation for the Returned Overseas Chinese Scholars (No. 2008-17), Ministry of Personnel of the People's Republic of China, and the Natural Science Foundation Project of Chong Qing (No. CSTC2007BB4332). The authors would like to thank Prof. Dingfei Zhang, College of Materials Science and Engineering, Chongqing University, for his assistances with FESEM characterization.

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