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Synthesis of bismuth sulfide three-dimensional architectures using ultrasonic radiation

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ABSTRACT

Bi_2S_3 hierarchical architectures (multipodlike- and flowerlike-structure) were successfully synthesized using thiourea as the sulfur source under ultrasonic radiation. A mixed solent system of glycol and nitric acid aqueous solution was employed for the tunable synthesis of Bi_2S_3. The results show that Bi_2S_3 multipodlike- and flowerlike-structure were consisted of nanorods, while the size and phase structure of Bi_2S_3 nanorods were severely dependent on the volume ratio of the solvent system. Furthermore, a remarkable Raman signal enhancement effect was observed in different architectures, suggesting a novel potential of Bi_2S_3 in nanosensor devices.

KEYWORDS

Nano materials;
Bi_2S_3;
Ultrasonic radiation;
Raman signal;
Scanning electron microscopy.

INTRODUCTION

Remarkable progress in the tunable synthesis of various nanomaterials (such as semiconductors, noble metals, alloys, and metal oxides) has been achieved in the past decades. Self-assembling the nanoscale building blocks into hierarchical architectures paves the prerequisite way to fabricate functional nanodevices, although both of them still remain as the great challenge.

Bismuth sulfide (Bi_2S_3) with a direct band gap (E_g) of 1.30 eV has been widely used as photovoltaic materials and photodiode arrays, as well as the thermoelectric cooling technologies derived from the Peltier effect[1,2]. A great deal of effort has been focused on the synthesis of different nanostructures of Bi_2S_3. For instance, Bi_2S_3 nanorods[3-6], nanowires[7-10], nanoribbons[11,12], microspheres[13-15], and flowerlike-structures[16-19] have been synthesized through the solvothermal processes, wet chemical routes and sonochemical methods with the assistance of biomolecules, polymers, ionic liquid, etc. Recently, a biomedical application of Bi_2S_3 nanoparticles as the injectable computed tomography (CT) imaging agent has been reported[20]. The PVP-coated Bi_2S_3 nanoparticles were demonstrated with excellent stability and biocompatibility, very long circulation time in vivo, and high X-ray absorption in particular, suggesting a promising potential in biomedical field.

In the present study, Bi_2S_3 hierarchical architectures including the flowerlike- and multipodlike-structure were tunably synthesizd using the ultrasonic radiation in a mixed solvent system. Although sonochemistry has been routinely utilized in the fabrication of various nanomaterials as one of the earliest preparation tech-

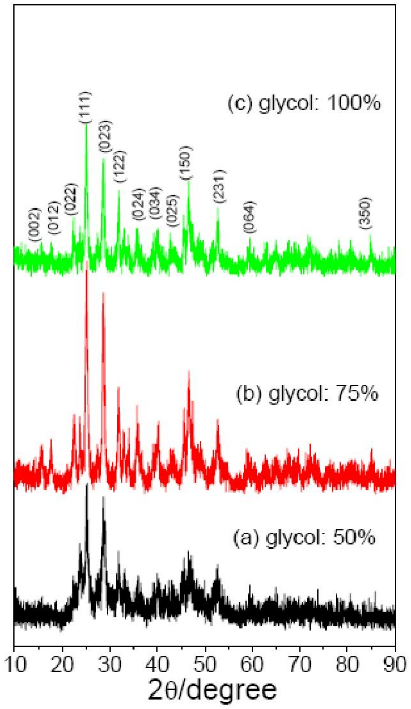

Figure 1 : XRD patterns of samples synthesized in the different solvent systems. (a) the glycol volume ratio of 50%; (b) the glycol volume ratio of 75%; (c) the glycol volume ratio of 100%

niques in the fields[21], few researches have been reported on the tunable synthesis of hierarchical architectures. Furthermore, the Bi_2S_3 flowerlike-structures consisted of nanorods display a remarkable enhancement of Raman signal.

EXPERIMENTAL

In a typical synthesis, bismuth nitrate [$Bi(NO_3)_3 \cdot 5H_2O$, 2 mmol] was dissolved into 20 mL glycol under magnetic stirring. Thiourea (Tu, 3 mmol) was dissolved into 20 mL of diluent nitric acid aqueous solution (0.025 M) under magnetic stirring. Then, Tu solution was added dropwise into bismuth nitrate solution and the mixture was treated using a ultrasonic probe (Ti-horn, 2 cm in diameter, 20 kHz, 80 W/cm^2; 88-1 Ultrasonic Instrument, Institute of Acoustics, CAS) after stirred magnetically for 16 h. The radiation was performed for 2 min followed with a interval of 2 min and five cycles were carried out. The mixture was placed for 2 h and cooled to room temperature. The precipitates were collected by centrifugation (10 000 rpm × 5 min), washed alternately with deionized water and ethanol, and dried in air at 60°C for 4 h. In the series of synthesis, the volume ratio of glycol and nitric acid solution was changed. In the case of glycol as the single solvent (100% glycol), Tu was added into the mixture after bismuth nitrate was dissolved.

The phases of samples were characterized by X-ray diffraction (XRD). The morphologies and structures of samples were observed using transmission electron microscopy (TEM, Tecnai G2-20, FEI Corp., Netherlands) and high-resolution field-emission transmission electron microscopy (HRTEM, JEM-2100F, JEOL, Japan). Raman spectra were recorded using inVia Laser Confocal Raman Microscope (Renishaw Corp., UK) at room temperature between 100 and 1500 cm^{-1}, excited with the 514.5 nm Ar$^+$ laser.

RESULTS AND DISCUSSION

The phases of samples synthesized in the different solvent systems were identified by XRD characterization. As shown in figure 1a-c, corresponding to samples synthesized with a glycol volume ratio of 50%, 75% and 100%, respectively, all the peaks can be indexed to the orthorhombic structure of Bi_2S_3 (JCPDS card No. 65-3884). The sharp peaks indicate the excellent crystalline nature of samples. Further decreasing the glycol volume ratio to 25% and 0%, the XRD diffraction patterns strongly imply the existence of unidentified impurities (data not shown). These results suggest that the volume ratio of glycol and nitric acid solution plays a crucial role in the formation of pure Bi_2S_3 crystals.

Figure 2 displays the SEM, TEM and HRTEM images of samples synthesized in the different solvent systems. As shown in Fig. 2a and b, multipodlike-structures consisted of nanorods were obtained when glycol was used as the single solvent. Nanorods consisted in multipodlike-structures are ca. 0.78 μm in average length and ca. 0.21 μm in average diameter. The perfectly aligned lattice planes and reduced FFT patterns (as shown in the insets of figure 2b, respectively) provide the strong confirmation for the well-crystallized nature of multipodlike-structures. The interplanar spacing of ca. 0.356 nm obtained from the HRTEM images can be ascribed to the adjacent (111) planes of Bi_2S_3 crystal. Flowerlike-structures were synthesized when the glycol volume ratio was adjusted to 50%, as shown in figure 2e and 2f. Nanorods consisted in flowerlike-

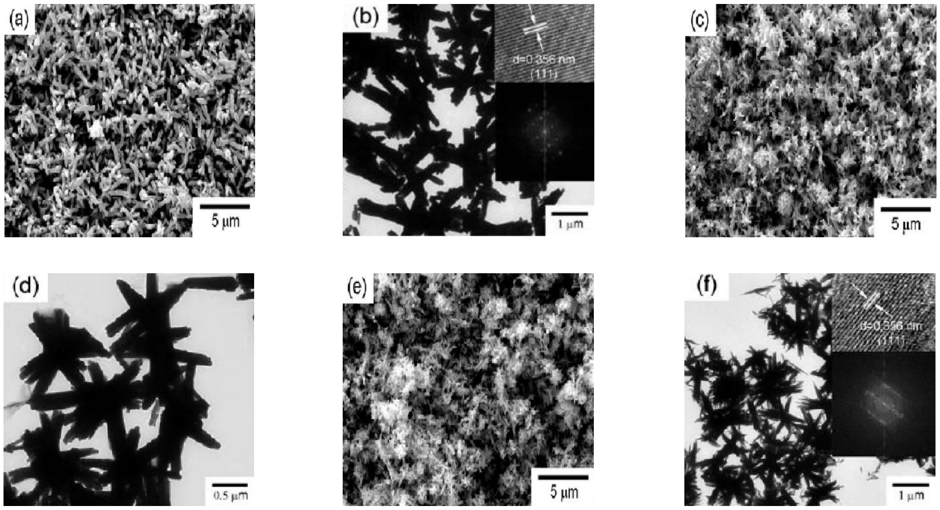

Figure 2 : SEM, TEM and HRTEM images of samples synthesized in the different solvent systems. (a) and (b): the glycol volume ratio of 100%; (c) and (d): the glycol volume ratio of 75%; (e) and (f): the glycol volume ratio of 50%. The insets in panel (b) and (f) show an enlargement of HRTEM images (upper-right) and the reduced FFT patterns (lower-right) of the sample

structures are ca. 0.53 μm in average lengthand and ca. 40 nm in average diameter. The single crystal nature of samples can be also confirmed by the perfectly aligned lattice planes and reduced FFT patterns. Both of the multipodlike- and flowerlike-structures was observed in the case of the glycol volume ratio at 75% (Figure 2c and 2d). Obviously, the sizes of nanorods in the architectures were severely influenced by the volume ratio of glycol and nitric acid solution in the solvent system.

Tu has been shown to control the morphological evolution of metal sulfides in the solution phase[9,13,22]. In the present studies, bismuth ions were coordinated with Tu to form the complex of$[Bi(Tu)_n^{3+}]$, which could be decomposed under the ultrasonic radiation and resulted in the formation of Bi_2S_3 multipodlike-structures. However, the decomposition of$[Bi(Tu)_n^{3+}]$ complex was accelerated in the presence of nitric acid solution due to the instability of Tu in the acidic environment, leading to the formation of more Bi_2S_3 nuclei compared with that in the absence of nitric acid solution. Therefore, flowerlike-structures consisted of nanorods in smaller diameter and shorter length was obtained, instead of the larger multipodlike-structures.

The Raman spectra of Bi_2S_3 nanostructures were recorded at room temperature between 100 and 1500 cm^{-1}, as shown in Fig. 3. A steep Raman absorption band consisted of two shoulder peaks at ca. 234.95 cm^{-1} and 252.36 cm^{-1} can be contributed to Bi-S bond, well agreed with that reported previously[9,13,22]. Very interestingly, a significant enhancement of absorption intensity in Raman spectra has been shown with the decrease of glycol volume ratio from 100% to 75% and 50% in solvent system, which is probably derived from the smaller size of nanorods in the flowerlike-structures. Although Raman shifts of Bi_2S_3 nanostructures have been reported in the literatures[23-26], the size-dependent Raman signal enhancement has been rarely reported[18,27,28].

CONCLUSIONS

In conclusion, Bi_2S_3 hierarchical architectures including multipodlike- and flowerlike-structure were successfully synthesized using thiourea as the sulfur source and glycol/nitric acid solution as the mixed solvent system under ultrasonic radiation. Particularly, the obtained Bi_2S_3 nanostructures display a significant Raman signal enhancement effect dependent on its size. The simple and low-cost route can be potentially employed to the synthesis of other metal chalcogenide hierarchical nanostructures.

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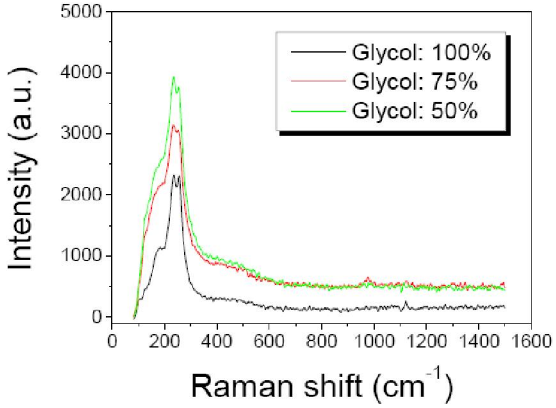

Figure 3 : Raman spectra of samples synthesized in the different solvent systems

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