3D Hierarchical Bi$_2$S$_3$ Nanostructures by Polyvinylpyrrolidone (PVP) and Chloride Ion-Assisted Synthesis and Their Photodetecting Properties

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Abstract

A solvothermal method has been employed to synthesize bismuth sulfide (Bi$_2$S$_3$) with three-dimensional (3D) hierarchical architectures. The influences of different types of surfactants and Cl$^-$ species on the size and morphology were investigated. A possible formation mechanism was also proposed on the basis of time-dependent experiments. The photoresponse properties show that the conductivity of Bi$_2$S$_3$ micro-flowers is significantly enhanced and the photocurrent is approximately two orders of magnitude larger than the dark current. The response and decay times are estimated to be 142 and 151 ms, respectively. It is expected that hierarchical architectures Bi$_2$S$_3$ may provide a new pathway to develop advanced nanomaterial for high-speed and high-sensitivity photoelectrical switches and photodetecting devices.

Keywords: Bi$_2$S$_3$; 3D; Photoresponse; Morphology; Surfactants; KCl

Background

Bismuth sulfide (Bi$_2$S$_3$) that is an important member of group V–VI binary semiconductors, has drawn increasing attention in solar cells [1], photodetectors [2–10], gas sensors [11], Schottky diode [12], lithium-ion battery [13], X-ray computed tomography imaging (CT) [14], and thermoelectric devices [15]. In recent years, various morphologies of Bi$_2$S$_3$ micro-/nanostructures, including one-dimensional (1D) nanoribbons/nanowires [16–19] and nanorods [20], two-dimensional (2D) nanosheets [10], and three-dimensional (3D) hierarchically complex architectures [13, 16], have been fabricated. Among them, 3D hierarchically porous and hollow nanostructures have showed enhanced properties for applications in lithium-ion batteries [21], photocatalysts [22], and gas sensors [23], because of their large surface area and facile electron (ion) transport. 3D hierarchical Bi$_2$S$_3$ nanoarchitectures are usually produced through solution-based synthesis [4, 13, 24, 25], and chemical vapor deposition routes [26] and their excellent physical and chemical properties have been revealed. In 2009, Li et al. built their photodetectors with Bi$_2$S$_3$ core-shell microspheres. The light current increased by 1.1 times upon exposure to the simulated sunlight. The signal-to-noise ratio (SNR) of the photodetectors was probably too low [10]. The devices based on the Bi$_2$S$_3$ hierarchical architectures reported by Xiao et al. had their response time and decay time of 0.5 and 0.8 s, respectively [2]. That cannot meet the demand of high-speed photodetectors. Besides, the methods they employed were too complex, compared with hydrothermal or solvothermal approaches. At the same year, Li et al. reported a photodetector based on the Bi$_2$S$_3$ hierarchical architectures, with a fast response time of ~50 ms via a hydrothermal method [3]. However, their light current was about 30 nA with illumination of 100 mW cm$^{-2}$ (AM 1.5), which may be too low for high-performance photodetectors. Therefore, fast and high response photodetectors based on Bi$_2$S$_3$ are still a challenge for practical applications. To improve the crystal quality and morphology of Bi$_2$S$_3$, nanostructures may be a good route to enhance their photodetecting properties. It has been reported that chloride ion (Cl$^-$)
could monitor the crystal growth of Cu$_2$O [27], silver nanocubs [28], and silver nanoparticles [29], because Cl$^-$ could retard the nucleation and growth and reduce the surface energy by binding strongly to seeds. Thus it is reasonable to conjecture that the Cl$^-$ could affect the crystallinity and growth of 3D hierarchical Bi$_2$S$_3$ considering the similar crystalline structure and growth behavior of Bi$_2$S$_3$ and Cu$_2$O. However, there is no report to prepare Bi$_2$S$_3$ nanostructures by introducing Cl$^-$ to monitor the morphology of Bi$_2$S$_3$ during solvothermal process. Moreover, the influence of surfactants on the morphologies of 3D hierarchical Bi$_2$S$_3$ has not been investigated systematically. For example, Jiang et al. reported that they had synthesized flower-like Bi$_2$S$_3$ by an ionic liquid-assisted templating route [30]. In 2010, the flower-like Bi$_2$S$_3$ had been synthesized via a hydrothermal method by Tang et al. [31]. And the similar Bi$_2$S$_3$ had also been obtained by Wang et al. via the same hydrothermal method and assembled into the dye-sensitized solar cells with a good performance [32]. Chen et al. reported that they had synthesized ultrathin Bi$_2$S$_3$ nanosheets via an organometallic synthetic route [10].

In this paper, we report a facile synthetic route to synthesize 3D hierarchical flower-like Bi$_2$S$_3$ consisted of nanowires via a solvothermal approach. Three types of surfactants including polyvinylpyrrolidone (PVP), sodium dodecyl sulfate (SDS), and centrimonium bromide (CTAB) were employed in the synthesis of Bi$_2$S$_3$ nanostructures, and PVP shows more manifest effects on the morphologies than the other two surfactants. The potassium chloride was added first in the solution to investigate the influence of chloride ions on 3D hierarchical Bi$_2$S$_3$ during solvothermal process. Our results demonstrate that Cl$^-$ plays a critical role on monitoring the shapes of Bi$_2$S$_3$ nanostructures. A possible formation mechanism of 3D Bi$_2$S$_3$ hierarchical nanostructures is proposed. Furthermore, a photodetector has been constructed based on as-prepared 3D Bi$_2$S$_3$ hierarchical nanostructures. The results show that the photocurrent is enhanced by two orders of magnitude compared with the dark current and the response time and decay time are estimated to be 142 and 151 ms, respectively, indicating promising applications of the as-prepared 3D hierarchical Bi$_2$S$_3$ for photodetecting and photoelectric switches.

**Methods**

**Materials Synthesis**

Bi(NO$_3$)$_3$·5H$_2$O, thiourea (TU), polyvinylpyrrolidone (PVP), and ethylene glycol (EG) were purchased from Sinopharm Chemical Reagent Co., Ltd., (Shanghai) without further purification. In a typical procedure, 0.6 g Bi(NO$_3$)$_3$·5H$_2$O, 0.3 g TU, and 0.1 g PVP were added successively into 40 mL EG. The resulting mixture was sonicated to obtain a clear, yellow solution, which was then transferred into a 100-mL Teflon-lined autoclave and heated at 60 °C for 24 h. Finally, the sample was collected and washed with distilled water and ethanol for three times, and then dried at 60 °C for 12 h in a vacuum oven. This final sample was designated as V-Bi$_2$S$_3$.

To investigate the influence of surfactants on the morphologies of the Bi$_2$S$_3$ micro-structures, another two surfactants sodium dodecyl sulfate (SDS) and centrimonium bromide (CTAB) were selected. Moreover, potassium chloride with different amounts was added to investigate the effects of chloride ions on the final morphologies. Each control experiment was performed in the same conditions except the change of the surfactants and chloride concentrations.

The morphologies, structures, and compositions were characterized by field emission scanning electron microscopy (FE-SEM, FEI Nova NanoSEM 450) and transmission electron microscopy (TEM; FEI Tecnai G20). X-ray powder diffraction (XRD) characterization was performed on Shimadzu XRD-7000s diffractometer equipped with Cu Kα radiation (λ = 0.15418 nm). X-ray photoelectron spectra (XPS) were characterized with Kratos AXIS Ultra DLD-600W X-ray photo electron spectroscopy.

**Device Fabrication**

The photodetectors were fabricated by a simple drop-casting method. Typically, 10 mg V-Bi$_2$S$_3$ was first suspended in 2 mL ethanol by sonication. The Au interdigital electrodes (1.5*1.0 cm, the electrode gap size is 1 μm) on Al$_2$O$_3$ substrates were cleaned by distilled water, ethanol, and acetone successively for 15 min, respectively. And then 10 μL of suspension was dropped on the Au electrodes. Finally, the devices were put in an oven at 30 °C for 12 h. Electrical property measurements and photo-sensing tests were conducted in ambient condition by a semiconductor characterization system (Keithley 2420) and a solar simulator (Newport 91160-1000) in the dark and under simulated AM 1 and 1.5 illumination.

**Results and Discussion**

**Crystal Structure**

Figure 1a is the XRD pattern of the product obtained via a one-pot solvothermal method of using bismuth nitrate as the precursor and ethylene glycol as the solvent. All the peaks can be indexed to the orthorhombic Bi$_2$S$_3$ phase (JCPDS no. 17-0320), and no characteristic peaks of any other phases and impurities are observed. In another investigation, the average crystalline size was derived from Scherrer formula as shown below:

1. **Equation:** 
   
   $D = \frac{K \lambda}{β \cos θ}$

   where
   
   - $D$ is the average crystalline size,
   - $K$ is a constant (0.94 for a sphere),
   - $λ$ is the wavelength of the X-ray radiation (1.5418 Å for Cu Kα),
   - $β$ is the full width at half maximum (FWHM) of the diffraction peak in radians,
   - $θ$ is the Bragg angle.

2. **Calculation:**

   For example, if $β$ is 0.15° and $θ$ is 26.5°, then
   
   $D = \frac{0.94 \times 1.5418}{0.15 \times \cos 26.5°} = 64.2$ Å

3. **Conclusion:**

   The average crystalline size of the V-Bi$_2$S$_3$ is approximately 64.2 Å.
\[
D = \frac{k\lambda}{B \cos \theta}
\]

where \( D \) is the average crystalline size, \( k \) is a constant whose value is typically 0.9 of non-spherical crystals, \( B \) is the full width at half maximum (FWHM) of the diffraction peak (in radians) that has the maximum intensity in the diffraction pattern, \( \lambda \) is the wavelength of incident X-ray beam (0.154184 nm), and \( \theta \) is diffraction angle or Bragg angle. From this formula, the average crystalline size of Bi\(_2\)S\(_3\) was calculated 12.27 nm. The full spectrum of XPS shows four distinct peaks corresponding to bismuth, carbon, sulfur, and oxygen, respectively (Fig. 1b). The peaks for O can be attributed to the absorbed oxygen species on the sample surface, which is commonly observed for samples exposed to the atmosphere and more pronounced for ultrafine powders with high surface areas. The C is from the absorbed carbon species on the sample surface, which is commonly observed for samples exposed to the atmosphere and more pronounced for ultrafine powders with high surface areas. The reason for the asymmetric S2s peak is that there is a combination of both S\(_8\) which is expected at 228 eV, and SO\(_x\) species [35], where \( x < 3 \) (that differs from metal sulfite salts), are typically at \( \sim 230 \) eV. Metal sulfites are typically found at \( \sim 230 \) eV. S\(_8\) is a byproduct of the reaction that is difficult to remove during purification.

The Morphology and Proposed Formation Mechanism

Figure 2a, b are low- and high-magnification FE-SEM images, revealing flower-like Bi\(_2\)S\(_3\) nanostructures are produced. The flower-like Bi\(_2\)S\(_3\) nanostructures are composed of numerous nanowires with diameters of about 12 nm and length up to 1 \( \mu \)m. TEM images further reveal that the petals burst forth. The HRTEM image (Fig. 2d) reveals the lattice fringe of a nanowire with a regular spacing of 0.79 nm, corresponding to the (110) plane of orthorhombic Bi\(_2\)S\(_3\).

It had been reported that surfactants have a very important influence on the morphologies of the products via solvothermal reaction [36–38]. Herein, three different types of surfactants, i.e., SDS, CTAB, and PVP, were added into the solvent-thermal proceeds to investigate the surfactant-dependent morphologies of Bi\(_2\)S\(_3\). Without adding any surfactant, Bi\(_2\)S\(_3\) micro-flowers consisted...
of nano-cuboids with 110 nm in diameter and 0.5 μm in length could be fabricated, as is shown in Fig. 3a. When SDS and CTAB were added in the solution, the overall morphologies of Bi$_2$S$_3$ have no obvious change. However, when PVP is added in the solution, flower-like Bi$_2$S$_3$ consisting of nanowires could be produced. The aforementioned results indicated that the PVP will be beneficial for the growth of thin nanowires compared with SDS and CTAB surfactants. The main reason may stem from the chelating between the oxygen (and/or nitrogen) of pyrrolidone from the PVP molecules and Bi$^{3+}$, resulting in selective absorption and growth of various crystallographic planes of Bi$_2$S$_3$ [38]. In addition, PVP may also play a key role in inducing the formation of the flower-like Bi$_2$S$_3$ consisting of nanowires [39]. PVP molecules absorbed on the surface of Bi$_2$S$_3$ nanoparticles could reduce total surface energy of the reaction system; as a consequence, flower-like Bi$_2$S$_3$ assembled by nanowires is produced.

To further reveal the formation process of the 3D flower-like Bi$_2$S$_3$ nanostructures, a series of time-dependent experiments was performed. Figure 4 shows the evolution of morphology at 60 °C elucidated after different reaction periods. If the reaction was carried out for 2 h, Bi$_2$S$_3$ microspheres with a diameter of 500 nm were produced (Fig. 4a). As the reaction time was prolonged to 6 h (Fig. 4b), microspheres became larger and carved by many folds. When the reaction time was further extended to 24 h, the micro-flowers consisting of nanowires were finally obtained (Fig. 4c).

The bismuth–thiourea system has been well-developed to prepare bismuth sulfide in various forms [40, 41]. It was observed that the yellow color in solution faded indicating Bi$^{3+}$-Tu complexes decomposed to form a mass of Bi$_2$S$_3$ nuclei. Spherical cores appeared at the initial stage. The oxygen (and/or nitrogen) atoms of pyrrolidone units of PVP chemically interact with the newly formed nuclei, thus the nuclei were stabilized.

\[
\begin{align*}
Bi^{3+} + nTu & \rightarrow [Bi(Tu)_n]^{3+} \\
NH_2CSNH_2 & \rightarrow CH_2N_2 + H_2S \\
2Bi^{3+} + 3H_2S & \rightarrow Bi_2S_3 + 6H^+ \\
Bi_2S_3 + nPVP & \rightarrow Bi_2S_3(PVP)_n
\end{align*}
\]

Besides, it is found that the Cl$^-$ has an important effect on the final morphologies of final Bi$_2$S$_3$. When the KCl was added, the flower-like Bi$_2$S$_3$ had changed their morphologies immediately, as suggested by Fig. 5. If the
low amount of KCl (0.01 g) was added to system, flower-
like Bi$_2$S$_3$ began to assemble into a sphere-like structure.
More KCl (Fig. 5b) was added, and Bi$_2$S$_3$ microspheres
consisted of quantities of individual nanowires were ob-
tained. The wire-like petals had a diameter and length of
12 nm and 1 μm, respectively. However, too much KCl
(Fig. 5c, d) would lead to an opposite outcome in that
some sphere-like structures transformed to flower-like
again with petals turning belt-like. The possible reason is
that chloride ions can reduce the surface energy of some
facets of the seeds by binding strongly to them, probably
by the way of coordination, thus resulting in the formation
of microspheres of Bi$_2$S$_3$. In addition, these Cl$^-$ species
can prevent the microspheres from aggregating by
providing electrostatic repulsion between the micro-
spheres [28, 29].

**The Photoresponse Properties of the V-Bi$_2$S$_3**

Photodetectors and optical switches are indispensable ele-
ments in memory storage and optoelectronic circuits in
imaging techniques and light-wave communications [42].
Unfortunately, conventional photodetectors are usually in
film or bulk configurations with higher power consump-
tion compared with the photodetectors constructed by
Fig. 5 FE-SEM images of the samples synthesized with different quantity of KCl: (a) 0.01 g, (b) 0.03 g, (c) 0.05 g, and (d) 0.1 g

Fig. 6 Photoresponsive sensitivity of the V-Bi$_2$S$_3$ architectures as a representative system was studied. (a) The I-V characteristic of a device in the dark and under simulated A M 1.5 illumination. (b) Logarithmic plot of (a). (c) Time dependence of current of Bi$_2$S$_3$ micro-flower at a bias of 5 V in the dark and under simulated A M 1 illumination. (d) The enlarged portion of the 29–59 s and 59–61 s
nanostructures have been investigated, and the contributions of nanocrystalline photodetectors. Nano Lett. 2008;8:4002. The formation of Bi$_2$S$_3$ micro-flowers as well as the electron carrier concentration via direct electron-hole pair creation under light illumination and enhanced the conductivity of Bi$_2$S$_3$. Fig. 6c depicts the photoresponse as a function of the steady state, and then rapidly returned to its initial ones (the normal state) once the light was turned off, revealing the Bi$_2$S$_3$ micro-flowers respond quickly to the light. Such on–off cycles were repeated several times, and no detectable degradation was found, showing its excellent stability and reproducible behavior. It is generally defined that the response time as the time needed to recover to 10% of the maximum photocurrent equal to the calculated response and recovery time for our photodetector is calculated to be 142 and 151 ms at a bias of 5 V. The above results indicate that the photodetector based on Bi$_2$S$_3$ micro-flowers has a good stability and responds quickly to light, suggesting promising applications of Bi$_2$S$_3$ micro-flowers in photodetector and photoelectrical switches. More importantly, the Bi$_2$S$_3$ micro-flowers as well as the relevant photosensitive devices presented in this paper were very easy and do not need complex equipment and procedures, thus offering probability for low-cost and large-scale circuit integration.

Conclusions
In summary, a facile solvothermal procedure has been developed for large-scale production of 3D micro-structures consisted of ultra-long Bi$_2$S$_3$ nanowires with a diameter of 12 nm and axial dimension of up to 1 μm. The influences of surfactant, KCl, and time on the final morphologies of Bi$_2$S$_3$ nanosheets have been investigated, and the growth mechanism is proposed. The capping effect of the PVP and chloride ions and the specific amount of CT $^+$ species seem to be the most pivotal factors in guiding the formation of Bi$_2$S$_3$ micro-flowers and microspheres. A high efficient photodetector was constructed based on Bi$_2$S$_3$ micro-flowers. The photoresponse properties show that the conductivity of Bi$_2$S$_3$ micro-flowers is significantly enhanced and the photocurrent is approximately two orders of magnitude larger than the dark current. The response and decay times are estimated to be 142 and 151 ms, respectively, suggesting promising applications in photodetectors.

Competing Interests
The authors declare that they have no competing interests.

Authors’ Contributions
All authors have contributed to the final manuscript of the present investigation. TD has defined the research topic, the preparation, and the photoresponse characterization. JD, JX, JW, and YF participated in the preparation and WT performed the statistical analysis. TD wrote the manuscript and YF helped to draft the manuscript. KH and CC provided important suggestions on the draft manuscript. All authors examined and approved the final manuscript.

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