Synthesis and Compactness Dependence on Flower-like Copper Germanate

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Flower-like CuGeO₃ has been obtained using a simple hydrothermal process by controlling the compactness. X-ray diffraction shows that the flower-like CuGeO₃ is composed of orthorhombic CuGeO₃ phase. Scanning electron microscopy displays that the size of each flower-like CuGeO₃ is about 3 μm which consists of the accumulation of dozens of CuGeO₃ nanorods with the diameter and length of less than 100 nm and about 1 μm, respectively. Compactness dependence results demonstrate that the compactness is the key factor for the formation of flower-like CuGeO₃. Free-standing CuGeO₃ nanowires can be obtained by improving the compactness. Hydrothermal temperature and reaction time have important roles on the size and formation of the flower-like CuGeO₃.


Keywords: flower-like CuGeO₃; compactness; hydrothermal process; electron microscopy

I. INTRODUCTION

Great research interest has been devoted to gemanate one-dimensional (1D) nanomaterials due to the novel physical properties for electrochemical sensors, catalysis, optical and nanoscale electronic devices [1–3]. Cd₂Ge₂O₆ nanowires [4, 5], In₅Ge₂O₇ nanowires [6], zinc germanate nanowires and nanorods [7–12], PbGeO₃ nanowires [13], strontium germanate nanowires [14], calcium germanate nanowires [15, 16] and Bi₂GeO₅ nanobelts [17] have been successfully synthesized by different methods, such as hydrothermal method, thermal evaporation and chemical vapour deposition (CVD) process. Among these germanates, copper germanate (CuGeO₃), as the first solid-state compound that undergoes a spin-Peierls transition, CuGeO₃ and its analogues with the SP transition were merely prepared by high temperature reaction processes, in which a floating-zone method was generally employed to ensure the growth of large single crystals [18]. In an opinion of the strong relationship between the structures and properties of CuGeO₃, it is of great significance to extend the research of CuGeO₃ 1D nanomaterials.

Single crystalline CuGeO₃ nanobelts have been synthesized by a simple hydrothermal route using cetyltrimethylammonium bromide (CTAB) as the surfactant at 180°C for 24 h [19]. The obtained CuGeO₃ nanobelts show distinct susceptibility behaviors in comparison with CuGeO₃ bulk crystals. Interesting magnetic properties of the layered CuGeO₃ nanobelts were also obtained. In our past research, by the combination of hydrothermal method and deposition process, single crystalline CuGeO₃ nanowires have been synthesized using GeO₂, copper sheets [20] and GeO₂, CuO, copper sheets [21] as the Ge raw material, Cu raw material and deposition substrate, respectively. The obtained CuGeO₃ nanowires display good optical and electrochemical properties. The CuGeO₃ nanowires can be used as a kind of novel electrochemical modified electrode material which exhibits a novel electrocatalytic effect to the electrochemical reaction of L-cysteine. The intensities of two electrochemical anodic peaks at the modified electrode are proportional to the concentration of cysteine, which can be used to detect cysteine sensitively [22].

Very recently, single crystalline CuGeO₃ nanowires in bulk have been successfully synthesized via a facile hydrothermal process using GeO₂ and Cu(CH₃COO)₂·H₂O as the raw materials in the absence of any surfactants by us so as to improve the yield of the CuGeO₃ nanowires [23]. The yield of the CuGeO₃ nanowires is higher than 80 wt.%. It is noticed that the compactness of the autoclave is a very important factor for the formation of 1D nanostructures with different morphologies [24]. The volume ratio of water in the autoclave is called compactness. In the paper, we report the synthesis of flower-like CuGeO₃ by controlling the compactness using GeO₂ and Cu(CH₃COO)₂·H₂O as the raw materials without using any surfactants. The compactness dependence on the formation of the CuGeO₃ nanostructures has been analyzed and the formation process of the flower-like CuGeO₃ is also discussed.

II. EXPERIMENTAL

High pure GeO₂ powders (purity: ≥99.99%) and Cu(CH₃COO)₂·H₂O (A.R. grade, purity: ≥99.0%) were
purchased from Sinopharm Chemical Reagent Co., Ltd. of China. All raw materials were used without further purification. In a typical procedure, 0.16 g GeO$_2$ and 0.305 g Cu(CH$_3$COO)$_2$·H$_2$O were dissolved in 20 mL deionized water under vigorous stirring. The compactness of the autoclave is 20 vol.%. Then, the mixture was placed into a 100 mL autoclave. The autoclave was maintained at 180°C for 24 h. Subsequently the autoclave was cooled naturally in air. The light blue precipitates were filtered, washed with deionized water for several times and dried at 60°C in air.

The light blue samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) spectrum. XRD pattern was carried out on a Bruker AXS D8 X-ray diffractometer equipped with a graphite monochromatized Cu-Kα radiation (λ = 1.5406Å). The samples were scanned at a scanning rate of 0.05°/s in the 2θ range of 20-80°. SEM observation was performed using JEOL JSM-6490LV SEM with a 15-KV accelerating voltage. FTIR spectroscopy (Perkin Elmer PE, WQF-410 spectrometer) was used at room temperature in the range of 4000-450 cm$^{-1}$ with a resolution of 4 cm$^{-1}$.

III. RESULTS AND DISCUSSIONS

The XRD pattern of the light blue products obtained from 180 °C for 24 h with the compactness of 20 vol.% is shown in Fig. 1. All indexed peaks in the spectrum are well matched with those of the orthorhombic structure CuGeO$_3$ (JCPDS Card No. 32-0333) which is same to that of the CuGeO$_3$ nanowires prepared from GeO$_2$, copper sheets [20] and GeO$_2$, Cu(CH$_3$COO)$_2$·H$_2$O [23] respectively. No other impurity peaks are detected in the spectrum further confirming that the obtained product is pure CuGeO$_3$.

The SEM images of the light blue products with different magnification are shown in Fig. 2. From the SEM images, it can be seen that the products exhibit flower-like morphology. So the products are defined as flower-like CuGeO$_3$. The size of each CuGeO$_3$ nanoflower is about 3 µm (Fig. 2(a)). The magnified SEM image (Fig. 2(b)) shows that the flower-like structures are composed of the accumulation of dozens of CuGeO$_3$ nanorods. The diameter of the nanorods in the flower-like CuGeO$_3$ is less than 100 nm and the length is about 1 µm. It is found that the nanorods originate from a single center arranging them in a spherical sharp exhibiting flower-like morphology. The morphology of the flower-like CuGeO$_3$ from a large amount of nanorods is similar to those of ZnO [25] and MoO$_3$ [26] flower-like morphology grown by hydrothermal process.

The FTIR spectrum of the flower-like CuGeO$_3$ obtained from 180°C for 24 h with the compactness of 20 vol.% is shown in Fig. 3. The absorption bands at 2800-3800 cm$^{-1}$ with the absorption peaks at 3407.60 cm$^{-1}$ and 2933.19 cm$^{-1}$ are the characteristic stretching vibration of hydroxylate (–OH) originating from water. Peaks at 1633.41 cm$^{-1}$, 1398.14 cm$^{-1}$ and 620.97 cm$^{-1}$ are assigned to the vibration of carboxylate (O–C=O) which is caused by the residue (CH$_3$COO)$^-$ in the product [27]. The absorption peaks at 710-861 cm$^{-1}$ are attributed to the vibration mode B$_{2u}$ and A$_g$ fundamental of the GeO$_4$ group of CuGeO$_3$ [28]. CuGeO$_3$ consists of basic building blocks of corner-sharing GeO$_4$ tetrahedra. Cu atoms are surrounded by six O atoms forming strongly deformed CuO$_6$ octahedra. Therefore, these absorption peaks at 854.31 cm$^{-1}$, 815.74 cm$^{-1}$ and 719.32 cm$^{-1}$ are attributed to GeO$_4$ group of CuGeO$_3$. The absorption peak at 528.39 cm$^{-1}$ corresponds to the Cu–O deformed vibration of CuGeO$_3$ [29].

The roles of the hydrothermal temperature and reaction time with the compactness of 20 vol.% on the formation of the flower-like CuGeO$_3$ are analyzed in order to understand the possible formation process of the flower-
Like CuGeO$_3$. Figure 4 is the SEM images of the products obtained from 180°C for 12 h, 6 h and 0.5 h, respectively. Flower-like CuGeO$_3$ with similar morphology is still observed with the decrease of the reaction time at 180°C. The size of the nanorods in the flower-like CuGeO$_3$ is similar with the reaction time decreasing to 12 h (Figs. 4(a) and (b)). However, the diameter and length of the nanorods in the flower-like CuGeO$_3$ decrease to about 50 nm and 500 nm, respectively with the reaction time decreasing to 6 h (Figs. 4(c) and (d)). Furthermore, some microscale particles are observed besides the flower-like CuGeO$_3$ when the reaction time continues 0.5 h (Figs. 4(e) and (f)). The diameter and length of the nanorods in the flower-like CuGeO$_3$ decrease to about 30 nm and 300 nm, respectively. These microscale particles act as a kind of intermediate reaction product forming the nuclei. The nanorods in the flower-like CuGeO$_3$ originate from nuclei of the microscale particles and grow continuously with the increase of the reaction time.

Figure 5 is the SEM images of the products obtained from 120°C and 80°C for 24 h, respectively showing the similar flower-like morphology. The diameter and length of the nanorods in the flower-like CuGeO$_3$ in Figs. 5(a) and (b) are similar to those synthesized from 180°C for 24 h. However, the diameter and length of the nanorods in the flower-like CuGeO$_3$ decrease to about 70 nm and 500 nm, respectively (Figs. 5(c) and (d)) when the hydrothermal temperature decreases to 80°C.

According to the SEM results synthesized from different reaction time and hydrothermal temperature with the compactness of 20 vol.%, it is suggested that the reaction time and hydrothermal temperature play important roles in the formation and size of the flower-like CuGeO$_3$. What is essential role on the formation of the flower-like CuGeO$_3$? It is known that the free-standing CuGeO$_3$ nanowires can be obtained by controlling the compactness of 60 vol.% [23]. Further compactness dependence on the formation of the flower-like CuGeO$_3$ is analyzed in order to understand the possible formation reason of the flower-like CuGeO$_3$. Figure 6 is the SEM images of the products obtained from 180°C for 24 h with the compactness of 40 vol.%, 60 vol.% and 80 vol.%, respectively.
Cluster-shaped structures composed of nanorods with the increased length of about 5 μm are observed when the compactness increases to 40 vol.% (Figs. 6(a) and (b)). When the compactness increases to 60 vol.%, a large amount of uniform free-standing CuGeO$_3$ nanowires with typical lengths of several tens of micrometers and average diameter of about 50 nm are obtained (Figs. 6(c) and (d)). No flower-like CuGeO$_3$ morphology is found from the products. The free-standing CuGeO$_3$ nanowires have a broad diameter distribution with the compactness increasing to 80 vol.% (Figs. 6(e) and (f)). The diameter of the CuGeO$_3$ nanowires increases to 0.1-2 μm. The results suggest that the compactness is the essential factor for the formation of the flower-like CuGeO$_3$.

Figure 7 shows the FTIR spectra of the products obtained from 180°C for 24 h with the compactness of 40 vol.% 60 vol.% and 80 vol.%. The FTIR spectra of the products obtained from different compactness exhibit absorption peaks at about 3421.81 cm$^{-1}$, 1633. 84 cm$^{-1}$, 856.56 cm$^{-1}$, 812.32 cm$^{-1}$, 723.84 cm$^{-1}$, 617.05 cm$^{-1}$ and 528.57 cm$^{-1}$. The absorption peaks are very similar to that of the products obtained from the compactness of 20 vol.% The results show that the CuGeO$_3$ can be formed from different compactness.

According to the present experiment results, the flower-like CuGeO$_3$ is considered to be formed by an assembled growth process. At the initial reaction stage of GeO$_2$ and Cu(CH$_3$COO)$_2$·H$_2$O, GeO$_2$ reacts with H$_2$O forming H$_2$GeO$_3$. The reaction between Cu$^{2+}$ and H$_2$GeO$_3$ yield CuGeO$_3$ cores. Therefore, nucleation process exists at the initial reaction stage of GeO$_2$ and Cu(CH$_3$COO)$_2$·H$_2$O forming CuGeO$_3$ crystals. The nanorods originating from the CuGeO$_3$ nuclei grow continuously with the increase of the reaction time and hydrothermal temperature. When the compactness of the autoclave is low, such as 20 vol.%, the CuGeO$_3$ nanorods mainly exist in the bottom of the autoclave with less water owing to the vaporization of water arranging themselves in a flower-like structure by an assembled process. With the increase of the compactness of the autoclave, the CuGeO$_3$ nanorods mainly exist in water resulting in the formation of the free-standing CuGeO$_3$ nanowires.

**IV. CONCLUSIONS**

In summary, flower-like CuGeO$_3$ with orthorhombic CuGeO$_3$ nanorods has been achieved by a hydrothermal route by controlling the compactness of 20 vol.%. No surfactants are necessary for the synthesis of the flower-like CuGeO$_3$. The diameter of the total flower-like structure is in the micrometer scale size. The diameter and the length of the nanorods in the flower-like CuGeO$_3$ are less than 100 nm and about 1 μm, respectively. Compactness dependence results demonstrate that the compactness is the key factor for the formation of the flower-like CuGeO$_3$ which can be explained by an assembled growth process.

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