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Controllable Hydrothermal Synthesis of $Cd_2Ge_2O_6$ Nanostructures

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Abstract

Various $Cd_2Ge_2O_6$ nanostructures, including nanorods, nanoparticles, nanowires and erythrocyte/flower/disc-like superstructures have been successfully prepared by hydrothermal methods, which are simply tuned by changing the reaction temperature, surfactants, and the molar ratio of Cd and Ge precursors in aqueous solution. These morphologies can be simply controlled by only selecting the reactants and controlling experimental conditions with excellent reproducibility. These studies about the $Cd_2Ge_2O_6$ nanostructures reveal that temperature is a crucial parameter to tune the morphologies from nanoparticles to nanorods. By adding various surfactants, different nanostructures such as flower/disc-like nanosticks could be obtained. Replacing $Cd(CH_3COO)_2 \cdot 2H_2O$ with CdO as the precusor results in the formation of ultralong nanowires with CTAB as surfactant. Molar ratio of GeO_2 to CdO was demonstrated as an important factor to influence the surface smoothness of nanowires. It is believed that the simple hydrothermal route may be the useful route to synthesize variable germanate nanostructures for various applications.

Keywords

Hydrothermal, $Cd_2Ge_2O_6$, Nanorods, Nanowires, Superstructures

1. Introduction

Metal germinates have attracted attention due to their applications in catalysis, adsorption, ion exchange, humidity sensors and high energy laser systems [1]-[3]. In recent years, considerable efforts have been devoted to synthesizing germinate nanomaterials, such as $CuGeO_3$ [4] [5], $In_2Ge_2O_7$ [6] [7], Bi_2GeO_5 [8], $ZnGeO_3$ [9]-[11] and $PbGeO_3$ [12]. However, reports about the fabrication of the $Cd_2Ge_2O_6$ nanostructures are still quite rare and

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the phase and morphology of the nanostructrues are still not well controlled. Thus, developing a simple route to synthesize various phases and shape for $Cd_2Ge_2O_6$ nanostructures is of fundamental importance. In recent years, hydrothermal synthesis has attracted attention because it can control the shape of materials easily, which is simply processed and in large scale. For example, Liu, *et al.* [13] reported the synthesis of a family of highly uniform metal germinate nanowires in a hydrazine monohydrate/H_2O binary solvent system, which facilitates CO_2 photocatalytic reduction into renewable hydrocarbon fuel in the presence of water vapor at room temperature. Huang *et al.* [14] used hydrothermal route to obtain $Cd_2Ge_2O_6$ nanorods photocatalyst for environmental purification of benzene in air with molecular oxygen under ambient conditions; Pei *et al.* [15] [16] synthesized $Cd_2Ge_2O_6$ nanowires and flower-like $Cd_2Ge_2O_6$ microstructures in the absence of any surfactants by hydrothermal treatment. Herein, we demonstrate a one-step hydrothermal route to synthesize $Cd_2Ge_2O_6$ nanostructures with well controlling of their morphologies, including nanorods, nanowires, erythrocyte-like and flower-like microstructures, which are simply tuned by changing the hydrothermal reaction temperature, surfactants, and the molar ratio of Cd and Ge precursors in aqueous solution.

2. Experimental Section

2.1. Synthesis

All of the chemical reagents are analytically pure and used as received without further purification. GeO_2, Ethylenediamine (EDA), Polyvinyl Pyrrolidone (PVP), Sodium Dodecyl Benzene Sulfonate (SDBS) and Cetyltrimethyl Ammonium Bromide (CTAB) were purchased from National Chemical Agent. $Cd(CH_3COO)_2{\cdot}2H_2O$ and CdO were purchased from Aladdin Industry.

2.1.1. GeO_2 and $Cd(CH_3COO)_2{\cdot}2H_2O$ as the Precursors

In a typical synthesis, 1.5 mmol GeO_2 and 3 mmol $Cd(CH_3COO)_2{\cdot}2H_2O$ was dissolved completely in 20 mL and 20 mL deionized water, respectively. Then the GeO_2 aqueous solution was transferred into a 60 mL Teflon-lined stainless steel autoclave, following dropwise adding of 20 mL $Cd(CH_3COO)_2$ aqueous solution. And more deionized water was added to reach 80% fill rate for the autoclave. Hydrothermal treatments were carried out at 180˚C, 160˚C, 140˚C or 120˚C for 24 h and then the autoclave was cooled down to room temperature naturally. White precipitates were collected by centrifugation, and washed with deionized water and ethanol several times to remove impurities. Finally, the precipitates were dried in air at 60˚C for 5 h.

2.1.2. GeO_2 and CdO as the Precursors

2 mmol GeO_2 was dissolved completely in 20 mL deionized water and then transferred into a 60 mL Teflon-lined stainless steel autoclave, following dropwise adding of 20 mL CdO aqueous solution (The molar ratio of GeO_2 to CdO is controlled at 1:1 and 2:1). Then 1 mmol CTAB was added into the uniform turbid solution under stirring and the hydrothermal treatment was carried out at 180˚C for 24 h, and then the autoclave was cooled down to room temperature naturally. White precipitates were collected by centrifugation, and washed with deionized water and ethanol several times to remove impurities. Finally, the precipitates were dried in air at 60˚C for 5 h.

2.2. Characterization

The products were characterized by X-ray diffractometer (XRD; Rigaku D/Max-2550 PC) equipped with Cu-Kα Radiation; scanning electron microscope (JEOL, JSM5600 LV) equipped with an X-ray energy dispersive spectrometer (EDS) (Oxford, IE 300 X).

3. Results and Discussion

To study the role of the temperature, we made four different experiments which were carried out at the temperature of 120˚C, 140˚C, 160˚C and 180˚C for 24 h. The microstructure and morphology of the as-prepared products were investigated by SEM, as shown in **Figure 1**. **Figure 1(a)** depicts the SEM image of erythrocyte-like $Cd_2Ge_2O_6$ prepared at 120˚C for 24 h. The SEM image demonstrates that the as-prepared $Cd_2Ge_2O_6$ are composed of nanoparticles with an average size of about 30 nm. The inset shows the high magnified TEM image of the nanoparticles. At higher preparation temperatures, these small particles grow into rod-shaped $Cd_2Ge_2O_6$. The

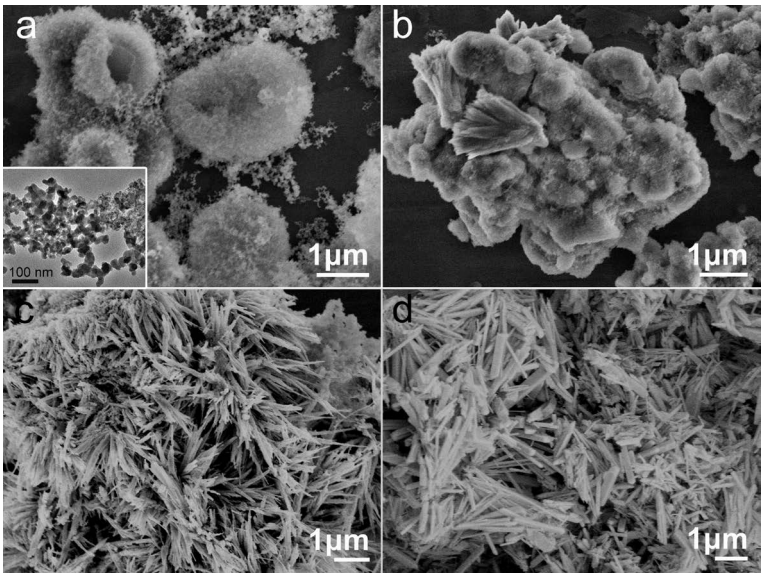

Figure 1. SEM images of the as-synthesized products that were carried out at (a) 120˚C; (b) 140˚C; (c) 160˚C and (d) 180˚C for 24 h. The inset is the high magnified TEM image of the nanoparticles.

product prepared at 140˚C is shown in **Figure 1(b)**, the $Cd_2Ge_2O_6$ particles getting larger in size and several short nanorods with 70 - 300 nm in width and 1 μm to 2 μm in length can be observed. The $Cd_2Ge_2O_6$ prepared at 160˚C (**Figure 1(c)**) contains a large quantity of short nanorods and nanospheres. At the 180˚C, the $Cd_2Ge_2O_6$ product is completely composed of nanorod-shaped nanostructure with the length ranging from hundreds nanometers to several micrometers, as shown in **Figure 1(d)**. These results indicate that the reaction temperature has an important effect on the morphology of the $Cd_2Ge_2O_6$ nanostructures. We observed that compared with the $Cd_2Ge_2O_6$ synthesized at low temperature, the products synthesized at 180˚C were more prone to form short nanorods structures. Therefore, the high temperature leads to the growth of nanorods but not the nanoparticles.

In order to further explore other parameters that might make impacts on the morphology of the products, we examined the role of surfactant in the synthesis of $Cd_2Ge_2O_6$ nanostructure. 0.5 mmol surfactant was completely dissolved in the GeO_2 aqueous solution before following dropwise adding of $Cd(CH_3COO)_2$ aqueous solution. The microstructure and morphology of the as-prepared products synthesized at 180˚C for 24 h were investigated by SEM, as shown in **Figure 2**. The $Cd_2Ge_2O_6$ disc-like microstructures prepared with EDA (**Figure 2(a)**) are constructed by massive nano-plates and each plate grows in a radial way from the center. As shown in **Figure 2(c)**, the as-prepared product with the existing of the SDBS is composed of abundant $Cd_2Ge_2O_6$ flower-like superstructures with a relatively good dispersion. High magnification SEM image reveals that the as-prepared hierarchical microstructures are constructed by many nanoparticles. Compared with above two types of superstructures, $Cd_2Ge_2O_6$ products synthesized with PVP and CTAB (**Figure 2(b)** and **Figure 2(d)**) were completely composed of short nanorods structures. Apparently, $Cd_2Ge_2O_6$ product prepared with CTAB was more prone to form relative long and uniform nanorods structures.

Different cadmium sources were tested to study their effects on the synthesis. When $Cd(CH_3COO)_2{\cdot}2H_2O$ was replaced by CdO, the final products were comprised of a large quantity of $Cd_2Ge_2O_6$ultralong nanowires with a length of 10 - 30 μm. **Figure 3(a)** and **Figure 3(c)** reveal the morphology of the as synthesized $Cd_2Ge_2O_6$ by adding CTAB as surfactant and the reaction was carried out at the molar ratio of GeO_2 to CdO of 2:1 or 1:1 at 180˚C for 24 h, respectively. The high-magnification SEM images (**Figure 3(b)** and **Figure 3(d)**) show that the diameters of the $Cd_2Ge_2O_6$ nanowires are 50 - 300 nm. Besides, we noticed that the surface of nanowires carried out at the molar ratio of GeO_2 to CdO of 1:1 is not as smooth as the other one made at the molar ratio of 2:1.

XRD was examined to identify the structure for the $Cd_2Ge_2O_6$ product obtained from the hydrothermal conditions of 180˚C for 24 h using CTAB as surfactant. As **Figure 4** shows, according to the standard value [Joint Committee on Powder Diffraction Standards (JCPDS) file card No. 43-0468], all the reflection peaks can be indexed to a pure monoclinic phase of $Cd_2Ge_2O_6$ and there are no other characteristic peaks from impurities [14]

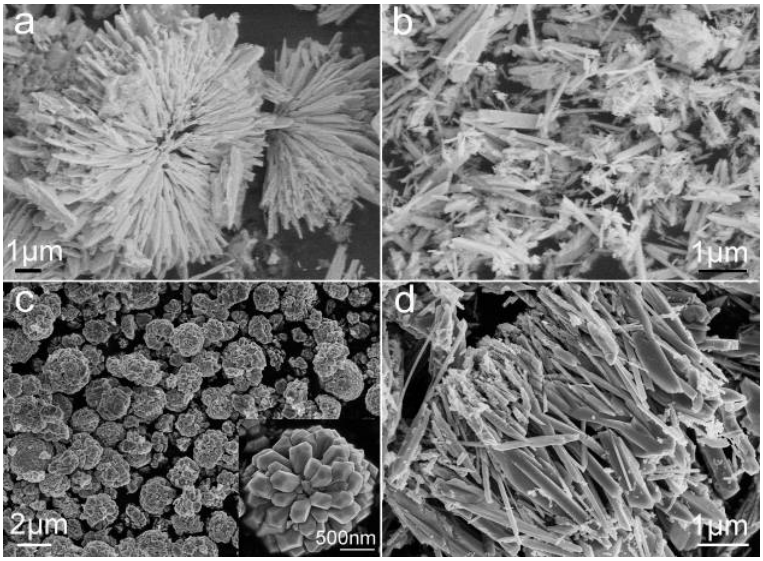

Figure 2. SEM images of the $Cd_2Ge_2O_6$ products synthesized at 180˚C for 24 h with (a) EDA; (b) PVP; (c) SDBS and (d) CTAB added as surfactant.

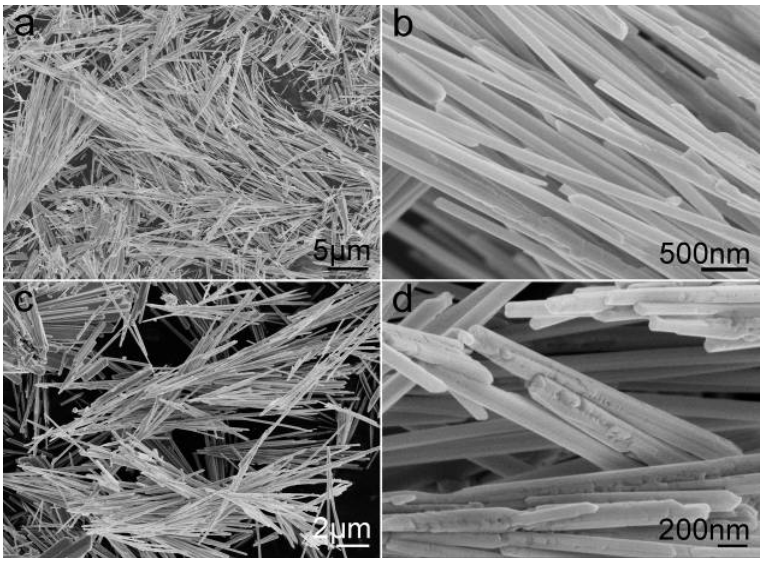

Figure 3. SEM images of the as-synthesized products with the molar ratio of GeO_2 to CdO of (a) 2:1 and (b) 1:1. CTAB was added as surfactant.

[17]. The strong and sharp diffraction peaks indicate good crystallinity of the product. Additional evidence of the formation of $Cd_2Ge_2O_6$ came from the energy dispersion X-ray analysis (EDS). **Figure 5(a)** shows a SEM image of the $Cd_2Ge_2O_6$ nanowires synthesized at 180˚C for 24 h with the molar ratio of GeO_2 to CdO of 2:1. The section in the yellow rectangle is taken for data collection. **Figure 5(b)** shows the energy dispersion X-ray spectrum of the as-prepared product. The peaks of Cd, Ge and O are easily found. Quantitative analysis shows that the molar ratio of Cd/Ge/O is 1:0.98:2.58, which is close to the stoichiometry in $Cd_2Ge_2O_6$.

In the above hydrothemral system, surfactants play a significant role in facilitating the nucleation and growth of various $Cd_2Ge_2O_6$ nanostructures, including nanorods, nanoparticles, nanowires and erythrocyte/flower/disc-like superstructures. At the initial period, H_2GeO_3 forms from the reaction of GeO_2 and H_2O. Then spherical nanoparticles spontaneously occur in the supersaturated solution via the hydrothermalreaction between Cd $(CH_3COO)_2$ or CdO and H_2GeO_3. Small nanoparticles may be activated and proceeded to assemble larger nanocrystals by a self assembled growth process so as to minimize the surface energies [18]. Then the spherical na-

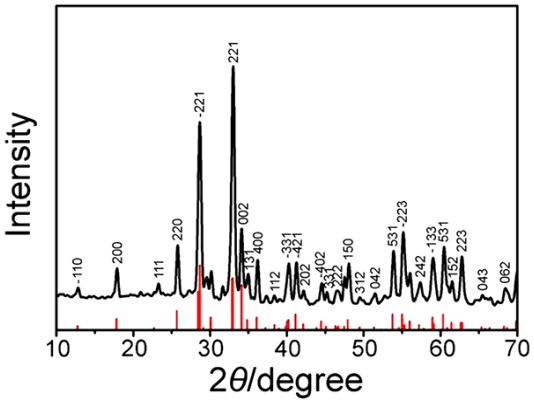

Figure 4. XRD pattern of the as-synthesized $Cd_2Ge_2O_6$ product prepared using GeO_2 and CdO as the precursors.

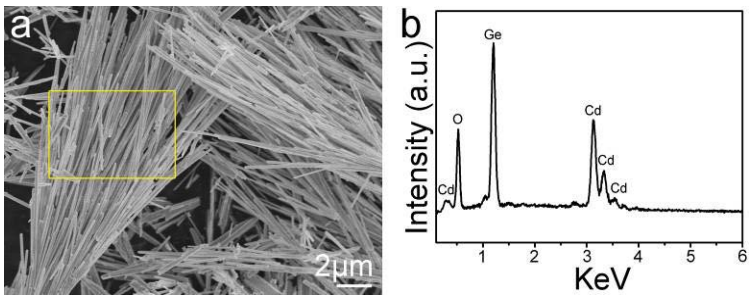

Figure 5. (a) A SEM image of the $Cd_2Ge_2O_6$ nanowires. The section in the yellow rectangle was taken for data collection; (b) Energy dispersion X-ray spectrum of the as-prepared product.

noparticles serve as the nuclei for the growth of the $Cd_2Ge_2O_6$ nanocrystals through an "Ostwald ripening" process [19]-[21]. With adding surfactants, such as EDA, PVP, SDBS and CTAB, the $Cd_2Ge_2O_6$ nanocrystals further grow and finally result in the formation of nanowires and erythrocyte/flower/disc-like superstructures.

4. Conclusion

In summary, we have synthesized various $Cd_2Ge_2O_6$ nanostructures, including nanorods, nanoparticles, nanowires and erythrocyte/flower/disc-like superstructures which can be achieved by simply tuning the hydrothermal reaction temperature, surfactants, and Cd precursor. These morphologies can be simply controlled by only selecting the reactants and controlling experimental conditions with excellent reproducibility. These studies of the $Cd_2Ge_2O_6$ nanostructures reveal that temperature is a crucial parameter to tune the morphologies from nanoparticles to nanorods. High temperature would lead to high aspect ratio of nanorods. By adding various surfactants, different nanostructures such as flower/disc-like nanosticks could be obtained. Replacing $Cd(CH_3COO)_2 \cdot 2H_2O$ with CdO as the precusor results in the formation of ultralong nanowires with CTAB as surfactant. Molar ratio of GeO_2 to CdO was demonstrated as an important factor to influence the surface smoothness of nanowires. Since the properties rely on the structure of materials firmly, it is believed that the simple hydrothermal route may be the useful route to synthesize variable germanate nanostructures for various applications.

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