

Dependence of growth conditions on copper germanate nanowires and their electrochemical characteristics

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Copper germanate (CuGeO_3) nanowires have been synthesized by the hydrothermal deposition process using GeO_2 and copper foil as the resource as well as the deposition substrate. The factors including hydrothermal temperature, pressure and duration of the process were investigated in order to analyze the processing parameters that control the formation process, morphology and size of the nanowires. The dependence of the nanowires properties on the growth conditions shows that the CuGeO_3 nanowires can be synthesized in a large range of different hydrothermal parameters from 400 °C to 250 °C. The hydrothermal pressure has an important effect on the formation and growth of the CuGeO_3 nanowires. The CuGeO_3 nanowires exhibit good electrochemical cyclic voltammetry characteristics owing to offering many advantages in sensing applications including their small size, high aspect ratio and conductance.

Keywords: *copper germanate nanowires, growth condition dependence, electrochemical characteristics*

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1. Introduction

One-dimensional (1D) nanowires have attracted considerable attention due to their potential use as building blocks for assembling active and integrated nanosystems [1–3]. Recently, a certain immediate promising application with ternary metal oxides nanowires as electrochemical sensors has been shown because of their high surface-to-volume ratio and excellent surface activities of 1D nanomaterials [4, 5]. Among the numerous ternary metal oxides materials, copper germanate (CuGeO_3) has been interestedly identified as the first solid-state compound that undergoes a spin-Peierls transition – the property previously associated only with molecular compounds [6]. The corresponding CuGeO_3 1D nanomaterials have received considerable attention due to their excellent electronic and optical properties [7]. The electronic properties of the CuGeO_3 suggest that when used as

electrode material they have the ability to mediate electron-transfer reactions with electroactive species in solution which can form potential building blocks for electrochemical sensors, offering the advantages in sensing applications including their small size, high surface-to-volume ratio and conductance.

Very recently, ternary CuGeO_3 nanowires have been synthesized via a simple hydrothermal deposition route by us, using GeO_2 and a copper foil as the resource as well as the deposition substrate under different hydrothermal conditions [8, 9]. The growth conditions, such as hydrothermal temperature, pressure and growth time have an important effect on the formation, growth, morphology and size of the CuGeO_3 nanowires, which is of great significance for optimizing the hydrothermal deposition parameters of the CuGeO_3 nanowires. In this paper, the growth condition dependence of the CuGeO_3 nanowires is analyzed in detail and the preliminarily electrochemical characteristics of the CuGeO_3 nanowires are reported. The research

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on the electrochemical properties of the CuGeO_3 nanowires is of value from the viewpoint of both fundamental scientific interest and its potential application in electrochemical sensor nanodevices.

2. Experimental

The CuGeO_3 nanowires were synthesized through a hydrothermal deposition route in an autoclave which is described elsewhere [8, 9]. The GeO_2 powders (purity: $\geq 99.99\%$) were purchased from Nanjing Germanium Factory Co., Ltd. in China. In a typical procedure, 1.0 g GeO_2 (purity: $\geq 99.99\%$) powders were mixed with 48 ml distilled water. Then the mixture was put into an autoclave. The copper substrate with the size of 6×2 cm was put into distilled water where it was cleaned using ultrasonic wave apparatus for 10 min in order to ensure appropriate cleanness of the surface. Then, the latter was fixed in a stainless steel bracket in the center of the autoclave. After the autoclave was sealed safely, it was heated to the temperature of $200\text{--}400$ °C, under the pressure of $1.2\text{--}8.0$ MPa and stirred at 100 rpm with a stirrer. The copper substrate was maintained at this stage for $4\text{--}12$ h. Subsequently, the autoclave was cooled down in air. The copper substrate with bulk light blue deposit was obtained.

The product was mechanically scrapped from the substrate. The samples for transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) examinations were prepared by putting several drops of the solution with CuGeO_3 nanowires onto a standard copper grid with a porous carbon film after the nanowire samples were dispersed into distilled water and treated for about 10 min using an ultrasonic wave apparatus. The transmission electron microscopy and high-resolution transmission electron microscopy observations were performed using JEOL JEM-2100 transmission electron microscope operating with 1.9 Å point-to-point resolution and a 200 kV accelerating voltage by a GATAN digital photography system. Scanning electron microscopy (SEM) observations were performed

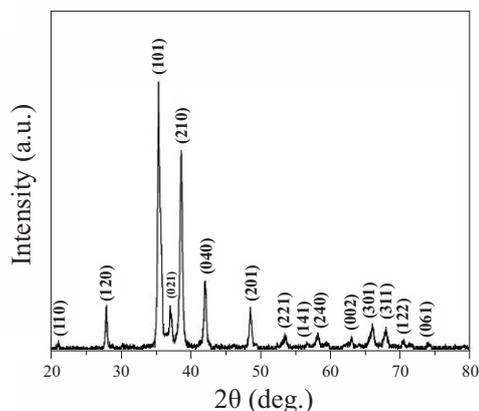


Fig. 1. XRD pattern of the CuGeO_3 nanowires grown at 400 °C, $7.5\text{--}8.0$ MPa for 12 h.

using JEOL JSM5410 SEM with a 15-KV accelerating voltage. X-ray diffraction (XRD) pattern was obtained using a Bruker AXS D8 X-ray diffractometer equipped with a graphite monochromatized $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406$ Å). The sample was scanned at a scanning rate of 0.05 °/s in the 2θ range of $20^\circ\text{--}80^\circ$. Electrochemical (EC) measurements were performed in an electrochemical working station LK2005A model. The CuGeO_3 nanowire modified glassy carbon electrode served as the working electrode, whereas a platinum plate and a saturated calomel electrode were used as the counter electrode and the reference electrode, respectively. EC cyclic voltammograms (CVs) were recorded from $-1.0\text{--}1.0$ V at a scan rate of 50 mV/s with the electrolyte of 0.1 M phosphate solution. The curve of current versus applied potential ($i\text{--}E$) was recorded.

3. Results and discussion

Fig. 1 shows the XRD pattern of the CuGeO_3 nanowires obtained in the hydrothermal deposition conditions of 400 °C, $7.5\text{--}8.0$ MPa for 12 h. The positions of all diffraction peaks agree with those of the orthorhombic phase of CuGeO_3 listed in the standard JCPDS card (32-0333), exhibiting the high crystallinity of the CuGeO_3 nanowires.

Representative TEM and HRTEM images of the CuGeO_3 nanowires obtained in the hydrothermal deposition conditions of 400 °C, 7.5–8.0 MPa for 12 h are shown in Fig. 2. Fig. 2(a) displays that the nanowires have a straight shape with smooth surface and a relatively uniform diameter of about 100 nm. The nanowires have flat tips and their length is longer than ten micrometers, reaching even several dozens of micrometers. However, some short rod-like structures with the length of about 1 micrometer are observed. They may originate from the fraction of the nanowires mechanically scrapped from the copper substrate and dispersion treatment using ultrasonic wave apparatus. The HRTEM image of a representative nanowire (Fig. 2(b)) shows a good single crystalline structure with no defects and dislocations. The corresponding fast Fourier transformation (FFT) diffraction pattern of the nanowire (inserted in the left-upper part of figure 2(b)) also indicates the single crystalline structure of the nanowires.

The factors including hydrothermal temperature, pressure and process duration were investigated in order to analyze the processing parameters that control the formation process, morphology and size of the CuGeO_3 nanowires. Fig. 3 shows the SEM images of the CuGeO_3 nanowires grown at different temperatures and pressures for 12 h. The CuGeO_3 nanowires still can be obtained when reducing the hydrothermal temperature below the supercritical hydrothermal temperature of 374 °C. The results demonstrate that the supercritical hydrothermal temperature is not the key factor for the formation and growth of the CuGeO_3 nanowires under hydrothermal deposition conditions. The nanowires can be easily obtained in different hydrothermal deposition conditions. The nanowires have a diameter ranging from 50 to 500 nm and the length exceeding 20 μm when the nanowires were synthesized at 350 °C and 300 °C, respectively (Fig. 3(a) and 3(b)). When the hydrothermal temperature decreases to 250 °C, the diameter of the nanowires (Fig. 3(c)) is similar to those synthesized in other hydrothermal conditions. However, the

length of the nanowires increases obviously reaching about 50 μm . The further decrease in the hydrothermal temperature and pressure to 200 °C and 1.3–1.6 MPa causes that the morphology and size of the products deposited on copper substrates change obviously (Fig. 3(d)). The rod-like structure is deposited on the copper substrate. The length of the structures decreases to about 10 μm and the diameter increases to about 900 nm. The CuGeO_3 nanowires can be easily obtained in a large range of hydrothermal deposition conditions by the hydrothermal deposition process using GeO_2 and copper foils as the starting materials. In fact, the amount of the deposition under the hydrothermal temperature of 250–400 °C is similar. However, the deposition on the copper foil substrates decreases obviously when the temperature decreases to 200 °C. The low hydrothermal temperature and pressure may confine the formation and growth of the nanowires. The preparation cost of the nanowires can be reduced obviously by decreasing the preparation temperature, pressure and growth time. Therefore, considering the preparation temperature, cost and quality of the CuGeO_3 nanowires, 250 °C is considered to be the proper temperature for the synthesis of the CuGeO_3 nanowires.

The growth time dependence of the CuGeO_3 nanowires grown at 250 °C demonstrates that the morphology and size of the nanowires are similar when the growth time decreases from 12 h to 4 h. The length of the CuGeO_3 nanowires grown at 250 °C for 8 h (Fig. 4(a)) and 4 h (Fig. 4(b)) is close to that of the CuGeO_3 nanowires grown at 250 °C for 12 h. The hydrothermal pressure can be controlled by changing the volume of the distilled water owing to the supply of the pressure by the water vapor. With the decrease in hydrothermal pressure from 2.4 to 2.2 MPa and from 1.4 to 1.2 MPa at 250 °C, the amount of the nanowires decreases obviously (Fig. 4(c) and 4(d)). Especially, a large amount of the particles with different sizes are observed on the copper substrates besides some nanowires when the hydrothermal pressure decreases to 1.4–1.2 MPa. The growth condition dependence of

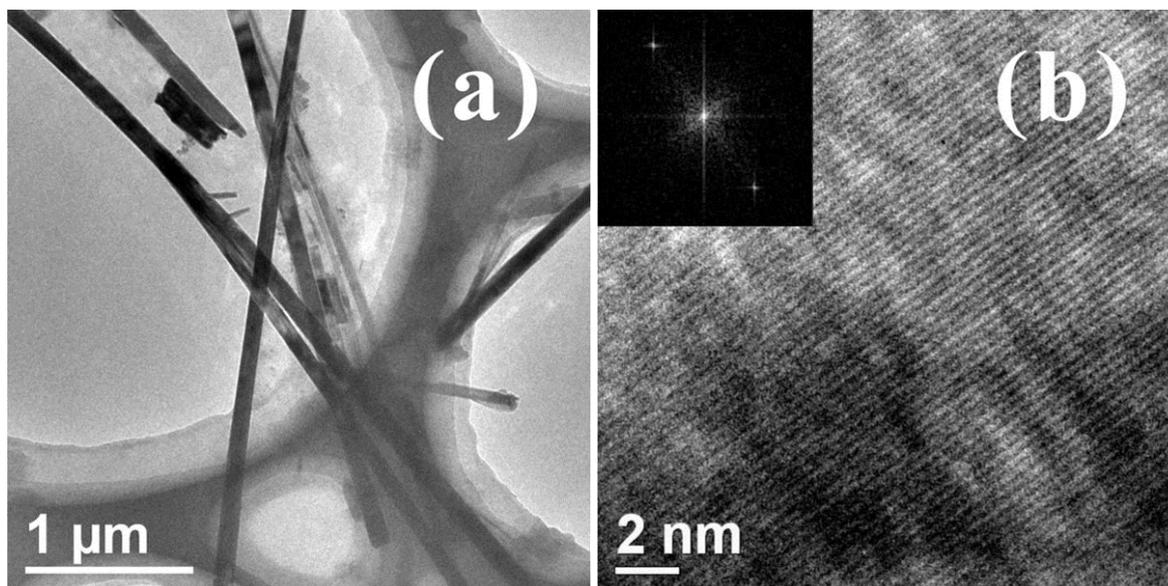


Fig. 2. Electron microscopy images of the CuGeO_3 nanowires grown at $400\text{ }^\circ\text{C}$, $7.5\text{--}8.0\text{ MPa}$ for 12 h. (a) TEM image, (b) HRTEM image.

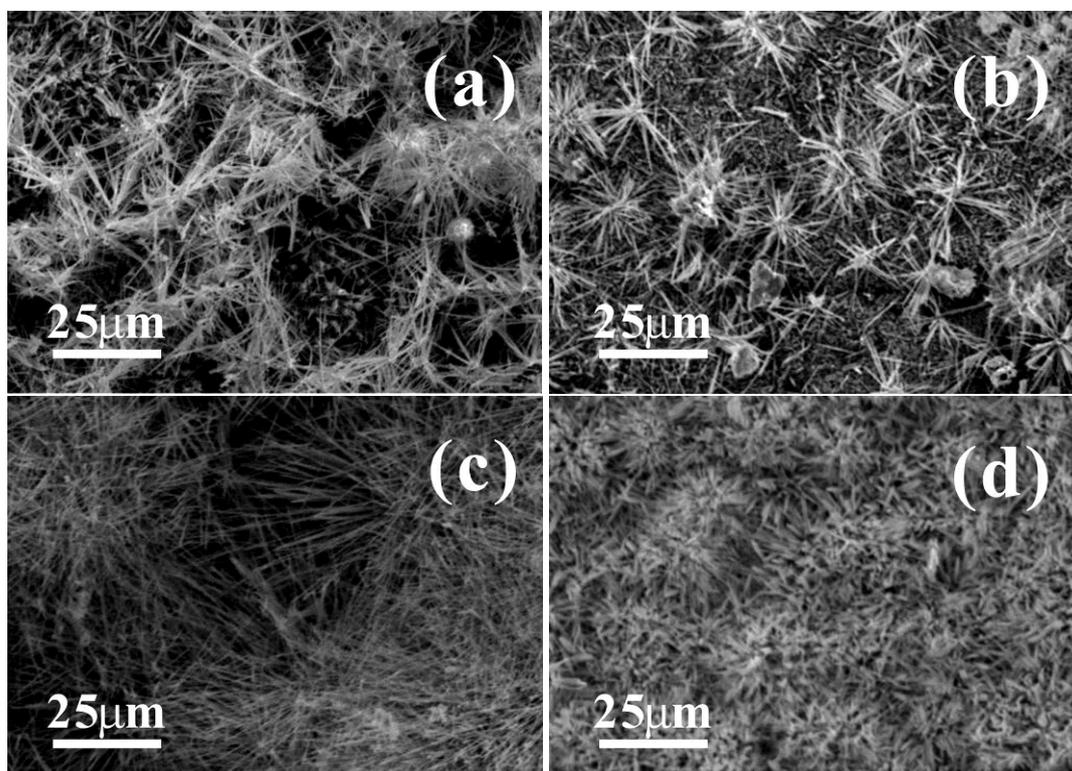


Fig. 3. SEM images of the CuGeO_3 nanowires grown at different temperatures under the hydrothermal pressure for 12 h. (a) $350\text{ }^\circ\text{C}$, $5.9\text{--}6.6\text{ MPa}$, (b) $300\text{ }^\circ\text{C}$, $5\text{--}5.7\text{ MPa}$, (c) $250\text{ }^\circ\text{C}$, $3.4\text{--}3.7\text{ MPa}$, (d) $200\text{ }^\circ\text{C}$, $1.3\text{--}1.6\text{ MPa}$.

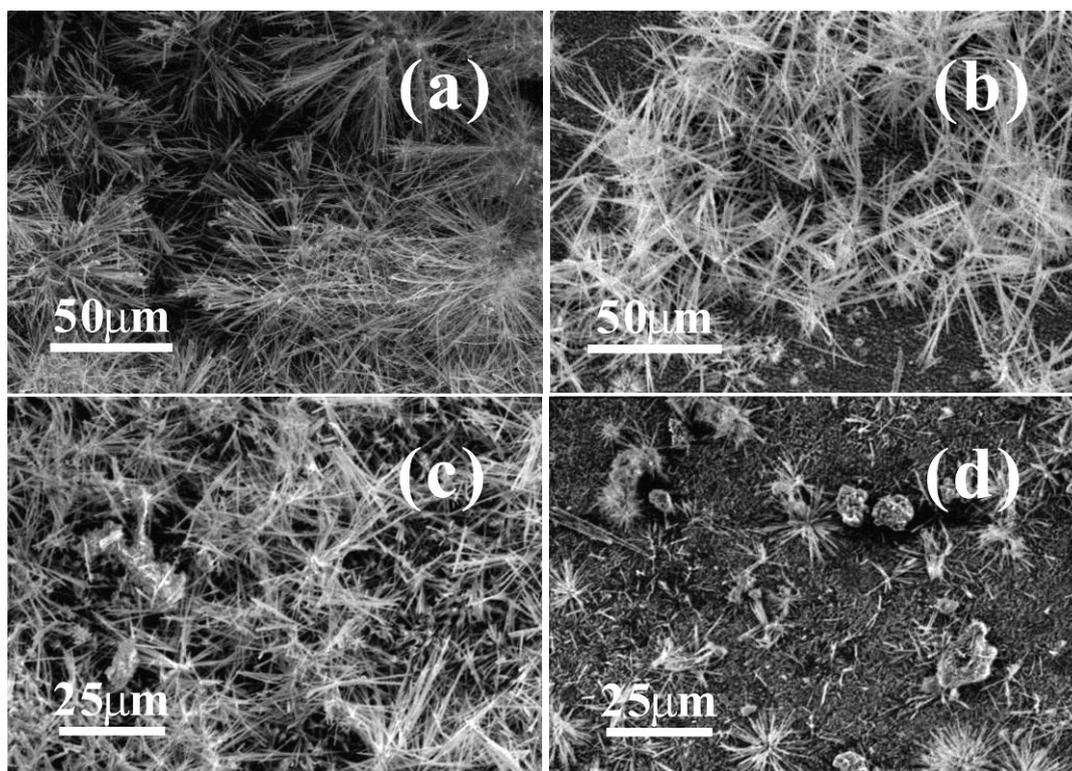


Fig. 4. SEM images of the CuGeO_3 nanowires grown under different hydrothermal pressures for different times at 250°C . (a) 3.3–3.6 MPa for 8 h, (b) 3.3–3.7 MPa for 4h, (c) 2.2–2.4 MPa for 12 h, (d) 1.2–1.4 MPa for 12 h.

the formation of the CuGeO_3 nanowires shows that the CuGeO_3 nanowires can be easily synthesized in a large range of different hydrothermal parameters. The results also show that the CuGeO_3 nanowires can be controlled by varying the hydrothermal deposition conditions.

The formation and growth process of the CuGeO_3 nanowires in different hydrothermal deposition conditions can be explained by the conventional nucleation and solid state growth mechanism [8]. Generally, CuO originates from the surface of the copper substrate owing to the oxidation effect. GeO_2 may play an important role in the formation and growth of the CuGeO_3 nanowires. The starting material – GeO_2 particles undergoes a conformation change from the solid state to the vapor phase in the nanocluster state under the hydrothermal conditions. The surface of the copper substrate is further oxidized owing to the existence of oxygen in the hydrothermal

atmosphere. The GeO_2 nanoclusters in the vapor phase are driven continuously by the flowing water vapor and the stirring of the stirrer mounted in the autoclave. Therefore, the GeO_2 nanoclusters deposit onto the copper substrate continuously and react with CuO to form CuGeO_3 nanoclusters. The CuGeO_3 nanoclusters absorb GeO_2 and CuO nanoclusters continuously to form CuGeO_3 , GeO_2 and CuO cores, resulting in the supersaturation state of CuGeO_3 and internal recrystallization process. The crystalline CuGeO_3 expels from the nanocluster cores resulting in the continuous growth of the CuGeO_3 nanowires.

The electrochemical properties of compound oxide nanowires and their application in the electrochemical sensors have gained significant interest lately [5, 9, 10]. In these compound oxide nanowires, the CuGeO_3 nanowires are now under intensive investigation as potential building blocks for electrochemical sensors which may replace

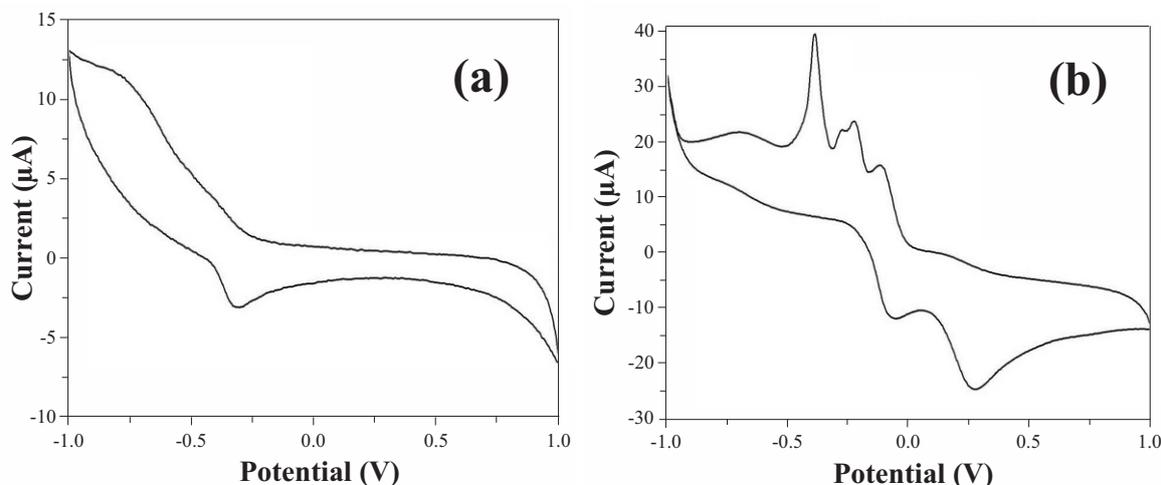


Fig. 5. CVs of the CuGeO_3 nanowire modified electrode in 0.1 mol/l phosphate solution of $\text{pH} = 7$. The CuGeO_3 nanowires were obtained under different hydrothermal conditions. (a) $400\text{ }^\circ\text{C}$ and 6.7–7.5 MPa. (b) $250\text{ }^\circ\text{C}$ and 3.4–3.7 MPa.

contemporary, time-consuming, sequential, and limited spectroscopy techniques, offering numerous advantages in sensing applications including their small size, high aspect ratio and conductance. Fig. 5 shows the cyclic voltammograms (CVs) of the CuGeO_3 nanowire electrode in a phosphate buffer solution of $\text{pH} = 7$ at a scan rate of 50 mV/s in the potential range of $-1.0\text{--}1.0\text{ V}$. The nanowires were obtained under the hydrothermal conditions of $400\text{ }^\circ\text{C}$, 6.7–7.5 MPa (Fig. 5(a)) and $250\text{ }^\circ\text{C}$, 3.4–3.7 MPa (Fig. 5(b)), respectively. It has been reported that the shape of CV shows the asymmetric CV behaviour which is asymmetric between the cathode process and the anode process, displaying the difference between the response current from that of polypyrrole nanowires and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanowires [11, 12]. Since the current for the same active weight represents the capacitance at the same sweep rate, obviously, the CuGeO_3 nanowire electrode possesses a high capacitance. Therefore, the CuGeO_3 nanowires may find promising applications in electrochemical cells. Similar to the high response current of the CV of manganese oxide nanowires [13], high response current is also observed in the range of $-0.1\text{ to }0.1\text{ V}$ (Fig. 5(b)) which may be caused by the reduction of the Cu^{2+} at the surface of the CuGeO_3 nanowire electrode.

The response in the positive range is a little higher than that in the negative range, indicating that the reduction of Cu^{2+} at the surface of the CuGeO_3 nanowire electrode to Cu^+ or Cu is a little more difficult than the oxidation of Cu^+ or Cu to Cu^{2+} . The result shows that the CuGeO_3 nanowires may also find promising applications in electrochemical sensors.

4. Conclusions

In summary, single crystalline CuGeO_3 nanowires have been synthesized by a simple hydrothermal deposition process. The CuGeO_3 nanowires are straight and smooth with flat tips. The temperature dependence of the growth of the CuGeO_3 nanowires shows that $250\text{ }^\circ\text{C}$ is the proper temperature for the synthesis of the nanowires. The hydrothermal pressure has an important effect on the formation and growth of the CuGeO_3 nanowires. The low hydrothermal temperature and pressure may confine the formation and growth of the nanowires. The CuGeO_3 nanowires exhibit good electrochemical cyclic voltammetry characteristics which may find promising applications in electrochemical sensors.

Acknowledgments

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