Controllable Preparation and Electrochemical Behavior of Nanostructured Zn_2GeO_4

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Abstract. A series of nanostructured Zn_2GeO_4 were prepared in a low temperature solvothermal process and characterized with transmission electron microscopy and X-ray diffraction. Then, the formation mechanism of nanostructured Zn_2GeO_4 was discussed. At last, their electrochemical behavior was investigated. The results indicate that the Zn_2GeO_4 nanorods can exhibit more excellent electrochemical activity.

Introduction

The application prospect of one-dimensional germanate nanomaterials in the electrochemical sensor [1], photocatalyst [2], and nano electronic devices [3] is very attractive. Thus, they were paid more and more attention. Therein, one-dimensional nanostructured Zn_2GeO_4 was especially concerned due to its excellent optical and photocatalytic properties. There were a large number of studies and reports [4,5,6]. However, from the present point of view, the research of Zn_2GeO_4 is mainly focused on its application in photocatalysis. Studies on the morphology of Zn_2GeO_4 and the relationship between the morphology and properties of Zn_2GeO_4 are relatively few. Therefore, it is necessary to carry out research in this area. In addition, it has been reported that the morphology of nanomaterials can be controlled by oleylamine and lactic acid [7,8]. Therefore, we have prepared Zn_2GeO_4 using mild hydrothermal method, and the morphology controlled by oleylamine and lactic acid was explored preliminarily. On this basis, we also investigated the electrochemical properties of the nanostructured Zn_2GeO_4.

Experimental

Nanostructured Zn_2GeO_4 was prepared in a low temperature solvothermal process. Typically, GeO_2 (0.52 g) and zinc acetate (2.20 g) were dissolved in deionized water (30 mL). Then, corresponding crystal modifier was added and stirred for about 1 h. After pH was adjusted to 8 by 10 mol L^{-1} NaOH solution, the solution above was transferred into a teflon-lined vessel (50 mL) and heated to 180 °C for 12 h. Subsequently, the autoclave was naturally cooled to ambient temperature. The precipitate was collected by filtration and washed with ethanol and water for several times, respectively. Finally, the resulting product was dried at 60 °C for 2 h.

The electrochemical behavior of the samples was measured using a CHI660E electrochemical system (Shanghai Chenhua Instruments, China) in a conventional three-electrode cell. The GCE coated with the nanostructured Zn_2GeO_4 was used as the working electrode. An Ag/AgCl electrode and a platinum electrode were used as the reference electrode and the counter electrode, respectively. Briefly, 5 mg of the samples were dispersed into 2 mL ethanol and ultra-sonicated for 30 min. Then, 10 μL of the suspension was dropped onto the GCE and dried in air. The supporting electrolyte was the mixed solution of KNO_3 (0.1 mol L^{-1}) and 5 mmol L^{-1} $K_3Fe(CN)_5/K_3Fe(CN)_6$ (1:1).

Results and Discussion

Fig. 1 shows the TEM images of the as-prepared nanostructured Zn_2GeO_4. When the crystal modifier is absent (Fig. 1a), the sample obtained is the short rods. And the length is about 100 nm. When oleylamine (0.1 mol L^{-1}) is introduced in the reaction system as a crystal modifier, the product is the mixture of long nanorods and short nanorods (Fig. 1b). The lengths are 100 nm and 500-800 nm, respectively. If the concentration of oleylamine increases to 0.16 mol L^{-1} (Fig. 1c), the product is basically long nanorods with the length of 500-800 nm. In addition, when lactic acid serves as a crystal modifier, the length of nanorods decreases rather than increases. The length decreases from 100 nm to 50 nm. And the change in the length can hardly be observed with the concentration increasing (Fig. 1d-e). However, we can find that both the high and low concentration of lactic acid make the size distribution of Zn_2GeO_4 nanomaterials become wider. Therefore, we believe that the morphology of Zn_2GeO_4 can be controlled through introduction of oleylamine or lactic acid.

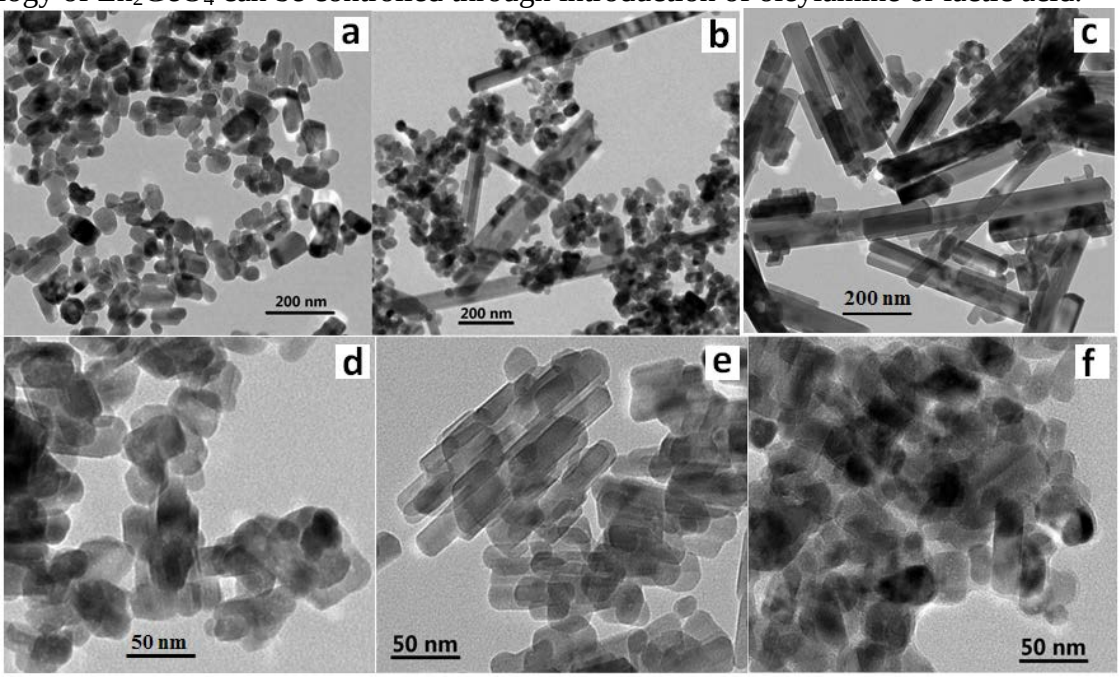


Fig.1. TEM images of Zn_2GeO_4 nanostructures prepared without crystal modifier (a) and with 0.1 mol L^{-1} oleylamine (b), 0.16 mol L^{-1} oleylamine (c), 0.16 mol L^{-1} lactic acid (d), 0.45 mol L^{-1} lactic acid (e) or 2.24 mol L^{-1} lactic acid (f).

Fig. 2 shows the XRD patterns of the as- prepared sample in the presence of oleylamine. We can see that when the pH was 8 (Fig. 2a) the XRD peaks of the resulting sample are narrow and sharp, indicating that the sample obtained possesses high crystallinity. In addition, compared with the JCPDS standard cards, the XRD patterns observed can match well with the JCPDS standard card (11-0687), indicating that the sample is hexagonal Zn_2GeO_4 nanorods with high purity. In order to explore the formation mechanism of Zn_2GeO_4 nanomaterials, we investigated the effect of pH on the phase of Zn_2GeO_4 nanomaterials. We can see that Zn_2GeO_4 can not be produced in the acidic environment (Fig. 2b). The XRD pattern of the product shows that the resulting product is GeO_2. In contrast, we can easily obtain Zn_2GeO_4 nanorods with high purity and high crystallinity in alkaline environment (Fig. 2a). This may be due to that the GeO_2 cannot be dissolved in acidic water, resulting in that the formation of Zn_2GeO_4 becomes by a heterogeneous reaction from homogeneous reaction. Therefore, the Zn_2GeO_4 generation speed is very slow so that little Zn_2GeO_4 is formed after 12 hours of reaction. In contrast, the alkaline environment would make the germanium acid monomer stable [9]. Based on the above results, we suggest that the formation mechanism of the Zn_2GeO_4 nanomaterials may be as follows: first, precursor GeO_2 hydrolyzed to form $HGeO^{3-}$. Then, Zn^{2+} and $HGeO^{3-}$ reacted to form Zn_2GeO_4 seed. Next, the Zn_2GeO_4 crystals grow gradually to form Zn_2GeO_4 nanorods.

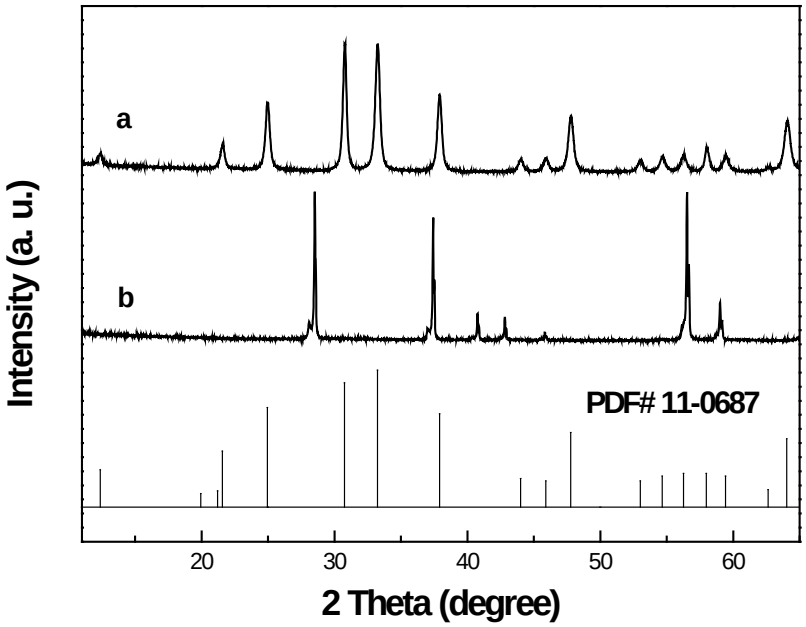
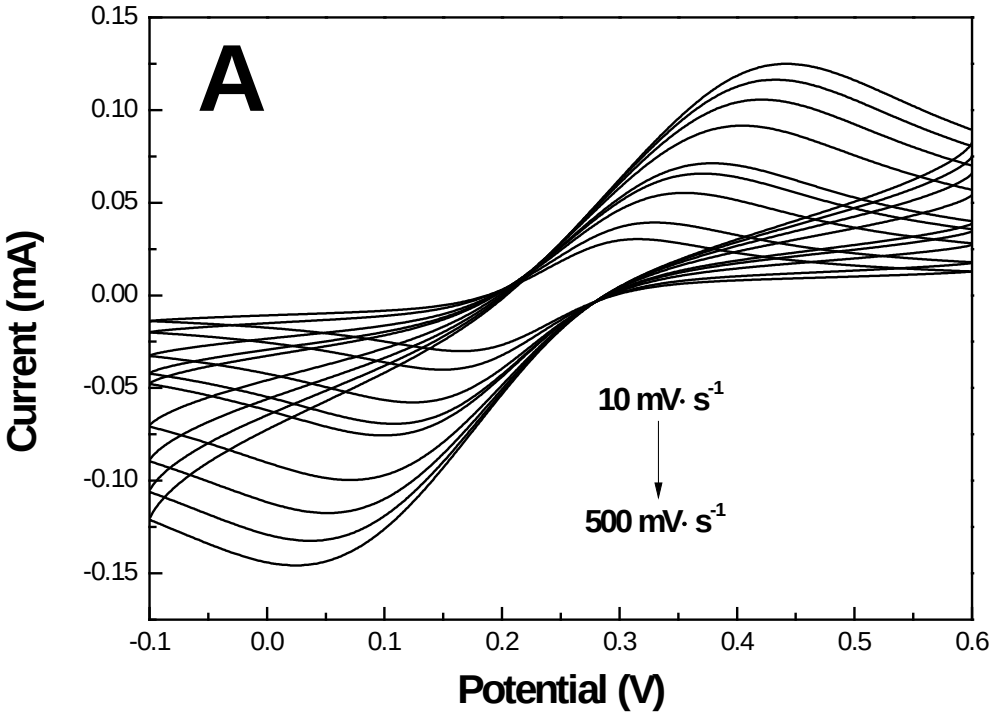


Fig.2. XRD patterns of products prepared with 0.16 mol L^{-1} oleylamine at pH=8 (a) and 1 (b).

Fig. 3 (A) shows the cyclic voltammograms of Zn_2GeO_4 nanomaterials at various potential scan rates. Meanwhile, the corresponding calibration plots of oxidation and reduction peak currents as a function of scan rate's root are also shown in Fig. 3. It indicates that both oxidation peak currents and reduction peak currents increase linearly with the scan rate's root. The corresponding linear equations are y = 0.01953+0.00491x and y = -0.00594x-0.01459, respectively. The linear correlation coefficients are 0.991 and 0.998. It indicates that the oxidation process of Fe^{2+} and reduction process of Fe^{3+} on the Zn_2GeO_4 nanomaterials modified electrodes are diffusion controlled processes.



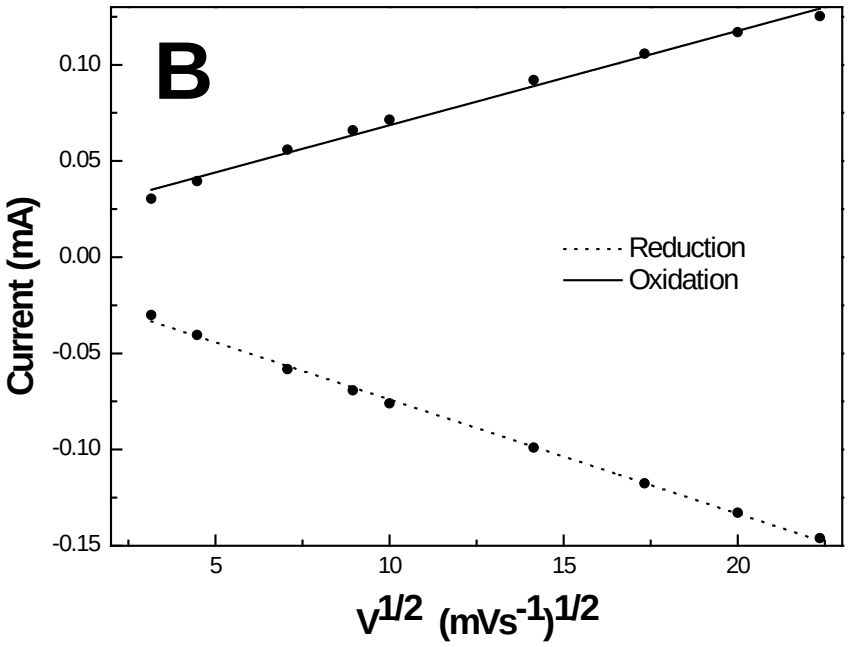


Fig.3. (A) Cyclic voltammograms of Zn_2GeO_4 nanomaterials prepared with 0.16 mol L^{-1} oleylamine at different potential scan rate. (B) The corresponding calibration plots of oxidation and reduction peak currents as a function of scan rate's root.

Fig. 4 shows the EIS curves of the Zn_2GeO_4 nanomaterials with various lengths. We can see that the semicircle diameters of the Zn_2GeO_4 nanomaterial with 50 nm (Fig. 4a), 100 nm (Fig. 4b), and 500-800 nm (Fig. 4c) are 2300 Ω, 1500 Ω, and 1200 Ω, respectively. It can be found that with the increase of the length of Zn_2GeO_4 nanomaterial, the semicircle diameters of the Zn_2GeO_4 nanomaterial were gradually decreased. The electron transfer resistance of the electrode is equal to the semicircle diameter of EIS and can be used to evaluate the interface properties of the electrodes. We can see that longer the length is, smaller the electron transfer resistance is. So, it can be deduced that the long Zn_2GeO_4 nanorods possesses better electron transport property in comparison with the short Zn_2GeO_4 nanorods.

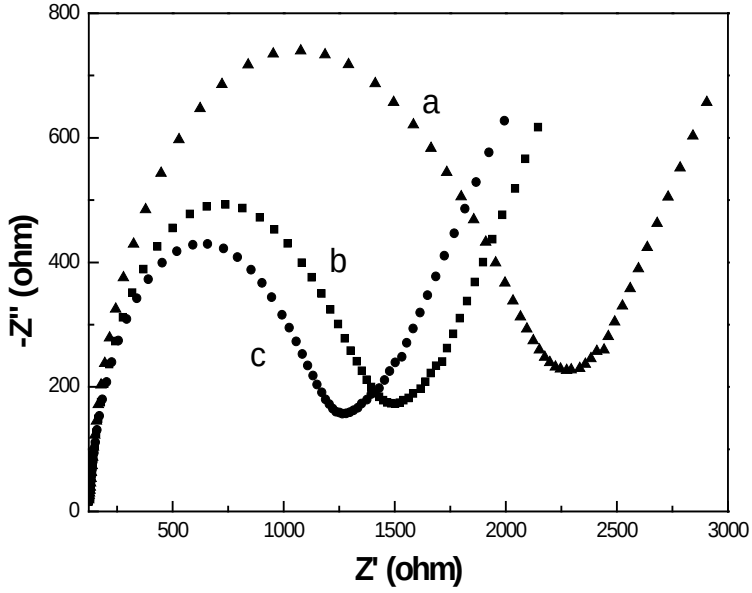


Fig.4. EIS of Zn_2GeO_4 nanomaterials with different lengths: 50 nm (a), 100 nm (b), and 500-800 nm (c)

Summary

In summary, we have successfully control the morphology of the Zn_2GeO_4 nanomaterials through tuning the kind and concentration of crystal modifiers. In addition, we also found that pH is one of the key factors for preparation of Zn_2GeO_4 nanomaterials under hydrothermal conditions. Finally, the long length of Zn_2GeO_4 nanomaterials is favorable to the electron transfer.

Acknowledgement

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