Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 20(2010) s211−s215
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Synthesis of ZnS nanoparticles by solid-liquid chemical reaction with ZnO and Na_2S under ultrasonic

SHE Yuan-yuan(佘媛媛)[1, 2], YANG Juan(杨 娟)[1], QIU Ke-qiang(丘克强)[1]

1. School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China;
2. Hunan Chemical Industry Vocation and Technology Institute, Zhuzhou 412004, China

Received 6 July 2009; accepted 30 December 2009

Abstract: A novel and simple solid-liquid chemical reaction route was proposed to synthesize ZnS nanoparticles. In the method, ZnS nanoparticles were prepared by reaction of ZnO and Na_2S in water with ultrasonic radiation at low temperature. The effects of process parameters on the properties of ZnS particles were investigated. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared spectroscopy (IR), thermogravimetry-differential thermogravimetry (TG-DTG) and fluorescence emission spectroscopy. The results show that these particles are good crystalline zinc blende with average size of 35 nm, and possess good IR transmittance in the range of 400 to 4 000 cm^{-1} and good thermal stability in oxygen.

Key words: ZnS nanoparticle; ZnO; optical property; ultrasonic

1 Introduction

Nanotechnology is a new kind of technology developing rapidly since 1980s. Nanoparticles attracted considerable attention in recent years because of their special properties, such as quantum size effects[1−2] and abnormal luminescence phenomenon[3−5]. As a kind of transition metal sulfides, ZnS nanoparticles show special photoelectricity properties, such as photoluminescence (PL) and electroluminescence (EL)[6−7], thus they have extensive application in lasers, sensors, infrared windows, displays, and many other fields[8−11]. ZnS particles have two kinds of structures: zinc blende structure (cubic crystal) and wurtzite structure (hexahedron). ZnS applied in luminescent materials generally has zinc blende structure[12].

There are many methods to prepare ZnS nanoparticles, which can be divided into two categories: physical method and chemical method. The chemical method mainly includes thermal decomposition method, micro-emulsion method, sol-gel method, and LB technique. However, these methods need high reaction temperature, vast use of organic solvents, high cost of equipment operation, and complex process control. In most cases, particles prepared by these methods are of poor uniformity and agglomerate easily[13−14]. XU et al[15−16] succeeded in preparing ZnS nanoparticles by reaction of Zn nanoparticles and Na_2S solution. However, the products are low purity. In this work, we present a new method to obtain ZnS nanoparticles without any stabilizer. Taking the normal ZnO and Na_2S as raw material, combining the solid-liquid chemical reaction and ultrasonic radiation, the cubic ZnS nanoparticles with good dispersion are obtained in aqueous phase under magnetic stirring.

2 Experimental

ZnS nanoparticles were prepared in a Na_2S solution-ZnO suspension system.

$$ZnO(s)+S^{2-}(aq)+H_2O(l)=ZnS(s, sph)+2OH^-(aq) \quad (1)$$

According to the chemical reaction isotherm equation:

$$\Delta_r G_m = \Delta_r G_m{}^{\theta} + RT\ln\left(C^2_{OH^-}/C_{S^{2-}}\right) \quad (2)$$

where $\Delta_r G_m$ and $\Delta_r G_m{}^{\theta}$ are the Gibbs free energy and standard molar Gibbs free energies of equation (1), J/mol, respectively; R is the gas constant (8.314 J/(K·mol); T is the temperature (K); C_{OH^-} and $C_{S^{2-}}$ are the concentration of OH^- and S^{2-} (mol/L), respectively.

If $\Delta_r G_m < 0$, the forward reaction will take place. The sign of $\Delta_r G_m$ is basically decided by $\Delta_r G_m{}^{\theta}$ when the

Corresponding author: QIU Ke-qiang; Tel: +86-731-88836994; Fax: +86-731-88879616; E-mail: qiuwhs@sohu.com

absolute value of $\Delta_r G_m^{\theta}$ is great. Therefore, in general case, if $\Delta_r G_m^{\theta}$ has a great negative value, $\Delta_r G_m$ will be also negative. The values of $\Delta_r G_m^{\theta}$ in this reaction under different temperature are shown in Table 1. It can be seen that, preparing ZnS from the reaction of ZnO and Na_2S solution is feasible. Furthermore, the solubility products of ZnO and ZnS in water at room temperature are 3×10^{-18} and 1×10^{-24}, respectively. ZnS is more difficult to dissolve in water than that in ZnO, which is beneficial to the forward reaction.

Table 1 Gibbs free energy change under different temperature

T/K	$\Delta_r G_m^{\theta}$/(J·mol^{-1})
298	−45 604
303	−45 278
313	−44 548
323	−43 717
333	−42 789
343	−41 766
353	−40 651
363	−39 446

A typical synthesis method yielding ZnS nanoparticles is described as follows. 2 g ZnO powder and 40 mL Na_2S solution (2.0 mol/L) were first mixed and radiated by ultrasonic for a period of time, then purged with argon to remove oxygen. After being magnetic stirred in 90 ℃ water bath for 2 h, the reaction mixture was quenched to room temperature immediately, and then washed with distilled water and ethanol for several times to remove unreacted Na_2S. The ZnS nanoparticles were finally obtained after vacuum-drying and grinding.

The X-ray diffraction spectrum of ZnS nanoparticles was obtained by using $CuK_{\alpha1}$ (λ=0.154 05 nm) irradiation on an X-ray spectrometer (Rigaku D/Max-2550V). Particle size and morphology were observed by using scanning electron microscope (KYKY2800) and transmission electron microscope (JEM-1230). The thermogravimetry-differential thermogravimetry (TG-DTG) curves were obtained by thermal weight analysis equipment (TGA/SDTA 851e) in pure oxygen atmosphere. The infrared spectrum was measured by Bruker FT-IRIFS-48 spectrum equipment. A fluorescence spectrophotometer (Hitachi F-2500) was employed to collect the photoluminescence spectrum.

3 Results and discussion

3.1 Product purity

Fig.1 shows the effects of different process parameters on the purity of ZnS particles. As the temperature increasing, the mass fraction of ZnS in the product gradually increases. This is expected, because the reaction is an endothermic reaction, and increasing temperature can enhance the forward reaction and further convert ZnO to ZnS. Increasing Na_2S concentration and prolonging the stirring time within a certain range will lead to a higher purity of the product, since both of them can make contributions to the complete consumption of ZnO.

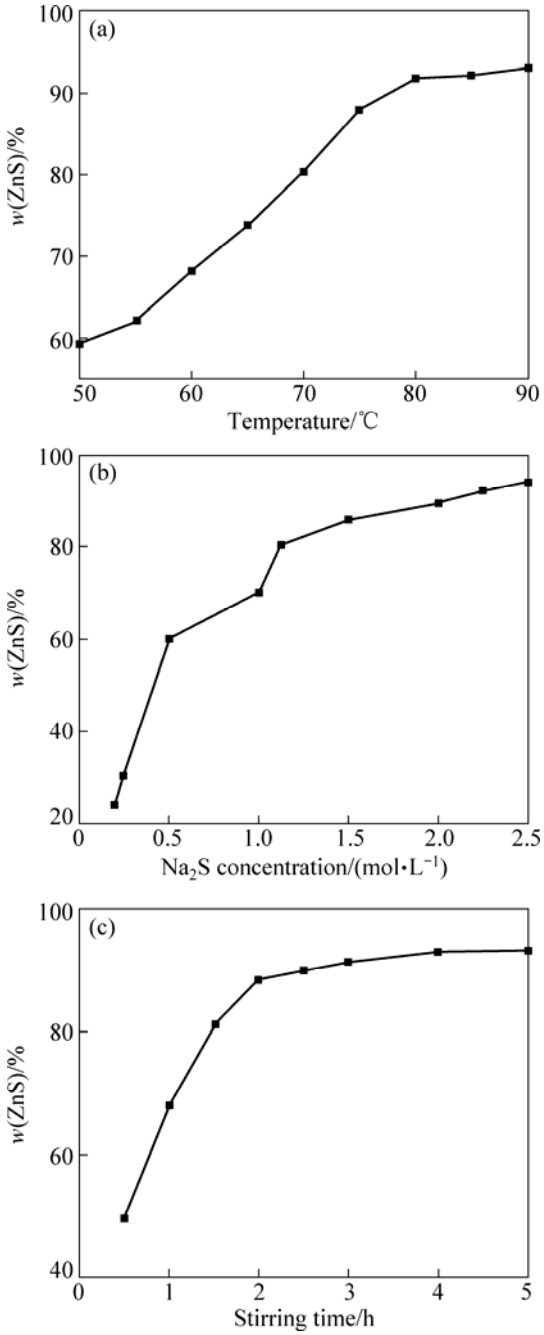

Fig.1 Effects of temperature (a), Na_2S concentration (b), and stirring time (c) on purity of ZnS particles

3.2 Product granularity

Fig.2 shows the effect of ultrasonic time on the average particle size of ZnS particles. It can be seen that, ultrasonic radiation before reaction can facilitate the

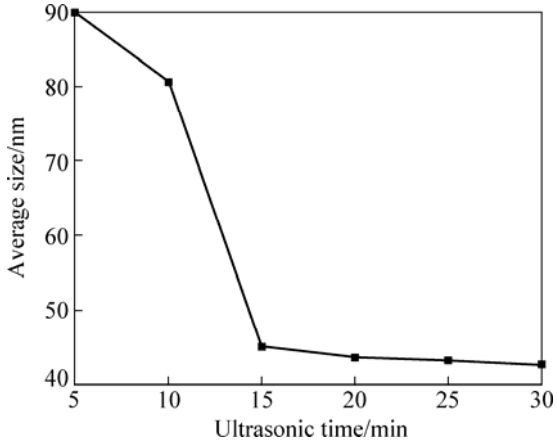

Fig.2 Effect of ultrasonic time on average size of ZnS particles

formation and stabilization of nanoparticles. Because of the cavitation of ultrasonic, the particles size decreases with extending of ultrasonic radiation time. The bubbles produced by ultrasonic field are radiated by ultrasonic at the same time. The impact effect of the cracked bubbles at liquid-solid interface results in the formation of small precursor particles. So ultrasonic radiation can accelerate the formation of the crystal in the inorganic supersaturated solution, increase nucleation rate and inhibit crystal growth. Then the fine grain can be obtained. In contrast, the size of ZnS particles obtained without ultrasonic radiation can not reach nanoscale, most of them are microscale.

3.3 Product morphology

The particle size and morphology of the samples were investigated by SEM and TEM. Fig.3(a) shows the SEM image of ZnO powder. The SEM image and TEM image of ZnS nanoparticles are shown in Figs.3(b) and (c), respectively. It can be seen that the ZnS sample consists of cubic particles with a narrow size distribution, and the average size of the particles is about 35 nm, which is much smaller than that of ZnO particles. In this work, fully crystallized ZnS nanoparticles are obtained at low temperature without calcining, which have small particle size and uniform distribution. The energy consumption of the preparation process is reduced, and the oxidation and agglomeration of ZnS powder are prevented at the same time.

3.4 XRD analysis

The XRD patterns for ZnS nanoparticles prepared with different Na_2S concentrations are shown in Fig.4. According to Fig.4(a), the diffraction peaks match the Bragg angles measured for bulk ZnS [111], [200], [220], [311], [222], [400], and [331] of the cubic crystalline with zinc blende structure. However, the diffraction

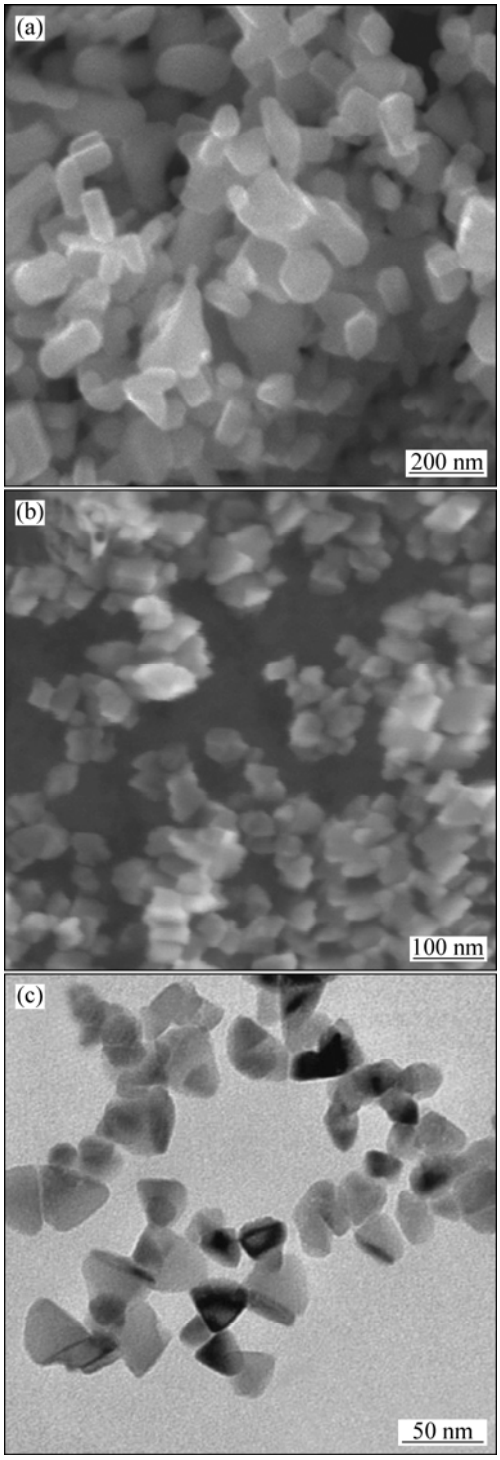

Fig.3 SEM images of ZnO powder (a) and ZnS particles (b), TEM image of ZnS particles (c)

peaks of ZnO [100], [002], [101], [103] and [112] are also found. It is indicated that ZnS prepared with Na_2S concentration of 1.125 mol/L is impure, mixed with a little unreacted ZnO. From Fig.4(b), ZnS prepared with Na_2S concentration of 2.0 mol/L is purer and less impurity diffraction peaks are found.

The mean particle sizes in diameter are 17.0 nm and 27.0 nm, respectively, which are determined by Scherrer

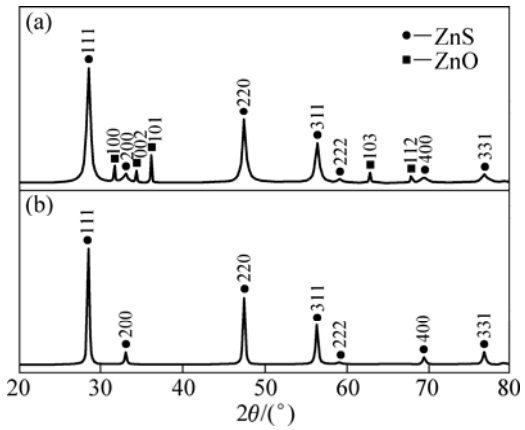

Fig.4 XRD patterns of ZnS prepared at Na_2S concentration of 1.125 mol/L (a) and 2.0 mol/L (b)

formula: $D_{hkl}=k\lambda/(\cos\ \beta\theta_{hkl})$, where *hkl* is the Miller indices, D_{hkl} is the mean particle size of crystal perpendicular to crystallographic orientation (*hkl*); *k* is a constant; λ is the wavelength of X-ray radiation; β is the full width at half-maximum of the (*hkl*) crystal face diffraction peaks; θ_{hkl} is Bragg diffraction angle of (*hkl*) crystal face. It is known that decreasing particle size results in a broadening of the diffraction peaks. The broadening of peaks in Fig.4(a) is more obvious than that in Fig.4(b), so the particle size in Fig.4(a) is smaller. The peaks of Fig.4(b) are much sharper than that of Fig.4(a), indicating that the product obtained under the condition of Fig.4(b) has more fully crystalline particles.

Compared the XRD pattern in Fig.4 with the XRD patterns of ZnS prepared by other researchers[15−16] with liquid reaction, ZnS prepared in this work performed sharper diffraction peaks, indicating that it has a better crystallinity.

3.5 IR spectrum

Fig.5 shows the IR spectrum of the ZnS nanoparticles. The stretch vibration adsorption of Zn—O at 420−460 cm^{-1} cannot be observed. It means that ZnS is not oxidized to ZnO during the preparation. This indicates that purging inert gas into the reacting system can prevent the oxidation of ZnS nanoparticles effectively. The stretch vibration absorption of O—H at 2 900−3 600 cm^{-1} also cannot be observed, which means that vacuum drying can remove the water adsorbed on the particles. There are few absorption peaks at 400−4 000 cm^{-1}, indicating that the prepared nano-ZnS is a nicer infrared-transmittance material.

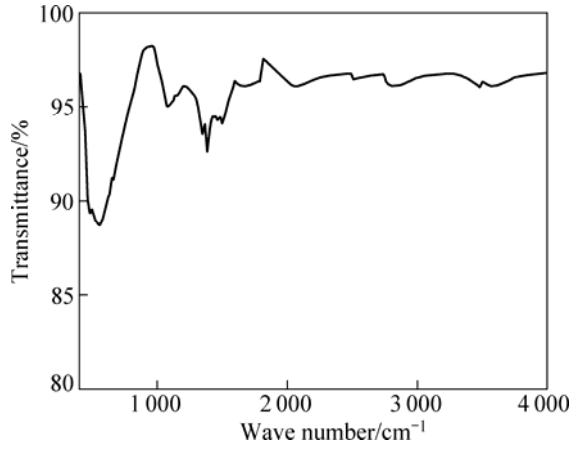

Fig.5 IR spectrum of ZnS nanoparticles

3.6 Thermoanalysis

TG-DTG measurement on the sample prepared with Na_2S concentration of 2.5 mol/L was carried out, as shown in Fig.6. Due to the strong water absorption of ZnS[17], it adsorbs water from oxygen, which leads to the slight increase of mass at 50 ℃. There is a mass loss around 100 ℃, which can be attributed to the elimination of adsorbed water on the particle surface. When the temperature is over 100 ℃, the mass of sample is almost constant until 570 ℃, and then has a rapid mass loss of about 14% at 620 ℃. It can be thus inferred that ZnS is oxidized to ZnO at 570 ℃ in oxygen[16]. The ultimate mass loss is about 17%. It can be concluded that ZnS particles possess good thermal stability in oxygen.

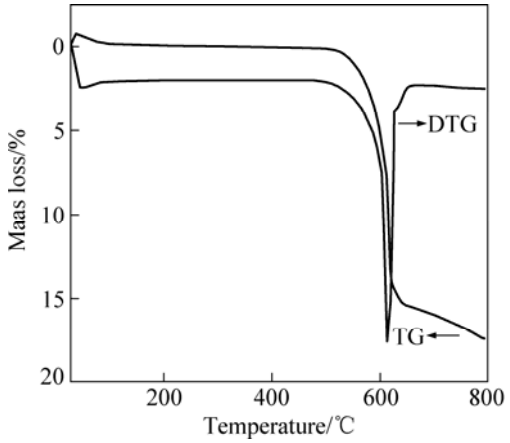

Fig.6 TG-DTG curves of ZnS nanoparticles

3.7 Fluorescence emission spectrum

In order to study the optical properties of the prepared ZnS nanoparticles, fluorescence emission spectrum analysis was carried out. Fig.7 shows that the ZnS nanoparticles prepared in this work have a single emission peak at about 445 nm. The intensity of emission peak is strong and the emission band is narrow, which further indicates the ZnS nanoparticles have a good crystallinity.

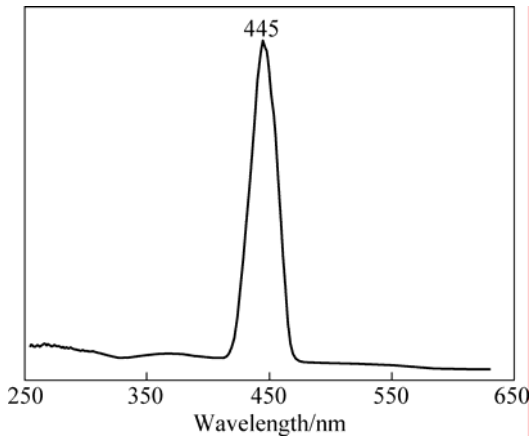

Fig.7 Fluorescence emission spectrum of ZnS

4 Conclusions

1) ZnS nanoparticles are synthesized by a simple solid-liquid chemical reaction without any surfactant. The preparation process has advantages of simple technology, high yield, cheap raw material and short preparation cycle.

2) The prepared ZnS nanoparticles are good crystalline cubic zinc blende with a uniform distribution and an average size of 35 nm. Few impurity peaks are found in the XRD patterns, indicating that the products are high purity. The prepared nanoparticles are nice infrared-transmittance materials with good crystallinity, infrared transparency and thermal stability.

References

[1] LI Li-ping, QIU Xiao-qing, LI Guang-she. Correlation between size-induced lattice variations and yellow emission shift in ZnO nanostructures [J]. Applied Physics Letters, 2005, 87(12): 124101−124103.

[2] SCHMIDT H M, WELLER H. Quantum size effects in semiconductor crystallites: Calculation of the energy spectrum for the confined exciton [J]. Chemical Physics Letters, 1986, 129(6): 615−618.

[3] XIN Xian-shuang, ZHOU Bai-bin, DU Hua, XU Xue-qin, SU Wen-hui. Preparation of ZnO nanoparticles and study on its optical property [J]. Chemical Research and Application, 2005, 17(3): 303−306. (in Chinese)

[4] CHENG Xing-wang, LI Xiang, ZHAI Fei-fei, YU Zhou, LONG Xue, LIN Peng-ting. Fabrication and photoluminescence study on ZnO nanostructured particles [J]. Journal of Aeronautical Materials, 2009, 29(1): 92−95. (in Chinese)

[5] NASUNO Y, KOHAMA N, NISHIMURA K, HAYAKAWA T, TANIGUCHI H, SHIMIZU M. Effect of perforated transparent electrodes on light transmittance and light scattering in substrates used for microcrystalline silicon thin-film solar cells [J]. Applied Physics Letters, 2006, 88(7): 1909−1911.

[6] WU Li-li, ZOU Ke, ZHAO Jin-bo, SHI Yuan-chang, WU You-shi. Controllable morphologies of ZnO nanocrystals and the photoluminescence property [J]. Journal of Synthetic Crystals, 2009, 38(3): 689−692. (in Chinese)

[7] CHENG Wen-de, WU Ping. Synthesis and strong blue light emission properties of ZnO tetrapod nanostructure [J]. Chinese Journal of Luminescence, 2006, 27(4): 608−613. (in Chinese)

[8] XU Hong-yan, LIU Xiu-lin, CUI De-liang, LI Mei, WANG Qi-long, JIANG Min-hua. Study on thick film gas sensors fabricated by using ZnO nanopowder [J]. Journal of Functional Materials and Devices, 2005, 11(2): 241−245. (in Chinese)

[9] DIMOS K, KOUTSELAS I B, KARAKASSIDES M A. Synthesis and characterization of ZnS nanosized semiconductor particles within mesoporous solids [J]. The Journal of Physical Chemistry B, 2006, 110(45): 22339−22345.

[10] DHAS N A, ZABAN A, GEDANKEN A. Surface synthesis of zinc sulfide nanoparticles on silica microspheres: sonochemical preparation, characterization, and optical properties [J]. Chemistry of Materials, 1999, 11(3): 806−813.

[11] WANG L P, HONG G Y. A new preparation of zinc sulfide nanoparticles by solid-state method at low temperature [J]. Materials Research Bulletin, 2000, 35(5): 695−701.

[12] ZHAO Z G, GENG F X, CONG H T, BAI J B, CHENG H M. A simple solution route to controlled synthesis of ZnS submicrospheres, nanosheets and nanorods [J]. Nanotechnology, 2006, 17: 4731−4735.

[13] CHAI L L, ZHU Y C, DU J, ZOU G F, XIONG K, QIAN Y T. One-step hydrothermal method to synthesize self-encapsulated ZnS micron core-shell spheres on a large scale [J]. Chemistry Letters, 2005, 34 (10): 1324−1325.

[14] KOLBA D M, ULLMANNA R, ZIEGLERA J C. Electrochemical nanostructuring [J]. Electrochimica Acta, 1998, 43(19/20): 2751−2760.

[15] XU J F, JI W, LIN J Y, TANG S H, DU Y W. Preparation of ZnS nanoparticles by ultrasonic radiation method [J]. Applied Physics A, 1998, 66(6): 639−641.

[16] XU J F, JI W. Characterization of ZnS nanoparticles prepared by new route [J]. Journal of Materials Science Letters, 1999, 18(2): 115−117.

[17] WONG E W, MAYNOR B W, BURNS L D, LIEBER C M. Growth of metal carbide nanotubes and nanorods [J]. Chemistry of Materials, 1996, 8(8): 2041−2043.

(Edited by LIU Hua-sen)