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Flower-like Se nanorods synthesized via carbamide-assisted hydrothermal routes

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Abstract Flower-like Se nanostructures consisting of clusters of nanorods with width of 40–100 nm and length of several 100 nm have been synthesized via a carbamide-assisted hydrothermal method. The optimal clusters are composed of nanorods protruding from a central point. FESEM and TEM demonstrate the flower-like morphology. The X-ray diffraction (XRD) pattern shows that the as-prepared flower-like Se nanostructures are of hexagonal phase.

Introduction

In recent years, synthesis of high quality semiconductor nanocrystals has been an important topic in the field of materials chemistry due to the excellent fundamental properties and functional applications of those novel materials [1]. One of the most elemental properties is quantum-confinement effect, which can lead to great differences in magnetic, optical, acoustic, electrical, thermal trait and superconductivity of nanostructures. Another one is surface effect, which has unique influence on the optical, photochemical, electrical and nonlinear optical properties of nanomaterials [2].

Several groups have focused on the synthesis and analysis of nanosemiconductors because of their potential application in a wide range of fields, such as new functional catalysts, solar battery, nonlinear optical materials, photochemical switches, etc [3]. One-dimensional (1D) nanostructures, such as nanowires, nanotubes, and molecular wires are currently being investigated in great detail for their unique electronic and mechanical properties and their potential implementation as devices [4]. The properties of nanostructures sensitively depend on their geometrical shape, configurations, and structure [5–7]. Control on morphology and size of nanomaterials has been a focus of considerable interest.

Solvothermal preparative routes, which further extend the usage of hydrothermal method, allow monodisperse low dimensional nanomaterials (metal and semiconductor) to be readily prepared with good optical quality and degree of crystallinity [8]. Although the conditions for synthesis of nanostructures with certain shape and size via solvothermal routes are not so easy to control and determine, it's considered as a relatively simple method to synthesize different kinds of nanostructures with attractive morphology and controllable size. Continued efforts are being made on shape and size control, dispersibility improvement, and facility of conditions of solvothermal method.

Simple synthesis of 1D II–VI semiconductor nanocrystals and nanorods by solvothermal method has been a focus recently; moreover, some interesting and attractive results were got [9]. Tellurium nanorods and nanowires have been successfully prepared in liquid phase by the microwave-polyol method without using any seed, or template or surfactant [10]. Qian et al. [11] successfully synthesized single crystalline Te nanowires with diameters ranging from a few nanometers to about 30 nm and lengths ranging from hundreds of nanometers to several micrometers and other semiconductor chalcogenide nanorods [12] by using the monodentate ligand *n*-Butylamine as a shape controller.

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Tellurium nanotubes were synthesized employing sodium tellurate ($Na_2TeO_4{\cdot}2H_2O$) as telluriumsource and formamide ($HCONH_2$) as a reductant [13].

Selenium is an important semiconductor, which can be used in the optoelectronics field, such as solar cell, selenium rectifier, etc. It's also an essential microelement for human beings due to its wide biological [13]. Selenium nanowires, nanorods, and nanotubes have successfully synthesized in aqueous solution by using cetyltrimethyl ammonium bromide (CTAB) as the soft template [14]. Single crystal trigonal selenium nanoplates have also been synthesized in a solid-solution-solid process under assistance of ethylenediamine [15].

In this paper, we focused on synthesis of Se nanorods with flower-like morphology by solvothermal method. Carbamide was determined as the solvent and reagent to control shape. As well known, most of growth with flower-like morphology appeared in multiple organic polymers, while we got a good result just with carbamide.

Experimental sections

All chemical reagents are of analytical grade and used as received without any further purification. In a typical experimental procedure, a mixture of 1.5 mmol (0.201 g) cadmium acetate ($Cd\ (Ac)_2{\cdot}4H_2O$), 1.5 mmol (0.402 g) sodium selenite anhydrous (Na_2SeO_3) and 2.073 g carbamide was dissolved in 40 ml distilled water and stirred for several minutes at room temperature, then this solution was transferred into a 50 ml Teflon-lined autoclave. The autoclave was sealed and maintained at 120 °C for 12–24 h or 160 °C for 12 h, respectively. It was then air-cool to room temperature. The precipitate was collected, washed with distilled water, and dried at 80 °C. The optimal brown sample was obtained under the proper condition (temperature = 120 °C, heating time = 12–16 h).

Powder X-ray diffraction (XRD) was carried on a D/MAX-500 X-ray powder diffractometer with Cu Kα radiation (λ = 1.5418 Å). The scanning rate of 0.020°/s was applied to record the patterns in the 2θ range of 15°–70°. Step-scan was set as 2.0 s per step for the sampling period. The samples for XRD characterization were prepared by casting a solution containing the selenium products onto a silicon wafer and allowing them to evaporate at room temperature. The overview morphologies of the crystals were observed by field emission scanning electron microscopy (FESEM), performed on a JSM-6700F at an acceleration voltage of 16.0 kv scanning electron microanalyses. Transmission electron microscopy (TEM), taken on a JEM-2000EX transmission electron microscope, was employed to observe the morphology and size of the as-prepared products. Selected area electron diffraction was also conducted by TEM analysis of the samples.

Results and discussion

The XRD pattern of the Se nanorods prepared by the carbamide-assisted hydrothermal method is shown in Fig. 1. Most of the peaks can be indexed as the hexagonal Se, although not of the same cell parameter (JCPDS 65-1876, #: 86-2244, *: 83-2437). The cell parameter of the main products is in accordance with JCPDS card 65-1876 (a = 4.363 Å, c = 4.959 Å).

Figure 2a–c shows the FESEM image of Se nanostructures synthesized by the carbamide-assisted hydrothermal method. The growth process was observed at different period and the flower-like morphology was shown in sequence. The temperature was 120 °C, the heating time for 2a is 12 h, while 2b is 16 h. Figure 2c is an electron microscopy image of Se nanostructures taken at a higher magnification. It shows that the aggregate is composed of individual small nanorods with diameter in the range of 40–100 nm and lengths of up to several 100 nm. It clearly reveals the radiate growth mechanism of Se nanorods. Bundles of Se nanorods with smooth surface protrude from the root of the flower-like Se nanostructures.

Although the growth of the sample synthesized with this simple method is not complete and the Se nanorods are not so uniform, the reproducibility is high, the conditions are facile and the experiment is very easy to manipulate due to the low temperature and simplicity of reactants. To demonstrate the influence of heating time and reaction temperature, the experiments have been operated under other conditions. The results indicate that there's no obvious evidence in accordance with the opinion that either higher temperature or longer heating time is beneficial to the complete growth of the flower-like Se rods. When the temperature was raised, just particles formed. And when the heating time was prolonged, there's no favorable

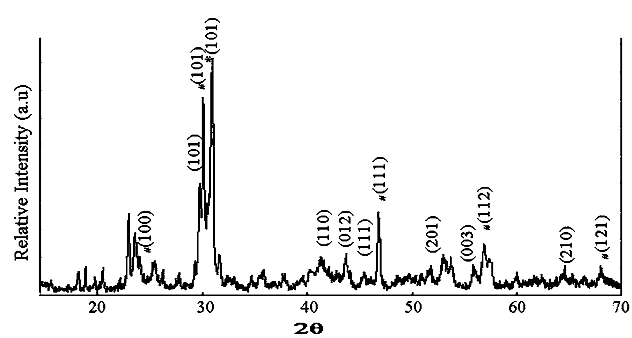

Fig. 1 XRD pattern of hexagonal Se nanostructure (some peaks overlap with each other)

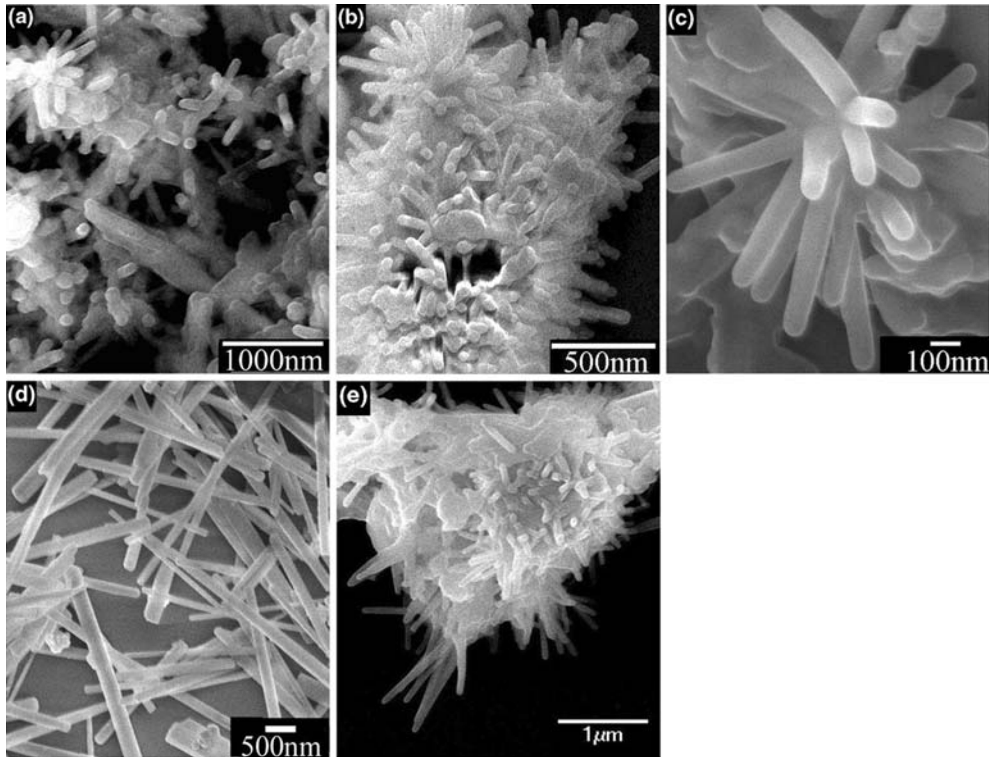

Fig. 2 FESEM images of nanorods (**a**) heating time is 12 h; (**b**) 16 h; (**c**) magnification images of smooth nanorods; (**d**) straight nanorods with DEA as reagent

outcome. It should be stated that the results were just obtained in a scope of temperature and heating time. The possible influence of increasing the temperature is complex. Some further research will be done in the future.

In the present route, we assume the formation of complex clusters at room temperature and the dissociation of organic ligands from complex clusters along specific directions during the hydrothermal process direct the anisotropic growth of Se. It is the chelation between carbamide and Cd^{2+} that makes the Se nanostructures formed and thanks to the aggregation of carbamide, so can the reaction to synthesize Se rather than CdSe (whose XRD pattern was in consistent with the value in JCPDC card (No.02-0330, a = 4.30 Å, c = 7.02 Å)) occurs. According to report [1], the weak acid radical in acetates is beneficial for the formation of nanocrystals. The flower-like growth can be attributed to the theory of nucleation. After the tiny Se nucleus form on the surface of the conglomeration, the anticipant Se nanorods grow from the conglomeration and show a flowe-like morphology. Straight CdSe nanorods were synthesized when carbamide was substituted with diethanolamine and the temperature was raised to 140–160 °C for 16 h, the SEM image was also shown in Fig. 2d. Comparatively, as the description above, when the temperature raised and urea used there's no rod-like formed. When Cd (Ac) $_2{\cdot}4H_2O$ was substituted with Zn (Ac) $_2{\cdot}2H_2O$, Se nanorods with a flower-like morphology were also obtained. The outcome was shown in Fig. 2e. It further indicated the effect of carbamide on the formation of this interesting morphology.

The TEM image in Fig. 3 was achieved to further characterize the as-synthesized Se nanorods. It's an image

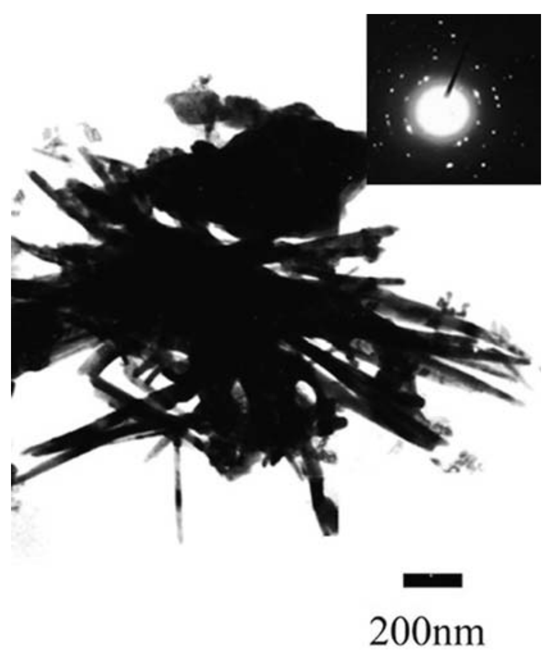

Fig. 3 TEM image of as-synthesized Se nanorods and the SAED pattern

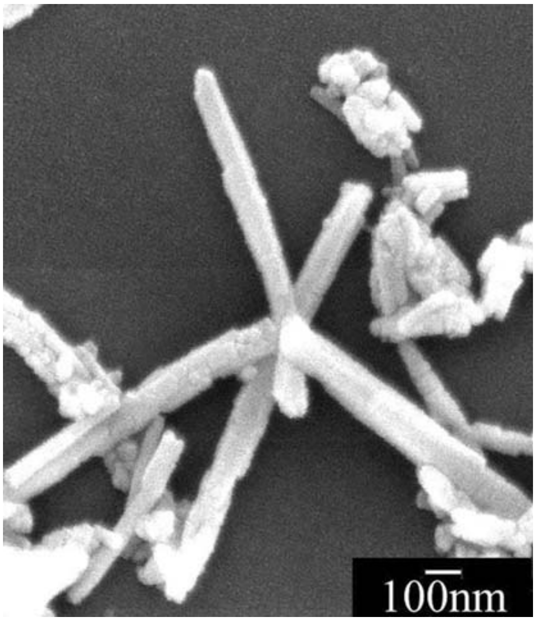

Fig. 4 SEM images of the "flower-like" nanorods (CTAB was added)

of a cluster. Lots of nanorods obtained from the growing flower-like nanostructures are observed, clearly identifying the morphology of the products. The corresponding selected area electron-diffraction (SAED) pattern (inset in Fig. 3) obtained from an individual nanorod reveals the crystalline features of the as-synthesized Se nanorods. The diffraction spots are not in line but circle, which indicates the structure, is not single crystal but polycrystalline.

CTAB was added considering the available effect of CTAB in synthesis of Se nanostructures [10], and the SEM images show that the nanorods grew longer while the surface became rougher (Fig. 4)

Conclusions

In summary, flower-like Se nanostructures consisting of nanorods with width within the region of 100 nm and length of several hundred nm have been synthesized via carbamide-assisted hydrothermal routes at 120 °C for 12–16 h. The rods have smooth surface. Carbamide was determined as the solvent and reagent to control the morphology. These nanorods protruding from the central point grew to form the flower-like shape. It is believed that the carbamide played a key role in the formation of flower-like morphology and anisotropic growth of Se in such a relatively low temperature. The growth mechanism is still under further discussion. These smooth flower-like nanorods may stimulate new research into the properties of semiconductor nanorods and find applications in optoelectronic field and other areas.

References

1. QU LH, Peng ZA, Peng XG (2001) Nano Lett 1:333
2. Fang JX, Lu D (1981) Solid Physics (II)
3. Yang J, Zeng JH, Yu SH, Yang L, Zhang YH, Qian YT (2000) Chem Mater 12:3259
4. Messer B, Song JH, Yang PD (2000) J Am Chem Soc 122:10232
5. Xia YN Yang PD Sun YG (2003) Adv Mater 15:353
6. (a) Joo SH, Choi SJ, Oh I, Kwak J, Liu Z, Terasaki O, Ryoo R (2001) Nature 412:169. (b) Pinna N, Weiss K, Urban J, Pileni (2001) MP AdV Mater 13:261
7. Thu J, Sli L, Dyang W, Manna L, Wwang L, Palivisatos A (2001) Science 292:2060
8. Murray CB, Norris DJ, Bawendi MG (1993) J Am Chem Soc 115:8706
9. Li YD, Sui M, Ding Y, Zhang GH, Zhuang J, Wang C (2000) Adv Mater 12:818
10. Zhang J, Zhang SY, Chen HY (2004) Chem Lett 33:1054
11. Xu LQ, Ding YW, Xi GC, Zhang WQ, Peng YY, Yu WC, Qian YT (2004) Chem Lett 33:592
12. Yang J, Xue C, Yu SH, Zeng JH, Qian YT (2002) Angew Chem Int Ed 41:4697
13. Xi GC, Peng YY, Yu WC, Qian YT (2005) Crystal Growth Design 5:325
14. Vogt TM, Ziegler RG, Graubard BI (2003) Int J Cancer 103:664
15. Zhu YJ, Hu XL (2004) Chem Lett 33:760