Available online at www.sciencedirect.com
SCIENCE DIRECT
Trans. Nonferrous Met. Soc. China 18(2008) 904−907
Transactions of Nonferrous Metals Society of China
www.csu.edu.cn/ysxb/

Fabrication of 2D and 3D dendritic nanoarchitectures of CdS

GU Li(谷 俐)

Biological and Chemical Engineering College, Jiaxing University, Jiaxing 314001, China

Received 14 March 2008; accepted 25 June 2008

Abstract: The controlled preparation of two-dimensional (2D) and three-dimensional (3D) dendritic nanostructures of CdS was reported. 2D dendritic patterns are obtained through the self-assembly of nanoparticles under the entropy-driven force. 3D dendritic needle-like nanocrystals are prepared through an aqueous solution synthesis regulated by oleic acid molecules. Their growth mechanism is presumed to be the selective binding of OA molecules onto growing crystal planes. Techniques such as SEM, TEM, XRD, and FT-IR were employed to characterize the morphologies and structures of the obtained products.

Key words: CdS; nanomaterial; semiconductor; self-assembly; dendritic pattern

1 Introduction

Recently, many efforts have been focused on the integration of nanoscale building blocks (e.g. nanorods/ nanowires and nanoparticles) into 2D or 3D ordered superstructures or complex functional architectures, which would offer opportunities to explore their novel optical, magnetic and electronic properties[1−4]. The species of complex nanoarchitectures include arrays[5−6], networks[4], superlattices[7], multi-arm structures[8], dendrites[9], and so on. The general preparation approach involves the usage of organic ligands and additives to alter the growth rate of various facets of a seed, which is inspired by the principles of mineralization in organisms[10−13]. Numerous elaborate nanostructures of inorganic materials, especially calcium and barium salts[13], were prepared. In addition, by means of the entropy-driven disorder-order phase transition, some complicated nanoarchitectures were also obtained, such as nanocrystal superlattices[7−14] and nanowire arrays[15]. Of various nanoarchitectures, fractal patterns (or dendrites) of inorganic materials are particularly attractive since the first report on the dendritic growth by NITTMANN and STANLEY in 1986[16]. This is because fractals are not only theoretically interesting but also practically important. Generally, fractal growth phenomena are usually observed in the far-from-equilibrium system and are also closely related to many processes of practical importance.

Cadmium sulfide (CdS), an important II-VI semiconductor, shows important applications in optical devices and light-emitting diodes[17−18]. Consequently, it deserves the efforts to fabricate various novel nanostructures. At present, there are numerous reports on the preparation and physical properties of quantum dots[19], nanorods[20], nanowires, nanobelts [21], and other nanostructures[22]. The creation of ordered superstructures of nanoscale CdS should still remain interests because of the possibility of achieving morphology-dependent optical properties. In this work, the preparation of 2D and 3D dendritic nanopatterns of CdS was reported.

2 Experimental

2.1 Fabrication of 2D dendritic nanopatterns

For the assembly of 2D dendritic structure of CdS, the primary process is to obtain nanoparticles with a narrow size distribution. Typically, stoichiometric cadmium chloride (0.114 g) and thioacetamide (0.037 g) were dissolved in 50 mL deionized water, which was kept at a constant temperature of 80 ℃ till yellow colloidal CdS was formed. The colloids were separated from the solution by centrifugal settling and washed several times

Foundation item: Project(50174059) supported by the National Natural Science Foundation of China; Project(Y406469) supported by the Science Foundation of Zhejiang Province, China
Corresponding author: GU Li; Tel: +86-573-83646195; E-mail: guli@mail.zjxu.edu.cn

with deionized water and absolute alcohol. After that, the obtained particles were re-dispersed ultrasonically in 50 mL absolute alcohol to give a homogenous yellow suspension. Then, 0.1 mL suspension was extracted and spread over the surface of a glass slide that was pretreated with hot nitric acid (65%). The glass slide was quickly transferred into a sealed container and kept undisturbedly for 24 h at ambient temperature, which was advantageous to the smooth volatilization of the solvent.

2.2 Fabrication of 3D dendritic nanocrystals

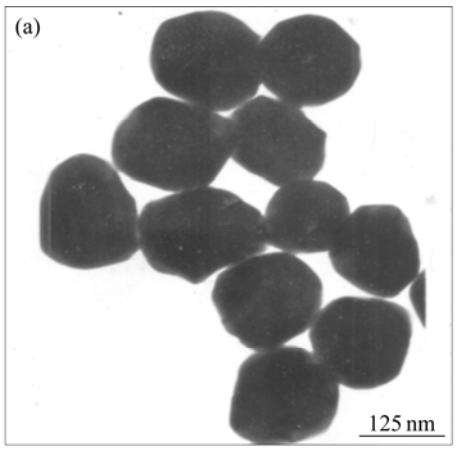
Firstly, 0.228 g cadmium chloride, 0.5 mL oleic acid(OA), and 10 mL absolute alcohol were dissolved in 40 mL deionized water. After ultrasonic dispersion for 10 min, milky solution was formed, which was then mixed with 10 mL aqueous solution containing 0.075 g thioacetamide homogeneously. After the mixed solution was stocked at 30 ℃ for 48 h, it can be seen that large amounts of faint yellow particles were suspended in the solution. The particles were separated from the solution and washed several times with hexane and absolute alcohol, respectively. Then, they were dried in a vacuum oven at 40 ℃ for further characterizations.

2.3 Characterization of 2D and 3D dendritic structures

Scanning electron microscopy(SEM) measurements were performed on a HITACHI−S570 microscope. Transmission electron microscopy(TEM) observations were performed on a HITACHI−H800 microscope operated at 200 kV. X-ray powder diffraction(XRD) patterns of the products were recorded on a Japan Rigaku D/max-r rotation anode X-ray diffractometer (Cu K_α, λ = 1.541 78 Å). Fourier transform infrared(FT-IR) spectrum of the products was recorded on a Bio-Rad FTS 575C instrument.

3 Results and discussion

Through the accurate control of experimental temperature, the reaction of cadmium chloride with thioacetamide can produce nanoparticles with a narrow size distribution, as learned from TEM observations (Fig.1(a)). It can be seen that the as-prepared nanoparticles are nearly monodispersed and present an irregular spherical profile. By statistic calculations on 200 particles, the average particle size is determined to be (95±6.2) nm, indicating the good monodispersity of the products. The good monodispersity of the as-prepared nanoparticles is advantageous to their subsequent assembly because it can efficiently prevent nanoparticles from severe aggregations[23]. Fig.1(b) displays the XRD pattern of these nanoparticles, which



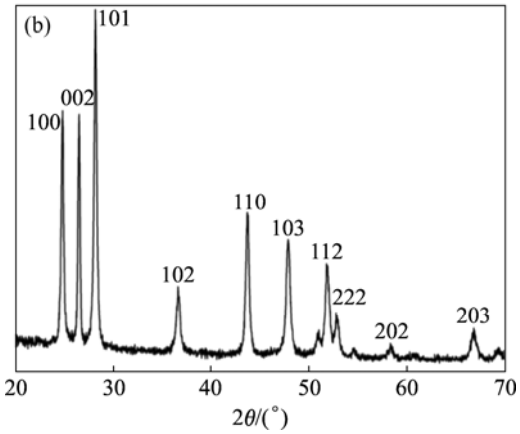


Fig.1 Typical TEM image(a) and XRD pattern(b) of monodispersed nanoparticles of CdS

can be readily indexed to the hexagonal structure of CdS (Joint Committee on Powder Diffraction Standards, JCPDS file, No. 77-2306). The strong and sharp reflections indicate that CdS nanoparticles are composed of well crystalline.

When these nearly monodispersed nanoparticles were dispersed in absolute alcohol and dropped onto the surface of a glass slide, they can assemble into dendritic nanopatterns spontaneously along with the volatilization of solvent, as observed by SEM (Fig.2). The low magnification image shown in Fig.2(a) reveals that there are large-area dendritic patterns covered on the surface of support. From the image with a high magnification (Fig.2(b)), it can be found that dendritic nanopatterns are quite regular, which are formed through the radial arrangement of CdS nanoparticles.

In terms of the diffusion-limited aggregation(DLA) model for interpreting fractal growth phenomena, the self-assembly of CdS nanoparticles into 2D dendritic nanopatterns should be directed by an entropy-driven disorder-order phase transition. It is understandable because fractal aggregations are ordered structures and are relatively stable in thermodynamics. When the solution containing CdS nanoparticles was dropped onto

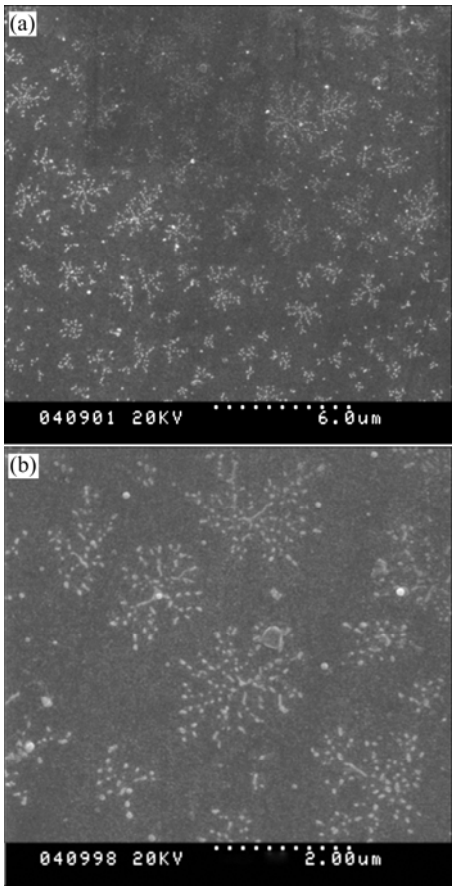


Fig.2 Representative SEM images of 2D dendritic nanoarchitectures of CdS assembled by CdS nanoparticles: (a) In low magnification; (b) In high magnification

the surface of support, parts of neighboring nanoparticles would aggregate to form skeletons for the subsequent fractal growth. Then, as the volatilization of the solvent, the force generated will drive other nanoparticles diffuse towards the skeletons and form peripheral branches.

In experiments, it was found that the volatilization temperature of the solvent influenced the assembled pattern dramatically. The ideal temperature for the formation of dendritic nanopatterns is in the range of 5−20 ℃. If temperatures are higher or lower than this level, the arrangement of CdS nanoparticles will be less ordered or disordered. This result is evident because the assembly of nanoparticles is associated with entropy. It is well-known that entropy is directly related to the temperature. Consequently, the variation of experimental temperatures will lead to the change of entropy, and in return, the degree of order of the assembled CdS nanoparticles is decreased.

In addition to the 2D dendritic nanopattern, by introducing OA molecules into the system, 3D dendritic CdS nanocrystals were obtained through the reaction of cadmium chloride with thioacetamide. The representative TEM and SEM images of 3D CdS dendrites are shown in Figs.3(a) and 3(b), respectively. They clearly reveal that the products have the 3D dendritic feature, which is comprised of large amounts of needle-like nanocrystals. XRD pattern of 3D dendrtitic nanocrystals is shown in the insert in Fig.3(b), which can be indexed to the cubic phase of CdS (JCPDS file, No. 21-829).

The formation of 3D dendritic nanocrystals should be related to the selective adhesion of OA molecules to grow facets[24−26]. This is because OA molecules are good organic additives in the morphology control of nanomaterials, which can bind to the surface of nanocrystals and hinder their growth. Usually, materials with a cubic crystal structure are prone to grow into spherical shape to minimize the surface tension. However, bound selectively by oleic acid, the surface tension and surface free energy of the growing crystals are altered and the growth rates of the nanocrystal along the bound crystal planes are slowed down or stopped[27], resulting in the far-from-equilibrium growth and the formation of dendritic patterns.

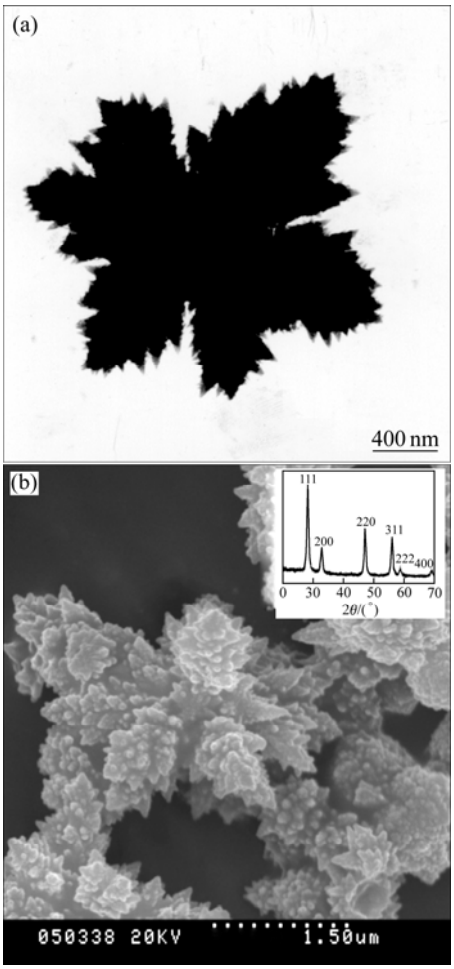


Fig.3 Representative TEM(a) and SEM(b) images of 3D dendritic nanocrystals of CdS (Insert is XRD pattern of 3D dendritic nanocrystals)

The existence of a strong interactions between OA molecules and dendritic CdS is confirmed by the FT-IR spectrum in the wavelength region of 4 000−500 cm^{-1} (Fig.4). Functional groups in OA chains, such as C═O, C—H, and —OH, can be identified easily from the spectrum, suggesting that OA is bound tightly to CdS because repetitive washings of the product by hexane could not remove them.

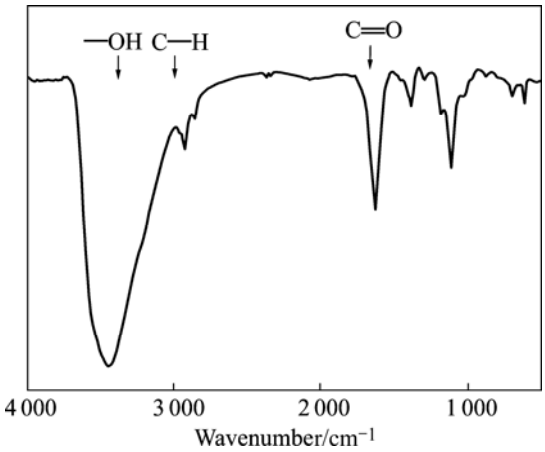


Fig.4 FT-IR spectrum of 3D dendritic nanocrystals of CdS

4 Conclusions

1) Two simple and convenient routes for the preparation of dendritic nanopatterns of semiconducting CdS are demonstrated. Under the regulation of OA molecules, 3D dendritic nanocrystals are synthesized.

2) Growth mechanism of CdS nanocrystals is presumed to be the selective binding of OA molecules onto growing crystal planes of seeds.

3) By means of the entropy-driven force, large-area 2D dendritic nanopatterns with nanoparticles as the building block are assembled onto the surface of glass slides.

4) The entropy-driven self-assembly of nanoparticles should provide a novel method for the fabrication of ordered nanostructures.

References

[1] COLLIER C P, VOSSMEYER T, HEATH J R. Nanocrystal superlattices [J]. Annual Review of Physical Chemistry, 1998, 49: 371−373.

[2] STEVEN L T, STEPHEN V P, ALEXANDER E R, ALEXANDER W. Self-assembly of cobalt nanoparticle rings [J]. Journal of American Chemical Society, 2002, 124 (27): 7914−7915.

[3] CAO M H, LIU T F, GAO S, SUN G B, WU X L, HU C W, WANG Z L. Single-crystal dendritic micro-pines of magnetic α-Fe_2O_3: Large-scale synthesis, formation mechanism, and properties [J]. Angewandte Chemie International Edition, 2005, 44(27): 4197−4201.

[4] CAO X B, XIE Y, LI L Y. Spontaneous organization of three-dimensionally packed microspheres into large-area nanowire networks [J]. Advanced Materials, 2003, 15(22): 1914−1918.

[5] CAO X B, XIE Y, YU F, YAO Z Y, LI L. Y. Magnetic force orientation of $Co_{23}B_{10}$ arrays inspired by magnetostatic bacteria [J]. Journal of Materials Chemistry, 2003, 13(4): 893−896.

[6] LI Y P, LU Y F, DOERR D W, ALEXANDER D R. Laser-assisted nanopatterning of aluminium using particle-induced near-field optical enhancement and nanoimprinting [J]. Nanotechnology, 2004, 15(11): 1655−1660.

[7] SUN S H, MURRAY C B, WELLER D, FOLKS L, MOSER A. Monodisperse FePt nanoparticles and ferromagnetic FePt nanocrystal superlattices [J]. Science, 2000, 287(5460): 1989−1992.

[8] JUN Y W, LEE S M, KANG N J, CHEON J. Controlled synthesis of multi-armed CdS nanorod architectures using monosurfactant system [J]. Journal of the American Chemical Society, 2001, 123(21): 5150−5151.

[9] XIAO J P, XIE Y, TANG R, CHENG M, TIAN X B. Novel ultrasonically assisted templated synthesis of palladium and silver dendritic nanostructures [J]. Advanced Materials, 2001, 13(24): 1887−1891.

[10] MANN S, MANN S. The chemistry of form [J]. Angewandte Chemie International Edition, 2000, 39(19): 3392−3406.

[11] JIN R C, CAO Y C, HAO E C, METRAUX G S, SCHATZ G C, MIRKIN C A, Controlling anisotropic nanoparticle growth through plasmon excitation [J]. Nature, 2003, 425(6957): 487−490.

[12] ZHANG Z P, SHAO X Q, YU H D, WANG Y B, HAN M Y. Morphosynthesis and ornamentation of 3D dendritic nanoarchitectures [J]. Chemistry of Materials, 2005, 17(2): 332−336.

[13] YU S H, ANTONIETTI M, COLFEN H, HARTMANN J, Growth and self-assembly of BaCrO4 and BaSO4 nanofibers toward hierarchical and repetitive superstructures by polymer-controlled mineralization reactions [J]. Nano Letters, 2003, 3(3): 379−382.

[14] PUNTES F, KRISHNAN K M, ALIVISATOS A P. Colloidal nanocrystal shape and size control: The case of cobalt [J]. Science, 2001, 291(5511): 2115−2117.

[15] GAO Y, JIANG P, LIU D F, YUAN H J, YAN X Q. Synthesis, characterization and self-assembly of silver nanowires [J]. Chemical Physics Letters, 2003, 380(1/2): 146−149.

[16] NITTMANN J, STANLEY H E. Connection between tip-splitting phenomena and dendritic growth [J]. Nature, 1986, 321(6071): 663−668.

[17] WANG Z L. Characterizing the structure and properties of individual wire-like nanoentities [J]. Advanced Materials, 2000, 12(17): 1295−1298.

[18] DESHMUHK I P, HOLIKATTI S G, HANKARE P P. A CdS: Sb photoelectrode for photoelectrochemical applications [J]. Journal of Physica D: Applied Physics, 1994, 27(8): 1786−1790.

[19] QI L M, COLFEN H, ANTONIETTI M. Synthesis and characterization of CdS nanoparticles stabilized by double-hydrophilic block copolymers [J]. Nano Letters, 2001, 1(2): 61−65.

[20] ZHANG P, GAO L. Synthesis and characterization of CdS nanorods via hydrothermal microemulsion [J]. Langmuir, 2003, 19(1) 208−210.

[21] IP K M, WANG C R, LI Q, HARK S K. Excitons and surface luminescence of CdS nanoribbons [J]. Appllied Physics Letters, 2004, 84(5): 795−797.

[22] SHEN G Z, LI C J. CdS multipod-based structures through a thermal evaporation process [J]. Crystal Growth Design, 2005, 5(3): 1085−1089.

[23] SAUNDERS A E, SIGMAN M B, KORGEL B A. Growth kinetics and metastability of monodisperse tetraoctylammonium bromide capped gold nanocrystals [J]. Journal of Physical Chemistry B, 2004, 108(1): 193−199.

[24] WANG W, EFRIMA S, REGEV O. Directing oleate stabilized nanosized silver colloids into organic phases [J]. Langmuir, 1998, 14 (3): 602−610.

[25] FANG J Y, STOKES K L, ZHOU W L, WANG W D, LIN J. Self-assembled. bismuth nanocrystallites [J]. Chemical Communication, 2001(18): 1872−1873.

[26] CAO X B, GU L. Spindly cobalt ferrite nanocrystals: Preparation, characterization and magnetic properties [J]. Nanotechnology, 2005, 16(2): 180−185.

[27] WANG Z L. Transmission electron microscopy of shape-controlled nanocrystals and their assemblies [J]. Journal of physical chemistry B, 2000, 104(6): 1153−1175.

(Edited by YANG Bing)