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Shape-Controlled Synthesis of 3D and 1D Structures of CdS in a Binary Solution with L-Cysteine's Assistance

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Abstract: A facile L-cysteine-assisted route was designed for the selectively controlled synthesis of 1D and novel, interesting 3D CdS spherical nanostructures constructed from CdS nanorods (or nanopolypods) in a binary solution. By controlling reaction conditions such as the molar ratio between $Cd(OAc)_2$ and L-cysteine and the volume ratio of the mixed solvents, the synthesis of various 3D architectural structures and 1D wirelike structures in large quantities can be controlled. This is the first reported case of the direct growth of novel 3D self-assemblies of CdS nanorods (or nanopolypods). The morphology, structure, and phase composition of the as-prepared CdS products were examined by using various techniques (X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), selected-area electron diffraction (SAED), high-resolution TEM, and Raman spectroscopy). On the basis of the results from TEM studies and our analysis, we speculate that in the present synthesis the L-cysteine dominates nucleation growth and the ethylenediamine (en)-dominated, oriented-assembly process. Interestingly, the products obtained show a gradient evolution in color from light-yellow to dark-yellow, which implies that their intrinsic optical properties change, possibly due to variations in their special morphologies and structures. This facile solution-phase L-cysteine-assisted method could be extended for the controlled preparation of other metal chalcogenides nanostructures with complex morphologies.

Keywords: cadmium · cysteine · nanostructures · photoluminescence · polypods

Introduction

Recently, the biomolecule-assisted-synthesis method has given a new and promising focus in the preparation of various nanomaterials, whose special structures and fascinating self-assembling functions allow them to serve as templates for the design and preparation of complicated structures.[1,2] Until now, many efforts have focused on using biomolecules as templates to assemble nanostructures. For instance, by using glutathione, highly ordered snowflake-like structures of Bi_2S_3 nanorods have been obtained,[3] and due to its double-helical structure, it has been demonstrated that DNA is useful in the assembly of nanoparticles into 2D or 3D structures[4] and in the ordered alignment of discrete 1D nanomaterials.[5]

Controlling the size and shape of nanocrystalline materials is a crucial issue in nanoscience research in the exploitation of novel properties. Considerable effort has led to the design of effective methods to synthesize 1D nanostructures such as nanowires,[6] nanobelts,[7] and nanotubes[8] due to the unique optical, magnetic, and catalytic properties of these structures. In contrast to 1D nanostructures, complex 3D architectures, such as branched Cu_2O crystals,[9] hierarchical structures from the self-assembly of polyhedral mesophase crystals,[10] mesocrystals as new kinds of superstructures with complex forms,[11] and tetragonal $PbWO_4$ microcrystals with special hierarchical structures,[12] may offer opportunities to explore their novel properties and, thus, have attracted broad attention in materials science. However, the successful synthesis of complex architectures is difficult and remains a great challenge. In particular, the realization of the controllable and selective preparation of 1D and 3D nanostructures remains difficult and has been rarely reported.

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As an important group II–VI semiconductor with extensive applications in optical and electronic nanodevices, CdS has received considerable attention for its 1D (or 3D) nanostructures.[13] In this paper, we report for the first time a facile L-cysteine-assisted method for the selectively controlled synthesis of 1D and novel, interesting 3D CdS spherical nanostructures constructed from CdS nanorods (or nanopolypods) in a binary solution. L-Cysteine ($C_3H_7NO_2S$), an amino acid and very important biomolecule, has a very significant effect on human-tissue development and, thus, has fascinated biologists, as well as chemists. We have used it as a sulfur source in our work. By controlling reaction conditions such as the molar ratio between $Cd(OAc)_2$ and L-cysteine, the volume ratio of the mixed solvents, and the reaction time, the synthesis of various 3D architectural structures and 1D nanowires in large quantities can be controlled. This is the first case of the direct preparation of novel 3D self-assemblies of CdS nanorods (or nanopolypods).

Results and Discussion

Figure 1 shows the XRD patterns of the as-prepared products at different volume ratios of water/ethylenediamine with the same initial reactant concentrations (concentrations of Cd^{2+} and L-cysteine were $0.02\,mol\,L^{-1}$ and $0.04\,mol\,L^{-1}$, respectively). The reflection peaks of the different products can be indexed as wurtzite CdS with lattice constants $a=4.139$ and $c=6.720$ Å, which is in good agreement with literature values (JCPDS Card No. 41-1049). No peaks of impurities were detected, revealing the high purity of the as-synthesized products. However, on comparing the peak intensities, the relative intensity of the peak corresponding to the (002) plane varied significantly from samples a–c to sample d, which shows the different tropism of the crystals.

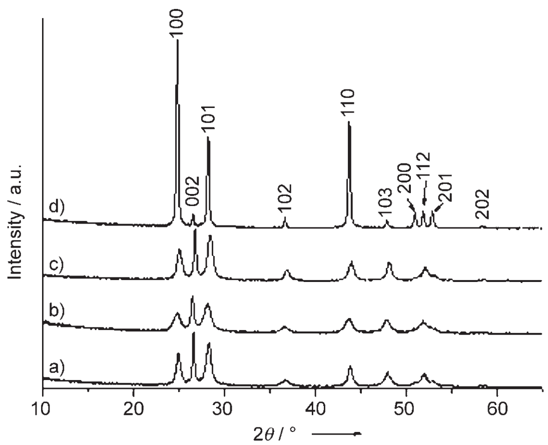

Figure 1. XRD patterns of CdS crystals obtained under different volume ratios of water/ethylenediamine: a) 2:1; b) 1:2; c) 1:4; d) 1:9. In all cases, the molar ratio of $Cd(Ac)_2$/L-cysteine = 1:2, with reaction for 24 h at 180 °C.

The morphologies of the as-synthesized products were examined by field-emission scanning electron microscopy (FESEM) and TEM. Figure 2a is a typical low-magnification FESEM image of the sample (from Figure 1a) obtained after aging at 180 °C for 24 h. This image indicates that these products are composed of homogeneous nanospheres with narrow diameter distributions of about 500–600 nm. These nanospheres are dispersed with good monodispersity (Figure 2a,b), although very few of them have discrepant diameters. High-magnification SEM images (Figure 2b,c) clearly reveal that the nanospheres are constructed from the assembly of nanorods. TEM images (Figure 2d,e and Supporting Information Figure S1) further confirm that these nanorods are highly directed to form radial arrays from the center to the surface of the spheres. Close examination of these images shows that the length and the diameter of the constituent nanorods are 250–300 and 15–20 nm, respectively, which yields a typical aspect ratio of around 14. The standard deviations of size distributions are estimated to be around 5.0 %. The high-resolution TEM image of an individ-

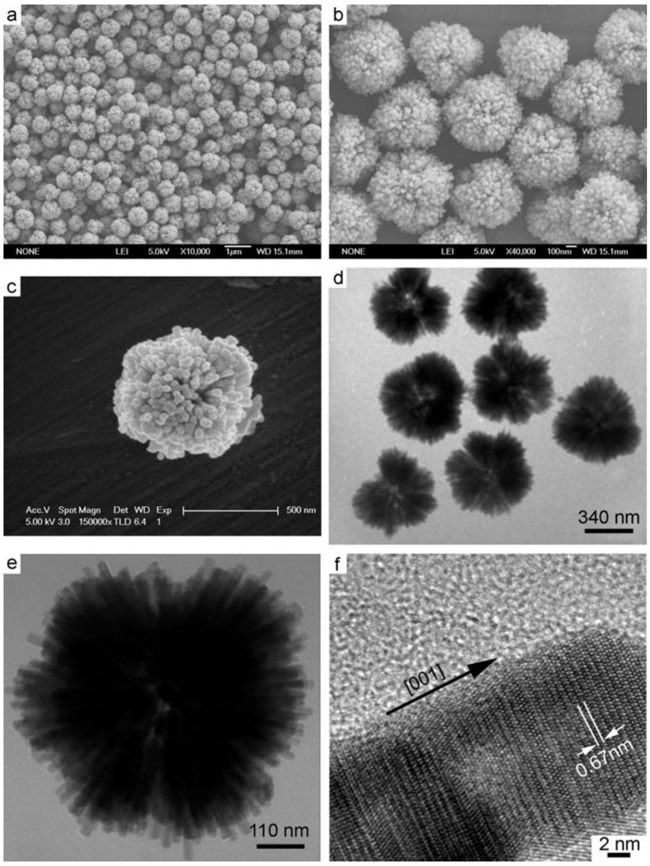

Figure 2. SEM and TEM images of the nanospheres. a) General view. b,c) Magnified SEM image, clearly showing that nanospheres are constructed from short nanorods. d,e) TEM images, revealing that nanorods are highly directed to form radialized arrays from the center to the surface of the spheres. f) HRTEM image of a nanorod.

ual nanorod (Figure 2f) confirms the single-crystal nature and the preferential [001]-direction growth.

In our experiments, the morphology of the products varied greatly as the volume ratio of water/ethylenediamine was decreased from 2:1 to 1:9 while keeping the other conditions constant. However, the crystal phase of the products did not change, which could be confirmed by the XRD pattern of the product fabricated under different volume ratios of water/ethylenediamine (Figure 1). An appropriate ratio of water/ethylenediamine is critical for the construction of superstructures (Table 1). At a volume ratio of water/ethylenediamine of 1:2, the samples obtained were found to contain CdS microspheres constructed from smaller spheres, as shown by the low-magnification FESEM image (Figure 3a). The magnified FESEM image (Figure 3b) clearly indicates that these composite smaller spheres possess polypod spherical structures. As shown in Figure 3c and d, urchin-like structures were obtained in the final products if just the volume ratio of water/ethylenediamine was decreased to 1:4 with the other conditions kept the same. Close observation of a typical broken urchin-like structure exhibited in Figure 3d indicates that the sphere was constructed from tightly self-assembled nanorod arrays. Interestingly, CdS nanowires with diameters of about 40–50 nm and lengths of up to several micrometers were obtained in the final products (Figure 3e,f) if the volume ratio of water/ethylenediamine was decreased to 1:9 with the other conditions kept unchanged. Thus, this method provides an efficient way for the selectively controllable preparation of 3D nanostructures and 1D wirelike structures of CdS. The conditions for preparing some typical samples by varying the ratios of the components of the binary solution are listed in Table 1. Notably, without the use of ethylenediamine, the as-prepared products consist of only large aggregates composed of particles that can be confirmed by SEM images (see Supporting Information, Figure S2). The successful preparation of these abundant and novel CdS morphologies suggests that the volume ratio in binary solution has a great influence on the shape of the products obtained.

Table 1. Summary of the experimental results indicating the influence of the composition of a mixed solution on the shape of the products.

Sample	V_{H_2O}/V_{en}	Phase	Morphology
a	1:9	CdS	long nanowires
b	1:4	CdS	urchin-like structures
c	1:2	CdS	polypod-like structures
d	3:7	CdS	urchin-like structures
e	2:3	CdS	urchin-like structures
f	1:1	CdS	urchin-like structures
g	2:1	CdS	spheres constructed from rods
h	4:1	CdS	spheres constructed from rods
i	pure water	CdS	irregular particles

The morphology and structure of the CdS nanowires were further analyzed by TEM and SAED. Figure 4a shows a low-magnification TEM image of a single CdS nanowire with a diameter of approximately 54 nm. The corresponding SAED pattern (inset) was recorded with the electron beam along the [010] zone axis of wurtzite CdS. The HRTEM image in Figure 4b, recorded at the area marked in Figure 4a, reveals that the nanowire is single-crystalline in nature and grows preferentially along the [001] direction (*c* axis), which is consistent with the SAED pattern.

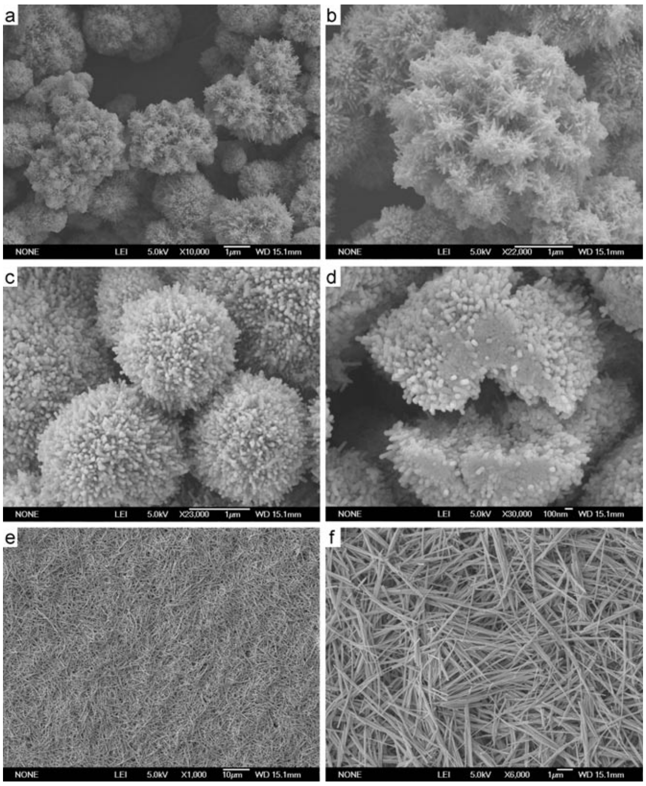

Figure 3. FESEM images of the samples prepared under different water/ethylenediamine volume ratios: a,b) 1:2; c,d) 1:4; e,f) 1:9. In all cases, the molar ratio of $Cd(Ac)_2$/L-cysteine = 1:2, with reaction for 24 h at 180 °C.

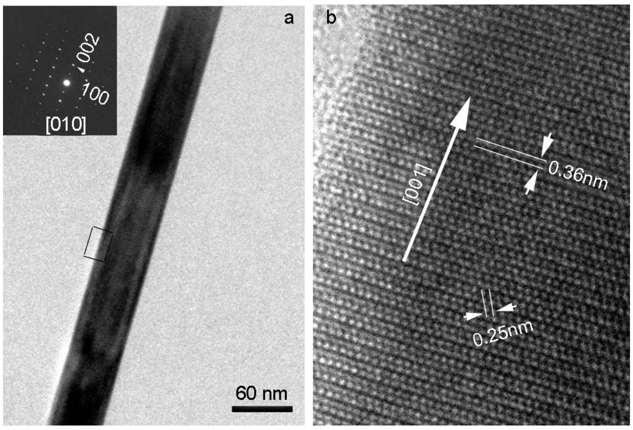

Figure 4. a) TEM image of an individual CdS nanowire. Inset is a SAED pattern taken along the [010] zone axis direction. b) HRTEM image of part of an individual nanowire (area marked with a rectangle in (a)). The fringe spacing of 0.36 and 0.25 nm observed in this image corresponds to the separation of the (002) and (102) lattice planes, respectively.

Notably, no spherelike 3D structures constructed from self-assembled nanorods (or polypods) could be obtained under similar conditions by replacing L-cysteine with thioacetamide or thiourea (Supporting Information, Figure S3). This indicates that the formation of these novel 3D structures may be dependent on the special properties and structure of L-cysteine. Furthermore, the molar ratio of Cd(OAc)$_2$ to L-cysteine has a significant effect on the final morphologies and structures of the products, if the other conditions remain the same (Supporting Information, Figure S4). An appropriate ratio of Cd^{2+}/L-cysteine is crucial to the construction of novel 3D structures.

In the current study, novel 3D nanostructures of CdS can be synthesized by using only L-cysteine as sulfur source in a binary solution with a suitable volume ratio of water/ethylenediamine. The detailed time-dependent experiments showed that the CdS particles are formed in the early stage and are then converted to spheres assembled from nanorods (Figure 5 and Supporting Information, Figure S5). From the results of TEM studies, XRD techniques (Supporting Information, Figure S6), and the above analysis, we speculate that in the present synthesis the L-cysteine dominates the nucleation-growth process and the en-dominated oriented-assembly process. The possible growth process is schematically illustrated in Figure 6. Based on observations from mass spectrometry, Burford and co-workers reported that metal ions could react with L-cysteine to form stable complexes.[14] Therefore, it is reasonable to conclude that, in our approach, the free Cd^{2+} can coordinate with L-cysteine to form an L-cysteine–Cd^{2+} complex that then decomposes to form initial amorphous CdS as nuclei for later growth (Figure 5a). The color change of the Cd(Ac)$_2$ solution upon addition of L-cysteine also confirmed this process. Subsequently, as the reaction proceeds, the initial amorphous CdS particles gradually crystallize, as demonstrated by the results shown in Figure 5, Figures S5 and S6. Simultaneously, as a structure-directing molecular-coordination template,[15] the complex reagent ethylenediamine, which contains more than one en-chelating atom in each molecule and possibly adsorbs onto the (010) and (100) planes of the incipient CdS nuclei, not only prevents the particles from agglomerating, but also influences the growth of these planes. This may allow the reaction to proceed more slowly to provide enough time for the anisotropic growth of the precursor originating from the match between the special CdS atomic surface structures and the linear molecular structure of ethylenediamine. Therefore, (001) is a high-energy face relative to the en-covered (010) and (100) faces. Direct evidence for this hypothesis requires further study and work is underway. The oriented attachment of the nanoparticles followed by crystallographic fusion of the (001) faces conforms to that described first by Penn and Banfield for TiO_2 nanocrystals.[16] This process guides the formation of 1D nanorods that assemble to form ordered 3D structures due to the direction-oriented role of ethylenediamine. Thus, the shape of the nanospheres constructed from the assembly of nanorods is dominated mainly by ethylenediamine. As mentioned above, if the amount of ethylenediamine increases to a certain level, a 1D wirelike structure is finally obtained, which further indicates that ethylenediamine dominates the whole growth process under the present experimental condition.

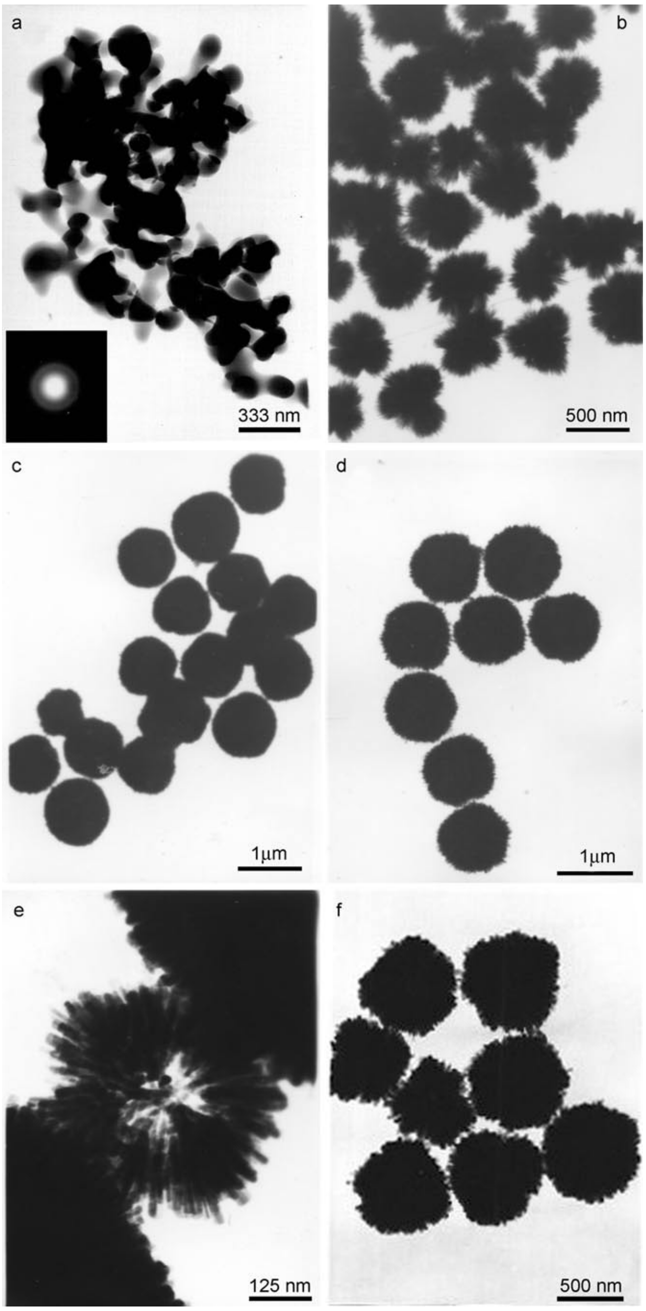

Figure 5. Shape-evolution process for different reaction times: a) 10 min; b) 30 min; c) 1 h; d,e) 4 h; f) 24 h. Volume ratio of water/ethylenediamine = 2:1, molar ratio of Cd(OAc)$_2$/L-cysteine = 1:2.

An interesting feature of these products is that they show gradient evolution in color from light-yellow to dark-yellow (samples 1–4, Figure 7) as the volume ratio of water/ethylenediamine increases. This implies that the intrinsic optical properties have changed. Therefore, the optical properties of these novel structures were studied.

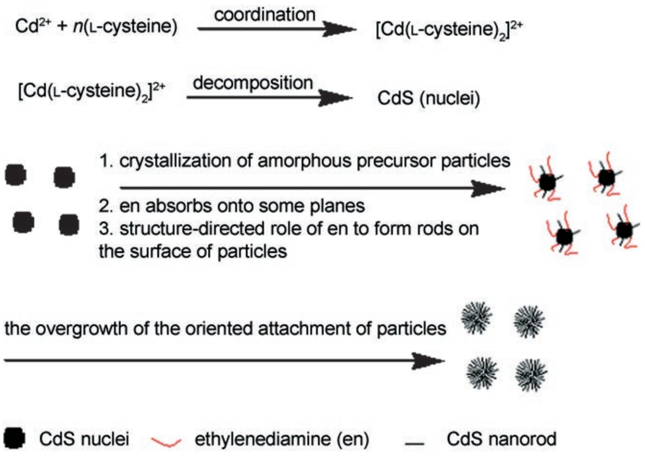

Figure 6. Schematic illustration of the formation and shape evolution of 3D CdS architectural structures by the synthetic process.

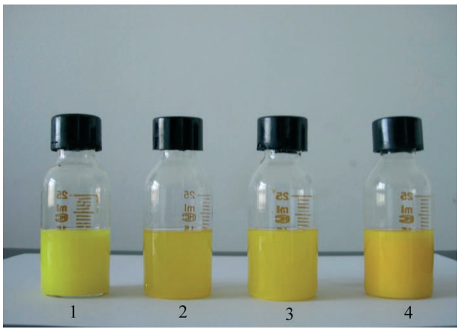

Figure 7. Color evolution of the as-obtained CdS products. Products 1, 2, 3, and 4 were prepared with volume ratios of water/ethylenediamine = 1:9, 1:4, 1:2, and 2:1, respectively. In all cases, the molar ratio of $Cd(Ac)_2$/L-cysteine = 1:2, with reaction for 24 h at 180 °C.

The Raman spectrum of the nanospheres constructed from short nanorods (Figure 8) displays three bands within the range 200–1000 cm^{-1}. The peaks located at around 295, 589, and 889 cm^{-1} correspond to the first-, second-, and third-order transverse optical (TO) phonon modes of CdS, respectively. No vibration modes due to impurities are observed. From previous reports, the first-, second-, and third-order TO phonon frequencies of single-crystalline CdS nanowires are 304, 607, and 908 cm^{-1}, respectively.[17] Relative to these results, the TO phonon peaks of the CdS nanostructures are all shifted towards lower frequency, which is probably due to the effects of small size and high surface area. The relatively broad, sharp, and symmetric peaks of the CdS nanostructures suggest that the CdS spherical structures constructed from short nanorods are highly crystalline, which is consistent with the TEM observations shown above. The Raman spectra of wurtzite crystals with other shapes (Figure 3) are similar to those of the wurtzite with spherical structures constructed from short nanorods (Figure 2).

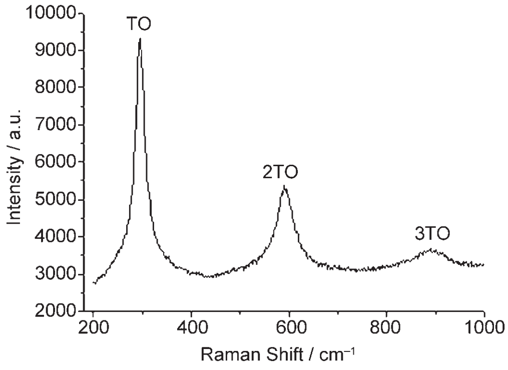

Figure 8. RT Raman spectrum of CdS spherelike structures constructed from nanorods.

Figure 9 shows the room-temperature photoluminescence spectra of the different microstructures, which were measured by using a Perkin–Elmer LS-55 luminescence spectrometer with an excitation-slit width of 5 nm and an emission-slit width of 5 nm. Curves 1–4 correspond to the wirelike structures (Figure 3e,f), the urchin-like structures (Figure 3c,d), the polypod structures (Figure 3a,b), and the spherelike structures constructed from nanorods (Figure 2). Each curve displays two distinct peaks; the one at 500–550 nm is the green emission component and the other at about 695 nm is the infrared band. These results are similar to those in previous reports for CdS nanocrystals.[13d,18] The green luminescence is usually attributed to near-band-edge (NBE) emission, whereas the latter (the infrared emission) could be associated with structural defects that may result from trap or surface states. As reported previously, the band-edge luminescence originated from the recombination of excitons and/or shallowly trapped electron–hole pairs. The excitonic emission at about 400 nm resulting from recombination of the bound excitons was detected in the CdS clusters in zeolite–Y.[19] The photoluminescence spectra at 298 and 77 K represented an infrared emission band with a maximum at 725 nm, which can be ascribed to trap emission.[18c] No direct recombination of the excitons was exam-

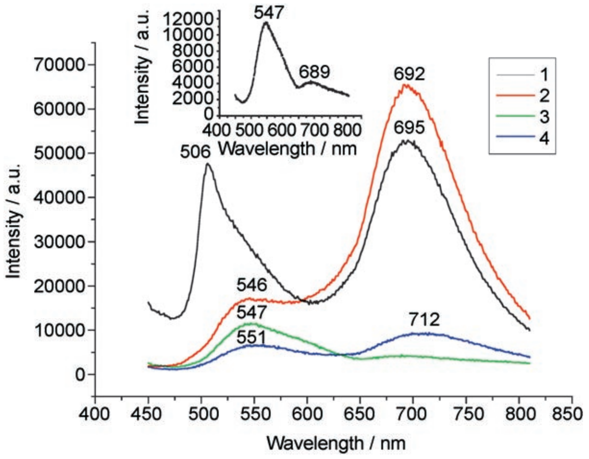

Figure 9. Photoluminescence spectra of CdS nanostructures. Curve 1 corresponds to the wirelike structures (Figure 3e,f); curve 2 to the urchin-like structures (Figure 3c,d); curve 3 to the polypod structures (Figure 3a,b); curve 4 to the spherelike structures constructed from nanorods (Figure 2). The excitation wavelength was 420 nm and all spectra were recorded at RT. Inset is an enlarged PL spectrum of curve 3.

ined. It is thought that the trap emission arises mainly from the excess of sulfur on the nanowire surfaces, but not from the low crystallinity of the particles. Notably, L-cysteine as a sulfur source is excessive in our reaction system. As a result, the infrared emission from the CdS nanostructures prepared in our work could arise from the trapped emissions. Relative to curve 1 in Figure 9, the green luminescence peaks of the 3D structures (curves 2–4) have not only red-shifted by about 40 nm, but show a large decrease in intensity, which may be relevant to the complexity of the 3D structures. More detailed study of this is required.

Conclusions

A simple procedure based on an L-cysteine-assisted method was developed to selectively and controllably synthesize CdS nanocrystals with 1D structures and novel 3D superstructures in high yield in a binary solution, by controlling reaction conditions such as the molar ratio between Cd(OAc)$_2$ and L-cysteine and the volume ratio of the mixed solvents. The formation mechanism of the 3D structures was investigated and the creation of such structures could be attributed to the L-cysteine-domination of nucleation growth and the en-dominated oriented-assembly process. Novel polypod structures, urchin-like structures, and wirelike structures can be synthesized by varying the volume ratio of water/ethylenediamine. The molar ratio of Cd^{2+}/L-cysteine also plays an important role in controlling the morphology. The difference in optical properties of these novel 3D structures could be related to their structural complexity and specialty. Further detailed investigation of the relationship between their structure and optical properties is required. In principle, this approach could be employed for the controlled synthesis of other semiconductor nanomaterials with complex shapes.

Experimental Section

All chemicals were of analytical grade and were used without further treatment. In a typical procedure, 1 mmoL cadmium acetate (Cd(Ac)$_2$·2H$_2$O) and 2 mmoL L-cysteine (C$_3$H$_7$NO$_2$S) were added to a given amount of distilled water and the mixture was dispersed to form a homogeneous solution by constant vigorous stirring. A given amount of ethylenediamine (en) was then added at RT to the solution, which was continually stirred for 10 min. The resulting mixture was transferred into a Teflon-lined stainless-steel autoclave (60 mL capacity) that was then sealed and maintained at 180 °C for 24 h. The system was then allowed to cool to ambient temperature. The final product was collected and washed with distilled water and absolute alcohol several times, then vacuum-dried, and kept for further characterization.

The products were characterized by XRD by using a Japanese Rigaku D/max-γA rotating anode X-ray diffractometer equipped with monochromatic high-intensity Cu$_{K\alpha}$ radiation ($\lambda = 1.54178$ nm). SEM images were taken by using a field-emission scanning electron microscope (FESEM, JEOL-6300F, 15 kV). Microscopy was performed by using a Hitachi (Tokyo, Japan) H-800 transmission electron microscope (TEM) at an accelerating voltage of 200 kV, and a JEOL-2010 high-resolution TEM, also at 200 kV. Raman spectra were recorded by using a Jobin Yvon (France) LABRAM-HR confocal laser micro-Raman spectrometer at RT. Photoluminescence (PL) measurements were recorded by using a Perkin–Elmer LS-55 luminescence spectrometer with a pulsed Xe lamp.

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