Single Crystalline Cadmium Sulfide Nanowires with Branched Structure

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Abstract In this article, we report the synthesis of branched single crystal CdS nanowires. This branched CdS nanostructure is prepared by a simple surfactant-directing method, which is of particular interest as it uses readily available reagents and provides a convenient route to high-yield single crystal nanowires but with branched shape. These branched nanowires have an average diameter of about 40 nm and length up to several micrometers. A possible mechanism has been proposed and the addition of surfactant dodecylthiol into the two mixed-solvents would play an importance effect on the structure of the product. Based on the mechanism, by controlling the synthesis conditions, such as the ratios between the surfactant, inorganic solvent, and organic solvent, other kinds of nanostructures based on CdS nanowires were also prepared. Photoluminescence (PL) measurement reveals that the branched CdS nanowires have a strong emission at about 700 nm which might be due to its special structure.

Keywords Cadmium sulfide · Nanowires · Branched single crystal

Introduction

Nanoscale semiconductors have attracted considerable attention in recent decades in both fundamental researches and technical applications because of their conspicuous optical and electronic properties [1]. The structures of semiconductor nanocrystallites, including size, shape, and dimension, play important roles to determine their physical properties [2]. One-dimensional (1D) nanomaterials, such as nanorods and nanowires, have been the focus of considerable interest because of their fundamental importance to study the dependence of various properties on dimensionality and size reduction as well as potential applications in optoelectronics, nanoelectronics, and nanobiotechnology [3–5].

Semiconductor nanowires are rising as versatile nanoscale building blocks for electronic and photonic nanodevices, such as electronic sensors, photodetectors, lasers, and light-emitting diodes [6–8]. Among semiconductors, cadmium sulfide (CdS) is one of the most important direct band gap II–VI semiconductors [9, 10]. It has been intensively studied because of its vital optoelectronic applications for laser light-emitting diodes and optical devices based on nonlinear properties [11–13]. By simply changing its size or morphology, it can easily tune emission in the visible range and engineer the band gaps over a wide range from visible to ultraviolet [14, 15]. Since the sizes, shapes, and crystalline structures are important factors for its intrinsic properties, sufficient controls on these characteristics inevitably become the key issues in the preparation of CdS nanomaterials. Up to date, various methods of manipulating the shape and size of CdS nanocrystals have been reported [16–18]. Star-like CdS nanocrystals were synthesized from a lyotropic triblock copolymer solution system [16]. Nanosized CdS spheres were synthesized in water-in-oil microemulsions with amphiphilic dendrimers [17]. Using mixed solvents of ethylenediamine and ethylene glycol, CdS nanotetrahedrons, pencil-shaped nanocrystals, tetrapods, prickly
spheres, and hexagonal nanoprisms have been prepared under solvothermal conditions [18]. As far as 1D shape-controlled preparation is concerned, CdS nanorods/nanowires/nanotubes have been fabricated by hydrothermal/solvothermal routes [19, 20], in situ micelle-template-interface reaction processes [21], ion beam syntheses [22], ultrasonic or microwave-assisted techniques [23, 24], hard template method [25], vapor transportation techniques [26], and so on. Stable and homogeneous CdS nanowires have been successfully obtained in aqueous SDS solutions [27]. Uniform and high aspect ratio CdS nanowires have been synthesized on a large scale by a solvothermal process in a mixed solvent of dodecanethiol and ethylenediamine [28]. A simple, one-step bench-top synthesis method using hexadecylamine as liganding solvent was reported for uniform luminescent 80–150 nm long CdS wires with ultra-narrow width (1.7 nm) [29]. With an anodic aluminum oxide (AAO)/Au/Si template, CdS nanowires could also be obtained through an electrochemical deposition process [30]. Although CdS nanowires with a wide distribution of sizes have been achieved by individually tailored routes, there are just few reports concerning the growth of new structure of CdS nanowires.

Surfactant-directed method has attracted the attention of many researchers and been broadly used in the preparation and morphology control of nanomaterials [31, 32]. Dodecanethiol, an important surfactant, has intensive applications in the preparation of nanoparticles and generally applied as a stabilizer of the resulting nanoparticles or a kind of post-treatment reagent [33, 34]. Recently, we have reported that using dodecanethiol as a co-directing agent, multi-armed CdS architectures can be synthesized through solvothermal technique [35]. In this communication, we developed this method to apply dodecanethiol in water–toluene system and a brand new wire-like structure: branched single crystal CdS nanowires can be prepared by this simple surfactant-directing method, which is of particular interest as it uses readily available reagents and provides a convenient route to high-yield single crystal nanowires but with branched shape. Furthermore, we have also been able to demonstrate a relationship between growth conditions and both the morphology and habitat of the 1D nanocrystal. Photoluminescence (PL) measurement reveals that the CdS nanowires have a very strong emission at about 700 nm which might be due to its special structure.

**Experimental**

The procedure involved adding cadmium chloride (CdCl₂) and thiourea (Tu) in an autoclave already primed with toluene, distilled water, and 1-dodecanethiol mixed in a certain ratio of 20:2:1. The reaction was carried out at 160 °C for 24 h. The CdS product was isolated by precipitation with ethanol, washing with toluene, and re-dispersing with ethanol before analysis. The products are characterized by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and PL Spectrum.

X-ray diffraction patterns were recorded on a Scintag diffractometer operated at 35 kV voltage and 30 mA current with Cu–Kα radiation (λ = 1.54178 Å). The samples were deposited on slides and dried at room temperature. SEM images were carried out on a Hitachi S-3500 N SEM. TEM images were obtained with a Philips 420 TEM with an accelerating voltage of 120 kV. High-resolution TEM (HRTEM) micrographs were taken on a JEOL-2010F TEM operated at 200 kV.

**Results and Discussion**

The XRD pattern of the prepared sample (as shown in Fig. 1) could be indexed to a pure hexagonal CdS wurtzite structure with lattice constants in accordance with literature (JCPDS card, No. 77-2306). No peaks due to any other phases were detected, indicating the high purity of the products. Strong peaks also confirmed the high crystallinity of the sample.

Figure 2a shows a TEM image with a low magnification of the sample. It could be seen that the product has a wire-like morphology in a large scale, which confirms the high yield of CdS nanowires. The average diameter is about 40 nm and length is up to several micrometers. Figure 2b displays a TEM image with a higher magnification, showing that the nanowires have fringy shape. One long nanowire seems to be assembled by several small and short nanorods/nanowires. The selected area electron diffraction (SAED) pattern (in inserted Fig. 2c) could be indexed as...
hexagonal CdS, which is in agreement with XRD analysis result. Figure 3 gives the details of the nanowire. Figure 3a, b show the middle sections of long nanowires, confirming that the long nanowires are not formed by two or several short nanorods/nanowire though they appear to be so. They are long nanowires but with branches. Figure 3c, d are the corresponding SAED patterns of the nanowires shown in Fig. 3a, b, which show diffraction spots, also confirming that the “assembled” nanowire might be single crystal although it has branches. The diffraction spots in two perpendicular directions could be indexed as (110) and (002), respectively, which means that the branched CdS nanowire might be with a preferred growth direction of [001]. HRTEM images of individual branched wire (Fig. 3e–g) show well-resolved lattice planes with inter-planar distances of 0.33 nm, consistent with the (002) d spacing of the CdS wurtzite structure. The result confirms that the branched CdS nanowires are single crystal in nature and have a growth direction of [001] in agreement with SAED analysis result.

Although the exact mechanism of the formation of these branched nanowires is difficult to know, it is no doubt relevant to the addition of surfactant dodecylthiol into the two mixed solvents of distilled water and toluene. These two solvents form a solvent–solvent interface, and dodecylthiol, which has a hydrophilic group and a lipophilic group, might exist in the interface. During the experiments, dodecylthiol would first react with cadmium ions and adsorb the ions into the interface. As reaction goes on,
sulfur source would attack the cadmium ions from one side of the interface to form CdS nanocrystals. During the growth process of CdS nanocrystals, dodecylthiol would confine the growth of CdS nanocrystals along the interface to form nanowires but as the sulfur source is provided from the water side, the nanowires would have tendency to grow into the water phase, which might lead to the formation of the branches. Based on this hypothesis, the behavior of surfactant in solution would play an important effect on the structure of the product. As is known, the behavior of surfactant in solution is affected by the concentration of the surfactant and the ratios between the surfactant, inorganic solvent, and organic solvent. So, all the experimental conditions, including the ratio between toluene and water and the ratio of dodecylthiol to metal ion, could determine the structure of final product. Different ratios would lead to different CdS structures. Figure 4a shows a typical SEM image of the product prepared with the ratio of toluene, water and dodecylthiol of 2:10:1, indicating that CdS nanowires with bundle-like structure can be obtained. TEM images shown in Fig. 4b, c also confirm that the product have a wire-like morphology but with bundle-like structure. The nanowires have an average diameter of 30 nm and length of several micrometers. Several nanowires aggregate to form a bundle. HRTEM images of individual nanowire (Fig. 4d) show well-resolved lattice planes with inter planar distances of 0.36 nm, consistent with the (100) d spacing of the CdS wurtzite structure. This result might be due to the different assembly behavior of dodecylthiol in different solvent ratios. The solvent ratio between toluene and water is not the only factor that can affect the structure of the final product, but the ratio between the metal ion and dodecylthiol can also lead to different structures. Figure 5a–c show TEM images and SAED pattern of the product prepared with the ratio between toluene, water, and dodecylthiol of 2:10:3. The product still has a wire-like morphology but more nanowires aggregate together compared with the product shown in Fig. 4. This might be due to the assembling ability of dodecylthiol. Higher dodecylthiol concentration would lead more CdS nanowires to assemble together. Similar result is found when the ratio between toluene, water, and dodecylthiol is 10:2:1. As shown in Fig. 5d, more branches are found in CdS nanowires compared with the product shown in Figs. 2 and 3.

PL measurement has also been carried out to evaluate the quality of the product. Figure 6 shows the room-temperature PL spectrum of the branched CdS nanowires. It displays a very strong infrared emission band centered at about 700 nm, which is close to those in previous reports for an infrared emission band of CdS nanocrystals [36].

![Fig. 4 a SEM, b, c TEM, and d HRTEM images of bundle-like CdS nanowires](image)

![Fig. 5 a, b TEM images and c SAED pattern of the product prepared with the ratio between toluene, water, and dodecylthiol of 2:10:3; d TEM image of the product prepared with the ratio between toluene, water, and dodecylthiol of 10:2:1](image)
This emission band is associated with structural defects, which may arise from the special structure of the branched nanowires [37].

Conclusions

In summary, a novel branched single-crystalline CdS nanowires have been prepared by a dodecylthiol-assisted technique in high yield. By controlling the synthesis conditions, such as the ratios between the surfactant, inorganic solvent, and organic solvent, other kinds of nanostructures based on CdS nanowires were also prepared. PL measurement reveals that the CdS nanowires have a very strong emission at about 700 nm which might be due to its special structure. In principle, this approach has promise for extension to other inorganic 1D nanowires.

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