Blue Luminescence of CdS Nanowires Synthesized by Sulfurization *

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Polycrystalline CdS nanowires have been synthesized by sulfurizing metal Cd nanowires deposited electrochemically within the nanochannels of porous anodic alumina (PAA) templates. Photoluminescence (PL) investigation shows that the CdS nanowires have an intensive and broad PL emission band peaked around 435 nm. The investigation results suggest that localized defects and excess S atoms existing in the CdS nanowires are responsible for this blue luminescence.

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One-dimensional (1D) semiconductor nanostructures have attracted considerable attention in recent years because of their importance in fundamental research and their potential applications in nanodevices.[1−3] A handful of examples of such materials, in particular cadmium sulfide (CdS) nanowires, an important II–VI group of semiconductors with novel optoelectronic properties and wide applications,[4−10] have been reported in the literatures by using different synthesis approaches, such as catalyzer-assisted vapour deposition,[4,5] solution-phase growth,[6,7] and template-assistant synthesis.[8−10] These well-aligned and well-distributed CdS nanowires would provide possibilities for observing interesting and useful physical phenomena.

Understanding the fundamental concepts of the role of structure on physical properties is a primary goal for studies of 1D nanostructures, and achieving that in the case of CdS nanowires is of importance. To the best of our knowledge, little research has been focused on the photoluminescence (PL) properties of CdS nanowires obtained by a template-assistant method.[8−10] Previously, Wang *et al.* found that singlecrystal CdS nanowires produced by physical evaporation have a strong red PL emission band around 750 nm, which has been ascribed to trapped emission related to surface and subsurface defects.[5] However, Zhan *et al.* reported that singlecrystal CdS nanowires formed by polymer-controlled growth can feature one strong narrow luminescence band at 380 nm, which has been attributed to a higher-level transition in CdS crystallites.[6] Why these singlecrystal CdS nanowires show different luminescence characteristics is unclear as yet, and further studies on the PL properties of CdS nanowires are therefore necessary to gain a fundamental understanding of the system.

In this Letter, we report the PL properties of polycrystalline CdS nanowires prepared by sulfurizing the metal Cd nanowires deposited electrochemically within the nanochannels of porous anodic alumina (PAA) templates. A blue luminescence band peaked around 435 nm has been observed in our CdS nanowires, which shows some differences from those reported previously.[5,6] Although the template synthesis of CdS nanowires as well as their arrays has been investigated extensively,[8−10] the physical properties such as the PL of these CdS nanowires synthesized via a template-assistant approach are not yet clear according to the existing literature.

Template synthesis of CdS nanowires is briefly discussed here. Firstly, metal Cd nanowires were fabricated by electrochemical deposition, which was similar to the preparation of metal Cu nanowires described previously.[11] A porous anodic alumina (PAA) template with a thickness of about 30 μm and nanochannel diameters of about 50 nm was prepared via an aluminium anodic oxidation process in a 0.3-M oxalic acid solution.[12] The metal Cd nanowires were electrodeposited in a conventional three-electrode aqueous bath, containing the mixture solutions of 0.2-M $CdCl_2$ and 0.1-M H_3BO_3. The deposition potentials were controlled in the range of $-0.68 \sim -0.7$ V (SCE, saturated calomel electrode) for 20–30 min at room temperature. Then the PAA template/Cd nanowire composite was obtained.

Subsequently, the sulfurization process was carried out. The PAA template/Cd nanowire composite was placed in a quartz boat and covered with pure S powder. The quartz boat was placed into the hot zone of a recrystallized alumina tube furnace. After the reaction chamber was evacuated by using a mechanical pump, the samples were heated up to 300°C within 30 min from room temperature and maintained at this temperature for 30 h to sulfurize the Cd nanowires completely. After sulfurization, the PAA template surface was cleaned with CS_2 to remove the remaining

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S powder, polished by using a 50-nm SiC polishing sandpaper to get rid of the CdS particles that stuck on the surface, and then the PAA template was totally removed by using a 1-M NaOH solution. Finally, the CdS nanowires were washed with ethanol and de-ionized water in turn and allowed to dry in air before characterization. The CdS nanowires were characterized by using powder x-ray diffraction (XRD, D/MaxrA, Cu K_α, $\lambda = 0.1542$ nm), scanning electron microscopy (SEM, JEOL JSM-6300), transmission electron microscopy (TEM, JEM-200CX), and photoluminescence (PL, HITACHI 850). All the experiments were performed at room temperature.

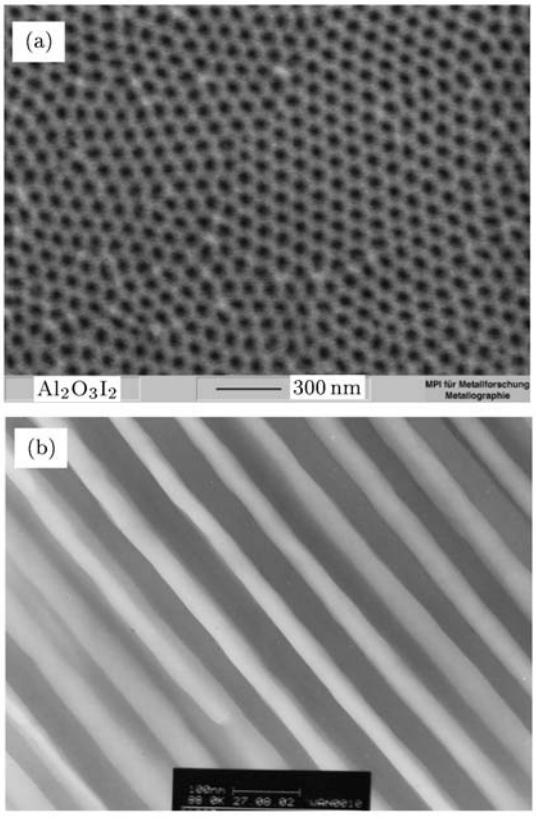


Fig. 1. SEM (a) and TEM (b) images of the PAA template with ordered nanochannels.

Figure 1 shows the SEM and TEM images of the PAA template used in this work, in which the highly ordered nanochannels with channel diameters about 50 nm are clearly seen. Due to their uniform and nearly parallel porous structures, PAA films have become ideal templates for the electrochemical deposition of the highly anisotropic, aligned nanowire arrays with wide range of materials.[13] Previously, metal oxide nanowires such as ZnO have been prepared by oxidation of metal Zn nanowires.[14] Furthermore, superconductive MgB_2 nanowires have been fabricated by reaction of B nanowires with metallic Mg.[15] These two-step synthesis approaches for the compound nanowires reveal that the sulfurization of

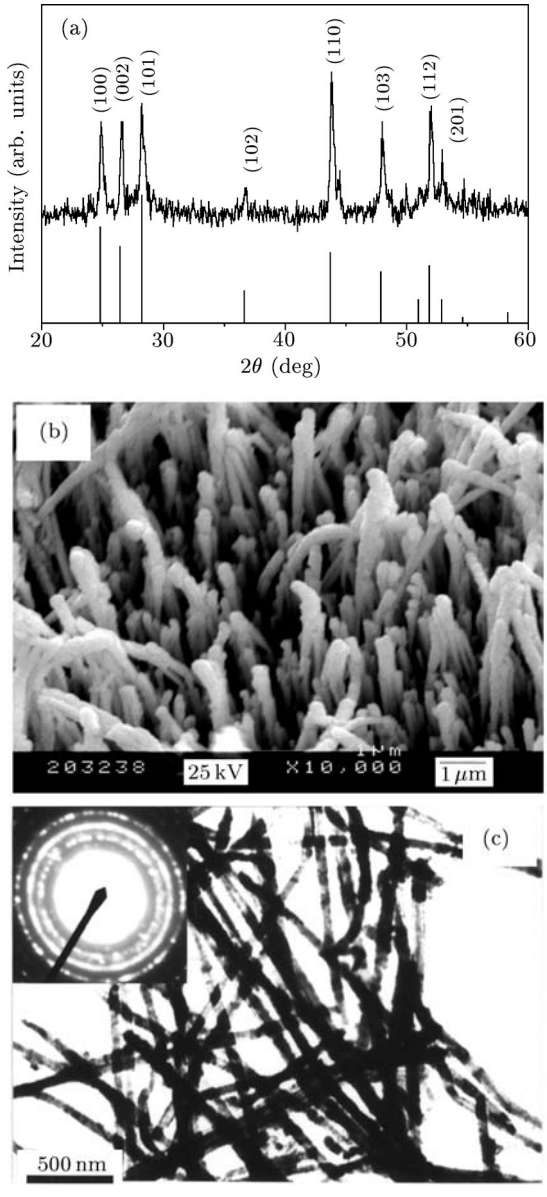


Fig. 2. (a) XRD spectrum of CdS nanowires with the straight lines corresponding to the line spectra of the bulk hexagonal structures of CdS provided by the JCPDS (File No. 06-0314). (b) SEM image of the CdS nanowires. (c) TEM image of CdS nanowires with the inset showing the SAED patterns of the CdS nanowires.

metal Cd used here given by the chemical equation

$$S + \text{Cd (nanowires)} \Rightarrow \text{CdS(nanowires)} \qquad (1)$$

is understandable, in which S atoms are expected to react with the metal Cd within the nanochannels of PAA template to form CdS nanowires. After the PAA template was totally removed, a typical XRD spectrum of the products was obtained, as shown in Fig. 2(a). It has been found that the XRD pattern of the products can be indexed as CdS of a pure hexagonal phase structure, which is very close to the values in the literature (straight lines inserted in Fig. 2(a), obtained from JCPDS Card, File No. 06-0314). Fur-

thermore, no other phases such as Cd or CdO were found, indicating that relatively pure CdS nanowires resulted from the reaction (1). The sharp and intensive XRD peaks also reveal that the as-prepared CdS nanowires are of highly crystalline structure.

The SEM image of the CdS nanowires prepared by sulfurization is shown in Fig. 2(b). It can be seen that large-scale arrays of CdS nanowires were produced. Figure 2(c) shows a typical TEM image of the CdS nanowires separated from the PAA template. It can be seen that the nanowires have uniform diameters of about 50 nm and the lengths of the nanowires are up to tens of micrometres. The inset in Fig. 2(c) shows the selected area electron diffraction (SAED) pattern taken from this area. No singlecrystal or cubic phase CdS nanowires were observed, implying that the CdS nanowires are polycrystal with hexagonal structure and no preferred growth directions. Similar results were found for the ZnO and MgB_2 nanowires by the two-step reaction approach.[14,15]

The room-temperature PL spectrum of our CdS nanowires is shown in Fig. 3. Using a 330-nm excitation light to pump the sample, a strong PL emission emerges around 435 nm. It should be pointed out that, in the present work, the PAA template has been totally removed by using NaOH solution due to its blue luminescence band.[16] Previously, the singlecrystal CdS nanowires formed by different synthesis approaches have shown different luminescence characteristics (750 nm[5] or 380 nm,[6] respectively), of which the PL mechanisms are still under discussion. Clearly, the PL characteristics of our CdS nanowires are different from not only the singlecrystal CdS nanowires,[5,6] but also the bulk CdS materials,[17,18] revealing that a new PL mechanism should be considered.

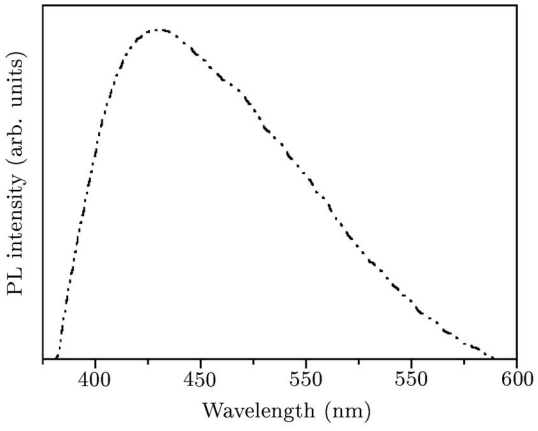


Fig. 3. PL emission spectrum of CdS nanowires. Excitation wavelength and filter are 330 nm and 390 nm, respectively.

It is well known that CdS is a wide-band-gap (E_g = 2.4–2.53 eV) semiconductor and typically has two emission bands: one is the green band around 2.4 eV, and the other is the red band at about 1.7 eV.[17,18] The former is attributed to gap or band-to-band emission and the latter is ascribed to trap or surface states.[17,18] Due to their 1D geometrical characteristics on a nanometre scale,[1–3] the CdS nanowires are expected to have different physical properties from their bulk materials; for example, a single luminescence band has been always observed in the case of the CdS nanowires.[5,6] However, compared to the data of CdS nanoparticles within the pore-free glass matrix[19] or mesoporous zeolite hosts,[20] the quantum-confined effects of our CdS nanowires would be slight due to their size (50 nm in diameter) being too large to produce a significant blue shift in the PL spectrum.[21] From the material science or physics perspective, the 'structure–property' relationship is very important and well documented. Therefore, we suggest that the polycrystal CdS nanowires would have more structural defects than the singlecrystal ones, such as grain boundaries, sulfur- and/or cadmium-related defects, which would exert an important influence on their luminescence properties. This assumption is reasonable if one considers the previous work on CdS nanoparticles loaded in zeolite-A hosts, in which a blue PL emission around 440 nm originated from the excess S atoms, a red emission around 660 nm produced by the S-vacancies, and a yellow-green emission band around 565–580 nm generated from the excess Cd atoms have been investigated in detail.[20]

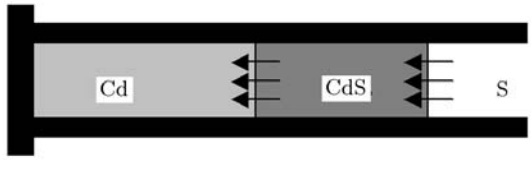


Fig. 4. Schematic diagram of the sulfurization process of CdS nanowires in a single nanochannel of PAA template.

Figure 4 shows a schematic diagram of a proposed sulfurization process in a single nanochannel of the PAA template, in which the S atoms reacted with Cd atoms to form CdS nanowire. From Fig. 4, it can be seen that the likely mechanism consists of S atoms diffusing through the formed CdS layer and reacting with Cd atoms to produce new CdS at the CdS/Cd interface. Thanks to the long-time sulfurization process (30 h), it is a reasonable assumption that the sulfurizing reaction would be complete, and no or extremely low concentrations of Cd atoms are present in the CdS nanowires. The absence of red and/or yellow-green emissions from trap or surface states[20] in this case also suggests that there were no superfluous Cd atoms in the CdS nanowires. However, it is likely that excess S atoms would be produced and would exist in the formed CdS nanowires after the sulfurization process. The localized defects and excess S atoms in the poly-

crystal CdS nanowires would therefore be responsible for the 435-nm PL emission band.

In summary, we have synthesized CdS nanowires by sulfurizing metal Cd nanowires deposited electrochemically in the nanochannels of a porous anodic alumina template. The obtained polycrystal CdS nanowires have an intensive blue emission around 435 nm, which originates from the localized defects, excess S atoms. The PL emission of the CdS nanowires in the visible region would suggest potential applications in the field of light-emitting devices.

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