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The selective synthesis of single-crystalline CdS nanobelts and nanowires by thermal evaporation at lower temperature

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Abstract

CdS nanobelts and nanowires were successfully synthesized by simple thermal evaporation of CdS powder at a temperature as low as 650 °C, using pure H₂ as a carrier gas. The morphology of the products could be conveniently controlled by adjusting the deposition parameters. Electron microscopy studies of the materials showed that the single-crystalline CdS nanowires have a diameter of 200 nm and a length of tens of micrometres, and the nanobelts are 100–200 nm in width, 30 nm in thickness and tens of micrometres in length. High-resolution transmission electron microscopy demonstrated that the nanobelts, which are different from the nanowires growing along the (0001) direction, have three types of growth direction: (2 $\bar{1}$ 10), (01 $\bar{1}$ 0) and (0001). It is demonstrated that a reductive carrier gas, such as hydrogen, plays an important role in the whole growth process of CdS nanowires and nanobelts.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One-dimensional nanostructured materials such as nanowires, nanotubes and nanobelts, have attracted much attention because of their novel physical properties and potential applications in nanoelectronic devices [1–4]. CdS, one of the most important II–VI group semiconductors (band-gap, $E_g = 2.4$ eV), is a vital optoelectronic material for laser light-emitting diodes and optical devices based on its nonlinear properties [5–8]. Many efforts have been made to synthesize one-dimensional CdS nanowires or nanobelts in the past few years. For example, Zhang and co-workers successfully fabricated CdS nanowires and nanobelts by the evaporation of CdS powders at 900 and 850 °C, respectively [9, 10]. Wu *et al* obtained hexagonal and cubic CdS nanowires by physical vapour deposition at 1000 °C, simultaneously [11]. Single crystalline CdS (hexagonal) nanobelts have been synthesized using thermal evaporation at temperatures ranging from 1000 to 1200 °C [12]. In addition, template-assisted electrochemical

deposition [13], laser-ablation [14], metal organic chemical vapour deposition [15] and solvothermal methods [16] have also been developed to synthesize CdS nanowires. Generally speaking, the thermal evaporation of CdS powder method is the most conventional for the preparation of CdS one-dimensional nanostructures because of its facile apparatus and low cost. However, this method [9–12, 17] requires an evaporation temperature higher than 850 °C. In addition, up to now, simultaneous selective growth of CdS nanowires and nanobelts is still a great challenge for scientists.

In this work, CdS nanowires and nanobelts were grown by a simple thermal evaporation of CdS powder at 650 °C. A reductive atmosphere of pure H₂ was used as a carrier gas to decrease the reaction temperature. Although it has been reported that the use of a reductive reagent in a reaction process can decrease the vapourization temperature in nanomaterial preparation [18–21], it has never been reported in a CdS system to the best of our knowledge. Furthermore, the effects of the temperature on the morphology of nanostructured CdS nanomaterials has been observed. The as-prepared structure of

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CdS nanowires and nanobelts were characterized and analysed using SEM and TEM techniques. The possible effects of the H₂ on the growth of CdS nanostructures were also discussed here.

2. Experimental method

The method for the synthesis of CdS nanowires and nanobelts is based on thermal evaporation of high-purity CdS powders (99.99%, SCR Company) under controlled conditions, with and without an Au catalyst, respectively. CdS powder was placed in the centre of an alumina boat, which was placed in the middle of a quartz tube that was inserted into a horizontal tube furnace [22]. Next to the boat filled with CdS powder, several boats were placed downstream of the gas flow. After the reaction chamber of the quartz tube was pumped to a vacuum of 1 Torr, the system where the pressure was maintained at 700 Torr was filled with pure H₂ gas with a constant flow of 30 standard cubic centimetres per minute (sccm) for the whole reaction process. Then the furnace began to heat at a rate of 10 °C min⁻¹ to 650 °C and was kept at this temperature for 2 h. After the furnace was cooled to room temperature, the H₂ gas flow was turned off. Yellow wool-like products (CdS nanobelts) were found on the inner wall of the alumina boat without the Au catalyst at a temperature zone of 350–450 °C and no products were found at the other positions. However, in the presence of the Au catalyst, yellow wool-like products (CdS nanowires) were observed on the bottom of the alumina boat at the temperature zone of about 550 °C. The temperature distribution along the length of the quartz tube was measured by a movable thermocouple. Here we used gold sols which contained a great deal of gold nanoparticles as a catalyst [23].

The as-synthesized products were characterized and analysed by x-ray diffraction (XRD) (Philips Panalytical X'Pert with Cu K α radiation), scanning electron microscopy (SEM) (Oxford Instrument, LEO-1530), transmission electron microscopy (TEM) (Hitachi, H-600 at 200 kV), high-resolution transmission electron microscopy (HRTEM) (Philips-FEI, TECNAL-F30), and energy-dispersive x-ray spectroscopy (EDX) attached to the HRTEM instrument. For HRTEM observations, the products were ultrasonically dispersed in ethanol and then placed on a Cu grid coated with carbon film.

3. Results and discussion

Firstly, we checked the evaporation system without a gold catalyst (i.e. when the Au catalyst was not used in the evaporation process of CdS powder at 650 °C), the inner wall of the alumina boat at temperature areas of 350–450 °C was bright yellow, which is the same colour as the CdS powder. In temperature regions lower than 350 °C or higher than 450 °C, no obvious yellow coloured products (nanobelts) were observed. However, in the boat loaded with Au catalyst, under the same experimental conditions, yellow products (nanowires) were observed in the temperature area of about 550 °C. These initial results imply that both the temperature and the catalyst play an important role in the formation of CdS nanostructures of different morphologies, and that CdS nanowires and nanobelts can be fabricated simultaneously at different temperature areas.

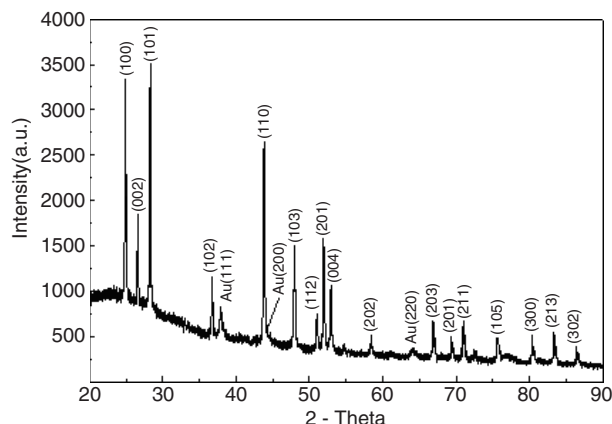


Figure 1. XRD pattern of the CdS nanowires.

The XRD pattern of the products shown in figure 1 reveals the crystal structure of the CdS nanowires. The diffraction peaks can be perfectly indexed to the hexagonal wurtzite-structured CdS (JCPDS 41-1049; lattice constants $a = 0.4136$ nm, $c = 0.6713$ nm). Also, some weak Au diffraction peaks were detected, which resulted from the minor Au catalyst particles. In addition, no diffraction peaks from CdO, Cd or other impurities were found in the products. Similarly, the diffraction patterns of the as-synthesized CdS nanobelts also belong to the hexagonal wurtzite-structure except that there are no Au peaks observed in the XRD pattern of the CdS nanobelts.

A representative SEM image shown in figure 2(a) reveals that the products deposited on the boat loading Au nanoparticles consist of large quantities of wire-like nanostructures with a length of several tens of micrometres. Figure 2(b) shows a typical TEM image of an individual CdS nanowire revealing that the products obtained have a diameter of about 200 nm. It was also found that the growth of CdS nanowires is initiated by the Au nanoparticle, which demonstrates that the growth process of CdS nanowires follows a vapour–liquid–solid (VLS) mechanism.

Figure 3(a) shows a representative SEM image of the as-grown CdS nanobelts with a typical length of several tens of micrometres deposited on the boat in the absence of Au catalyst. It can be seen from a high-magnification SEM image (figure 3(b)) of several individual CdS nanobelts that their geometrical shape is belt-like and these nanobelts are about 100 nm wide and 20–30 nm thick. A ripple-like contrast also appeared in the TEM image (figure 3(c)) of an individual CdS nanobelt which is distinct from the nanowires and consistent with some other nanobelts reported in the literature [24–26]. The chemical composition of the products was further confirmed by EDX characterization, as shown figure 3(d). The EDX spectrum of the nanobelts or nanowires indicates the presence of Cd and S, and the ratio of Cd and S determined from the spectrum is 50.2:49.8, which is consistent with the stoichiometry of CdS within the range of experimental error. In addition, no particle was observed at the ends of the nanobelts, which implies that the growth process of CdS nanobelts follows a vapour–solid (VS) mechanism.

Figures 4(a) and (b) show the typical HRTEM images of CdS nanowires which indicate that the nanowires grow along

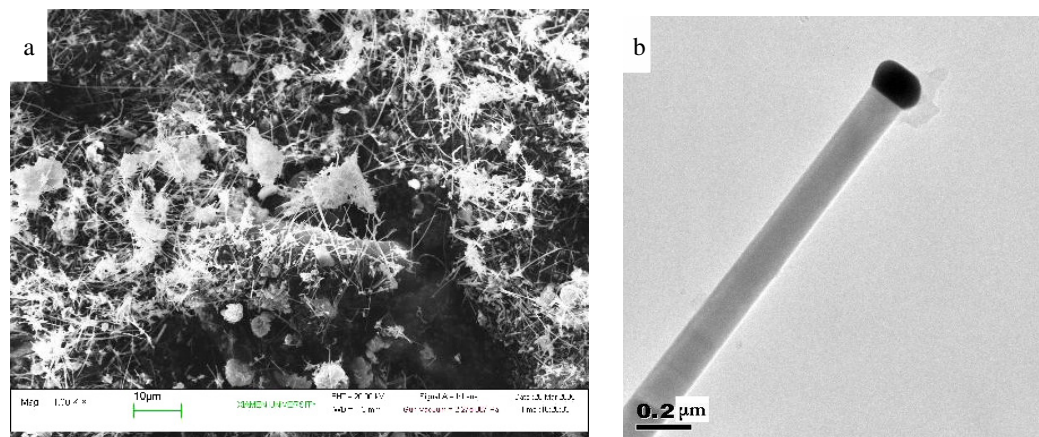


Figure 2. (a) SEM image of the bulk CdS nanowires; (b) TEM image of an individual CdS nanowire with an Au nanoparticle located at its tip.

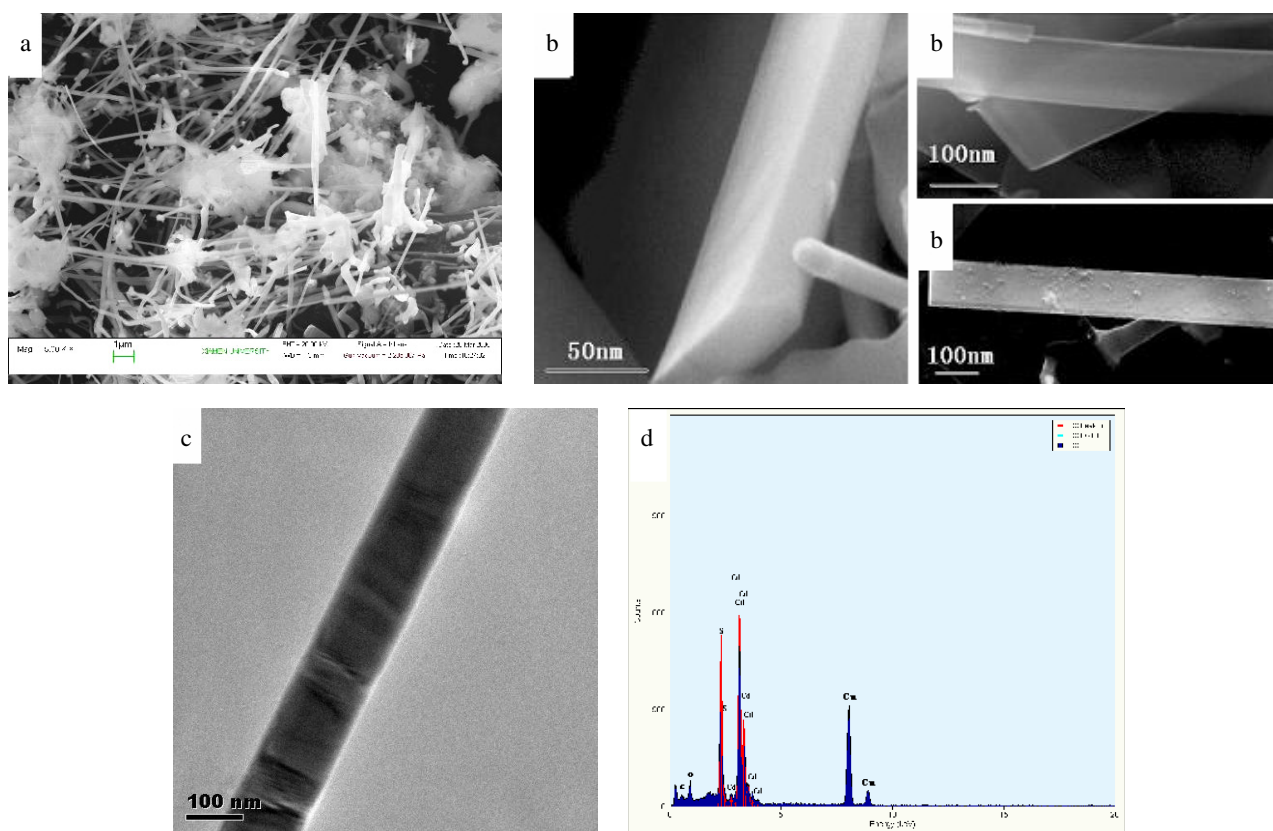


Figure 3. (a) Typical SEM of the bulk CdS nanobelts; (b) SEM images of several individual CdS nanobelts revealing the rectangular-like cross-section of them; (c) TEM image of an individual CdS nanobelt; (d) EDX spectrum taken from an individual CdS nanobelt.

the $[0001]$ direction ($d_{0002} = 0.34$ nm) and are enclosed by the $\{01\bar{1}0\}$ or $\{2\bar{1}\bar{1}0\}$ side plane (see figure 4(c)). Macroscopically, a crystal will commonly develop into a three-dimensional object with well-defined, low index crystallographic faces. During crystal growth, they tend to maximize the area of the $\{01\bar{1}0\}$ and $\{2\bar{1}\bar{1}0\}$ facets because of the lower energy trend in the crystal growth.

Figures 5(a)–(c) show the typical HRTEM images of CdS nanobelts with three types of growth direction, which is

distinct from the growth of CdS nanowires. The three types of growth direction are $\langle 2\bar{1}\bar{1}0 \rangle$ ($\pm[2\bar{1}\bar{1}0]$, $\pm[1\bar{2}\bar{1}0]$, $\pm[1\bar{1}20]$) $d = 0.207$ nm, $\langle 01\bar{1}0 \rangle$ ($\pm[01\bar{1}0]$, $\pm[10\bar{1}0]$, $\pm[1\bar{1}00]$) $d = 0.358$ nm and $\langle 0001 \rangle$ ($\pm[0001]$) $d = 0.674$ nm, respectively. These images reveal that there are no defects and no dislocations in the nanobelts and the surfaces of the nanobelts are clean, atomically sharp and without obvious sheathed amorphous phase. Figures 5(d)–(f) show the fast fourier transform (FFT) results corresponding to figures 5(a)–(c),

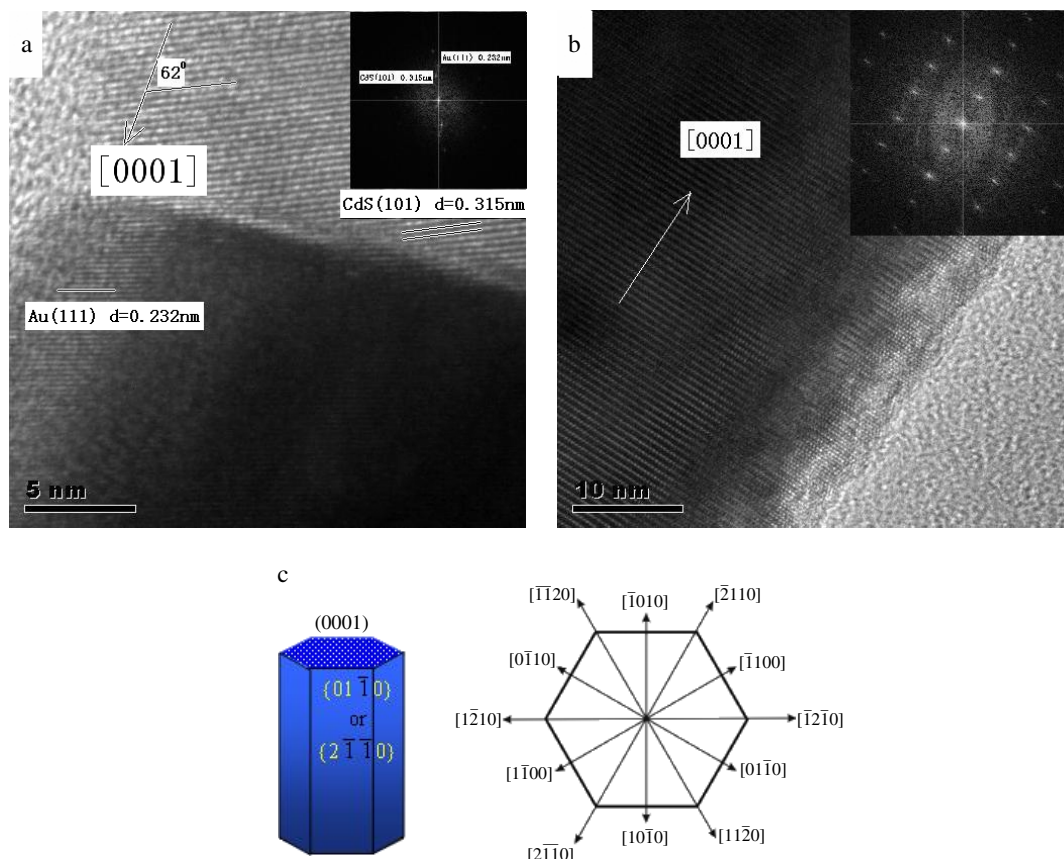


Figure 4. (a) HRTEM image of the CdS nanowires with an alloy droplet; (b) HRTEM image of CdS nanowires growing along the [0001] direction (inset images are the corresponding FFT patterns); (c) typical growth morphology of CdS nanowires and corresponding facets (left) and cross-sectional view of CdS nanowires (right).

Table 1. The growth directions of CdS nanobelts and their surface planes.

Structural type	I	II	III	IV	VI	VII
Growth direction	[0001]		[01 $\bar{1}$ 0]		[2 $\bar{1}$ $\bar{1}$ 0]	
Top surface	$\pm(01\bar{1}0)$	$\pm(2\bar{1}\bar{1}0)$	$\pm(2\bar{1}\bar{1}0)$	$\pm(0001)$	$\pm(0001)$	$\pm(01\bar{1}0)$
Side surface	$\pm(2\bar{1}\bar{1}0)$	$\pm(01\bar{1}0)$	$\pm(0001)$	$\pm(2\bar{1}\bar{1}0)$	$\pm(01\bar{1}0)$	$\pm(0001)$

respectively. In addition, we also observe more nanobelts growing along the $\langle 0001 \rangle$ direction than other types of nanobelts in our sample, which is in agreement with the lowest surface energy theory of crystal growth. Analysis of the selected-area electron diffraction (SAED) pattern (figure 5(g)) taken along the $[2\bar{1}\bar{1}0]$ zone axis indicates that the as-grown CdS nanobelts have single-crystal characteristics. Strictly speaking, the nanobelts are not one-dimensional nanostructures. Thus CdS nanobelts have six types of growth structure, which can all be observed in our sample. Table 1 shows the growth directions of six types of nanobelt and their top surface and side surface planes.

Although the growth of CdS nanowires in our system still follows the conventional VLS mechanism, formation of compound semiconductor nanowires through the VLS mechanism can be complicated by the presence of nonmetal as most compound semiconductors have a relatively higher melting points (e.g., CdS, melting point: 1750 °C). Moreover, unlike the single component nanowires, the VLS process

of compound semiconductor nanowires is not yet well understood. In the growth process of CdS nanowires, authors believe that the process involves reduction of CdS powder by hydrogen to form Cd and H₂S at a higher temperature. The Cd vapour is transported to, and reacts with, Au catalyst located downstream at a lower temperature to form alloy droplets. As the droplets become supersaturated, crystalline CdS nanowires are formed, possibly by the reaction between Cd and H₂S at a low temperature. The presence of H₂S is not expected to significantly change the Cd–Au phase diagram, at the same time it acts as the sulfur source during the CdS nanowire growth. That is to say, H₂ plays a role of ‘catalyst’ in the formation of nanowires, it has been reported that carbothermal/hydrogen reduction can help oxide powder to form nanowires [18–21].

On the other hand, as for the thermal evaporation method, there are several processing parameters that can be selected properly and controlled precisely. The type of carrier gas is one such parameter which could greatly affect the nucleation and

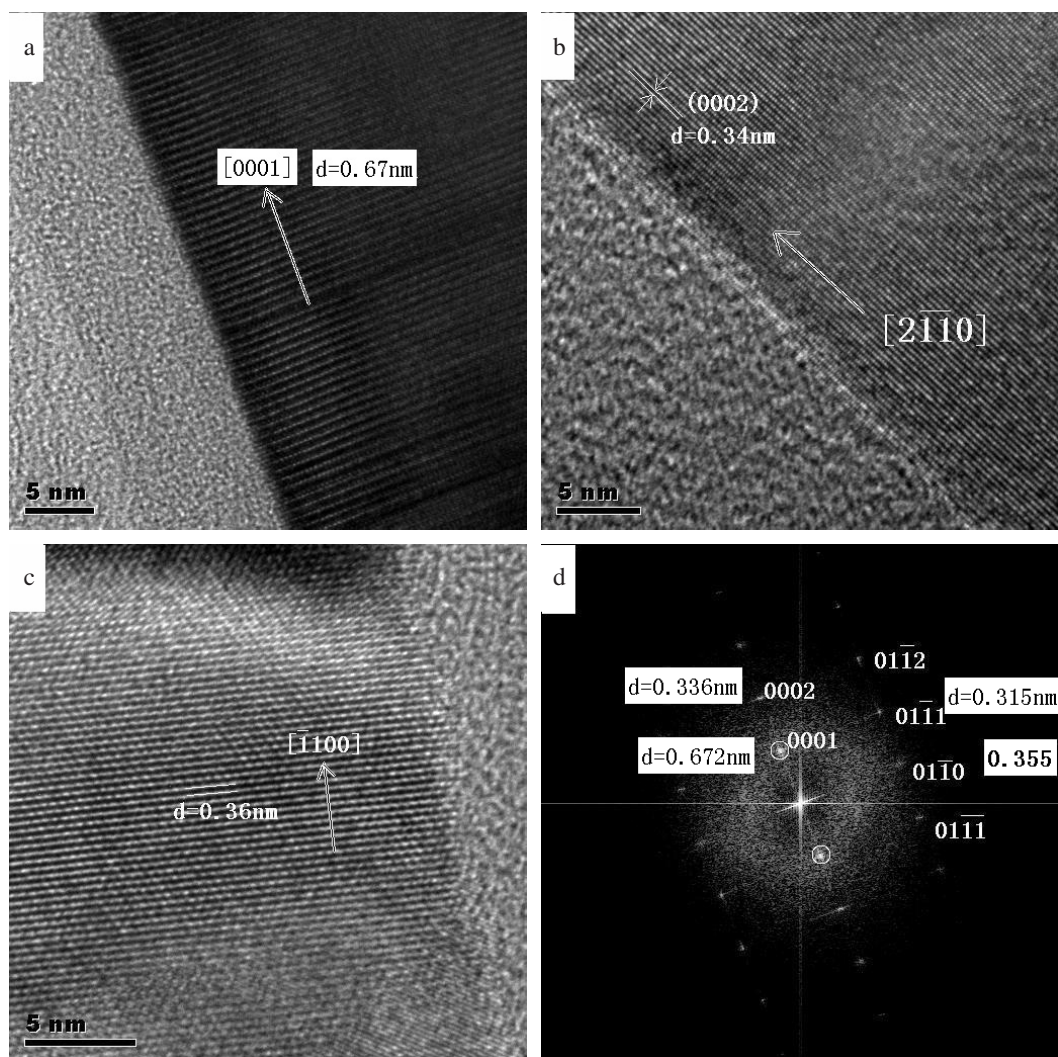


Figure 5. (a), (b), and (c) HRTEM images of the CdS nanobelt reveal three types of growth directions of the CdS nanobelts: $\langle 0001 \rangle$, $\langle 2\bar{1}10 \rangle$, and $\langle 01\bar{1}0 \rangle$; (d), (e), and (f) Fourier transform patterns are corresponding to the images of (a), (b), and (c), respectively; (g) SAED pattern of the CdS nanobelts taken along the $[2\bar{1}10]$ zone axis.

growth kinetics of CdS nanobelts, although the VS mechanism seems to be more complex than the VLS mechanism. In addition, we speculate that the carrier gas could also affect the sublimation process of the materials. For example, hydrogen, as a reductive gas, could decrease the sublimational point of CdS (CdS sublimational temperature: 900°C in N_2 , Therefore, the evaporation temperature of CdS is often higher than 850°C). Actually, the fact that a reductive atmosphere can decrease the temperature of chemical vapour deposition compared with the inert atmosphere, has been known for many years [27]. In our experiments, the use of H_2 facilitates not only sublimation of CdS powder but also growth of CdS nanobelts. When we did not use H_2 gas but inert gas (Ar gas) as a carrier gas, no CdS nanowires/nanobelts were obtained at 650°C , which also indicates the importance of H_2 gas. However, it should be noted that, in addition to carrier gas, both deposition temperature and Au catalyst also have great effects on the formation of nanostructures. These systematic investigations have been conducted in our laboratory, and are

expected to explain the difference in the growth of nanowires and nanobelts.

4. Summary

In conclusion, single-crystalline CdS nanowires and nanobelts are fabricated simultaneously by a simple thermal evaporation at a lower temperature— 650°C . Accordingly, CdS nanowires were grown via the catalyst-assisted VLS process in the temperature zone of about 550°C , and CdS nanobelts were grown via the VS process without any catalyst in the temperature zone of $450\text{--}350^\circ\text{C}$. HRTEM characterization revealed that the CdS nanobelts have three types of growth direction: $\langle 2\bar{1}10 \rangle$, $\langle 01\bar{1}0 \rangle$ and $\langle 0001 \rangle$, which is different from CdS nanowires growing along the $[0001]$ direction. The pure H_2 gas, as a carrier gas, plays an important role in the whole growth process, which might not only facilitate the nucleation and growth of CdS nanowires and nanobelts but also make the sublimation of CdS powder easier. This simple, energy saving

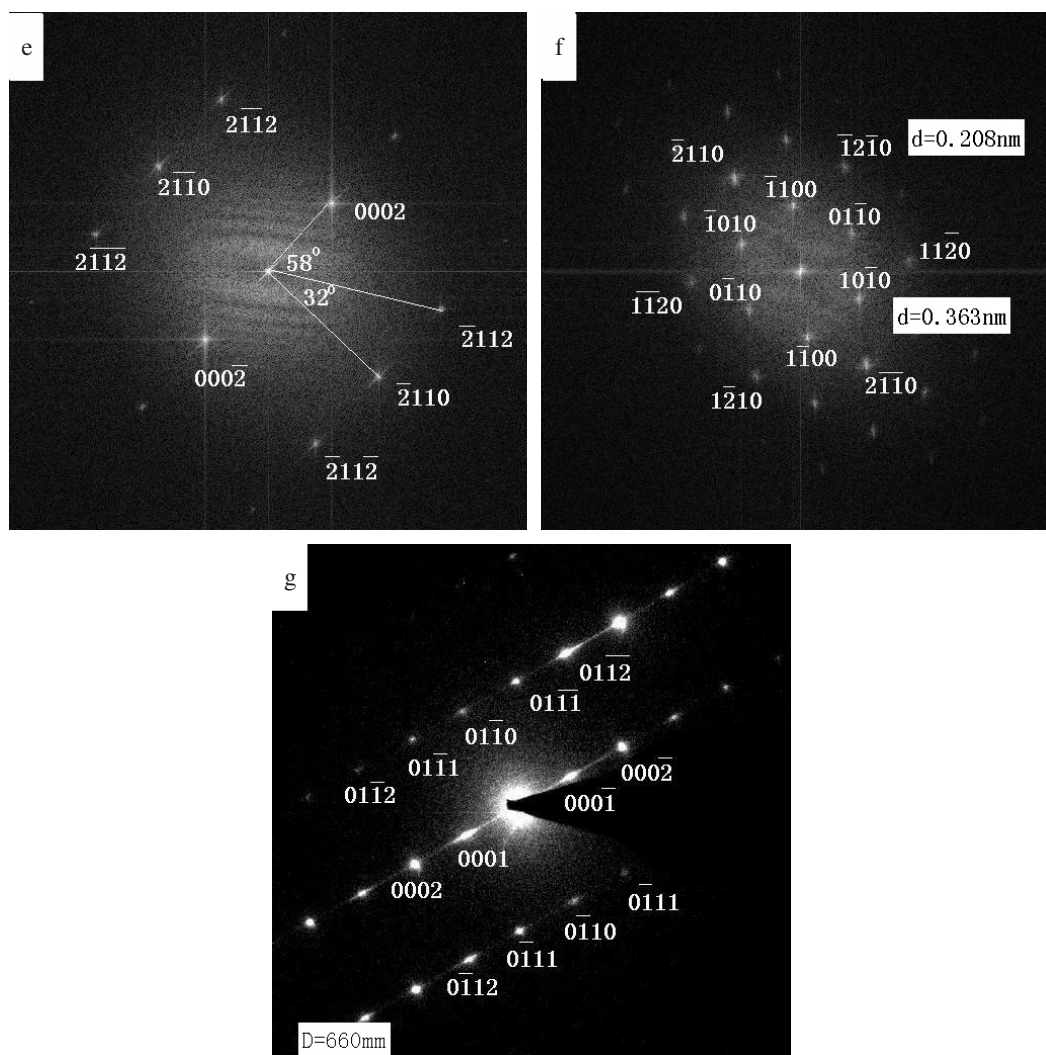


Figure 5. (Continued.)

and low cost method is able to synthesize high quality CdS nanostructures with high yield and, therefore, can open many opportunities for the use of these structures as optoelectronic devices.

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