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# Solvothermal synthesis of CdS nanowires templated by polyethylene glycol

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## Abstract

CdS nanowires were solvothermally synthesized from $Cd(NO_3)_2$ and S powder using ethylenediamine as a solvent and polyethylene glycol (PEG) as a template. Hexagonal CdS with $P6_3mc$ space group was detected using XRD and SAED, results which are in good accordance with those obtained by the simulation. SEM, TEM and HRTEM revealed the gradual development of nanowires in the [0 0 1] direction with a number of atoms aligning in a crystal lattice. Raman spectra of different products showed the fundamental and overtone modes at the same wavenumbers of 300 and 601 $cm^{-1}$, respectively. Their relative intensities at different molecular weight PEG were influenced by the anisotropic geometry of the products. Their photoluminescence peaks were detected at the same wavelengths of 518 nm. A formation mechanism for CdS nanowires was also proposed to relate to the experimental results.

*Keywords:* CdS nanowires; Solvothermal synthesis; Ethylenediamine; Polyethylene glycol

## 1. Introduction

Presently, the synthesis of luminescent materials with different morphologies is of increasing interest due to their importance in technological applications. CdS is one such material with a 2.42 eV band gap at room temperature [1,2]. It has applications for optoelectronic devices, light emitting diodes, and solar cells [1,2]. CdS has been successfully synthesized into micro- and nano-crystals with different morphologies, such as nanoribbons [3], nanobelts [4], nanoflowers [5], nanospheres [6], nanorods [6–8], hexagons [9], nanoparticles [10,11] and dendrites [12]. To our best knowledge, solvothermal synthesis is one of the most efficient methods used to synthesize CdS with different morphologies. It is simple, convenient and inexpensive. Ethylenediamine functions as a solvent and ligand [7], but the synthesized nanowires are of irregular morphology and low aspect ratio [7,13,14]. Some polymers such as PAA, PAN, PVP and PVA have been used to modify the surface chemistry of the crystals and the concentration of soluble species for crystal growing. This has resulted in an improvement in the length and diameter uniformity of CdS nanowires [13,14]. The purpose of the present research was to solvothermally synthesize CdS nanowires in ethylenediamine containing different molecular weights and amounts of polyethylene glycol (PEG).

## 2. Experiment

Each 0.005 mol of $Cd(NO_3)_2$ and S powder was dissolved in $NH_2CH_2CH_2NH_2$ (ethylenediamine, abbreviated to en), a bidentate ligand. Different molecular weights and amounts of polyethylene glycol were added. The mixtures were stirred and put in home-made stainless steel autoclaves. Reactions proceeded at 200 °C for 72 h. The precipitates were washed with de-ionized water and ethanol, and dried at 80 °C for 24 h. They then were characterized using: X-ray diffraction (XRD) operating at 20 kV, 15 mA, and using the K$\alpha$ line from a Cu target; transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM), as well as selected area electron diffraction (SAED) operating at 200 kV; scanning electron microscopy (SEM) operating at 15 kV; a Raman spectrometer using a 50 mW Ar laser with 514.5 nm wavelength; and a luminescence spectrometer using a 210 nm excitation wavelength ($\lambda_{ex}$). The interpreted patterns were also compared with those simulated using CaRIne Crystallography 3.1 software [15].

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## 3. Results and discussion

### 3.1. XRD

XRD spectra (Fig. 1) correspond to hexagonal CdS with $P6_3mc$ space group (JCPDS reference # 41-1049) [16] although the products were synthesized using different solutions. In PEG-free solution, the (0 0 2) intensity was the most dominant relative to those of the (1 0 0) and (1 0 1) peaks, showing that atomic ordering nucleated along the *c*-axis. The (0 0 2) peak became less dominant when PEG was added, especially for PEG with a molecular weight of 20,000. At heavier molecular weight PEG, the (1 0 0) and (1 0 1) peaks increased at a greater rate than the (0 0 2) peak. XRD spectra became sharper and narrower with an increase in molecular weight PEG. Two peaks diffracting from the (1 0 2) and (1 0 3) planes at $2\theta = 36.62^\circ$ and $47.84^\circ$ are characteristics of the hexagonal phase [17]. Calculated lattice parameters [18] ($a = b = 0.4138$ nm, $c = 0.6721$ nm) are in accordance with those of the JCPDS software [16]. The present research detected no oxygen contamination in the products, as confirmed by XRD analysis.

### 3.2. SEM

SEM images of the products that were synthesized in different solutions are shown in Fig. 2. In PEG-free solution (Fig. 2a), the product was composed of nanoparticles in clusters. When 0.50 g PEG with a molecular weight of 6000 was added (Fig. 2b), nanowires mixed with nanoparticles in cluster were detected. The wires were rather short. In a solution containing 0.10 g PEG with the molecular weight of 10,000 (Fig. 2c), the nanowires became longer, but their surfaces were uneven. When more PEG with the same molecular weight was added (Fig. 2d, e), the nanowires were much longer and the surfaces were smoother. At these stages, nanoparticles no longer existed in the products. The nanowires were the longest (several microns) and their surfaces became the smoothest at 0.50 g PEG with molecular weight of 20,000 (Fig. 2f). Compared to previous products synthesized using a solvothermal method, the present nanowires were longer than those synthesized in: en solvent with [14] and without [19,20] adding PVA; those of Mn-doped CdS nanowires in de-ionized water containing PEG400 [1]; those of CdS nanowires synthesized in en with PEG400 as a surfactant [21]; and those of CdS nanowires/PVA composite films [13]. However, for a large scale hydrothermal synthesis using PEG as a capping agent, the products were composed of hierarchical dendrites [12]. The present research found that both the amount and molecular weight of PEG had an influence on the formation of CdS nanowires. When PEG was added, it adsorbed onto the surfaces of nanoparticles. Hence, their lateral growths were inhibited, while growths in the axial lengths were accelerated.

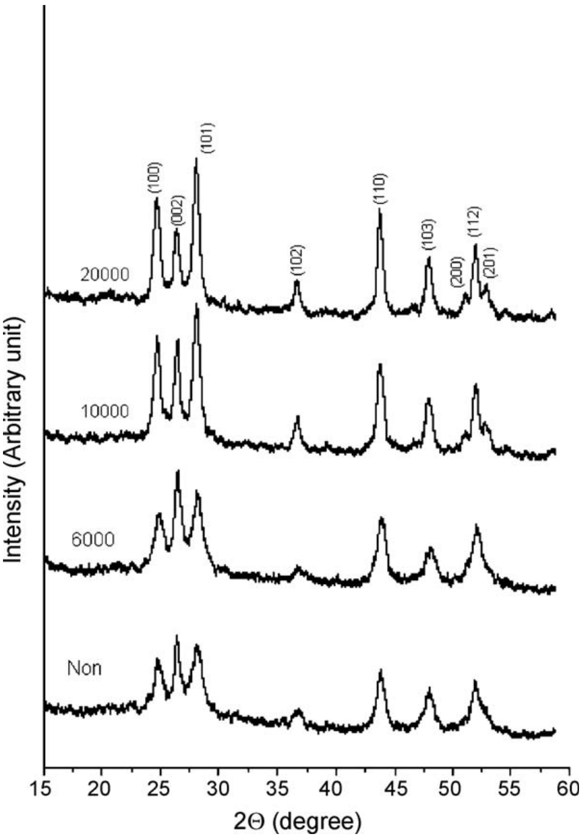

Fig. 1. XRD spectra of the products synthesized in PEG-free solution and the solutions containing 0.50 g PEG with different molecular weights.

### 3.3. TEM and HRTEM

TEM and HRTEM images (Fig. 3) show the morphologies of products synthesized in different solutions. In PEG-free solution (result not shown), the product was composed of very short nanowires. When different amounts and molecular weights of PEG were added, nanowires (Fig. 3a–c, f) with different length were detected. High magnification images (Fig. 3d, f, h) showed that the nanowires were composed of a number of atoms in lattice arrays. Growth of the nanowires was in the [0 0 1] direction, although they were synthesized in different solutions. Some defects, caused by mismatching of lattice planes, were also detected. HRTEM images (Fig. 3e, i) at the respective circles of Fig. 3d and h show a number of well-resolved (0 0 2) crystallographic planes composing the nanowires. The [0 0 1] direction is normal to the (0 0 2) plane. The defects (Fig. 3i), caused by the mismatch of (0 0 2) planes composing the nanowire, were clearly detected. Another HRTEM image (Fig. 3g) at the ellipse of Fig. 3f shows a number of (1 0 0) lattice planes in systematic array. The (1 0 0) planes are parallel to the [0 0 1] direction. The spaces (*d*) of (0 0 2) and (1 0 0) planes correspond very well with those of the JCPDS software [16]. The detection of these planes was also in accordance with the gradual development of the (0 0 2) and (1 0 0) peaks, characterized by XRD.

### 3.4. SAED and simulation

SAED patterns (Fig. 4a, c) of the products appear as periodic arrays of bright spots which were caused by electron diffraction through the crystallographic planes of single crystals. The

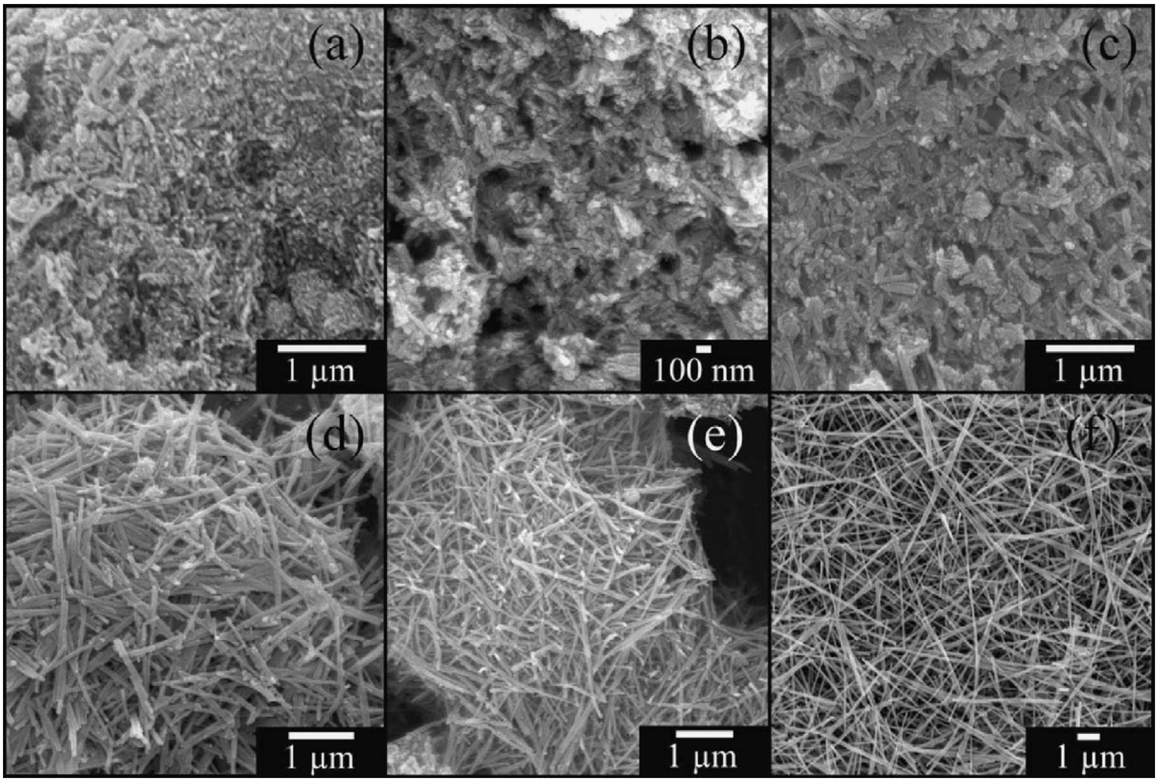

Fig. 2. SEM images of CdS synthesized in (a) PEG-free solution, (b) the solution containing 0.50 g PEG with the molecular weight of 6000, (c–e) the solutions containing 0.10, 0.25 and 0.50 g PEG with the molecular weight of 10,000, and (f) the solution containing 0.50 g PEG with the molecular weight of 20,000, respectively.

patterns were then interpreted [22]. The calculated angles between any pair of directions belonging to these planes, and interplanar spaces determined from (*h k l*), are in accordance with those of the diffraction patterns on the films. The patterns correspond to (0 0 2), (1 1 0) and (1 1 2) planes of hexagonal CdS with $P6_3mc$ space group (JCPDS reference # 41-1049) [16]. Calculated electron beams [22] are in the same directions of $[\bar{2}\,2\,0]$. They are the directions in which electron beams were sent to the crystal facets. Diffraction patterns with $[\bar{2}\,2\,0]$ zone axis were simulated (Fig. 4b, d) [15]. The simulated spots with the specified crystallographic planes are in systematic and symmetric arrays. The present analysis shows that interpreted and simulated patterns are in good accordance.

### 3.5. Raman analysis

Raman spectra (Fig. 5) show two main peaks corresponding to the first and second longitudinal optical (LO) phonon modes, which were polarized in the *x*–*z* face with strong coupling to excitons along the *c*-axis [23]. The 1LO and 2LO, corresponding to the fundamental and overtone modes [23,24], were detected at 300 and 601 $\text{cm}^{-1}$, respectively. This is in accordance with other results [25]. Each of the modes was at the same wavenumber although the products were synthesized in different solutions. The vibration frequencies were influenced by such parameters as the atomic weights of Cd and S, and the vibration constant of bonding between Cd and S atoms in a crystal lattice. Intensity ratios of 2LO/1LO in PEG-free solution and in the solutions containing PEG with molecular weights of 6000, 10,000 and 20,000 were 0.29, 0.47, 0.51 and 1.33, respectively. The ratios increased by adding PEG, and by increasing the molecular weight of PEG. Their relative intensities were strongly influenced by the anisotropic geometry of the crystals. The 1LO peaks became weaker and the 2LO peaks stronger in intensity. Differences in intensities of the 1LO and 2LO modes were caused by the difference in product morphologies, which influence the strength of the electron–phonon interaction [17].

### 3.6. Proposed mechanism

A solvothermal reaction is defined as any chemical reaction in a non-aqueous solvent or a solvent at supercritical or near supercritical conditions above room temperature and atmospheric pressure in a tightly closed system. Different products such as bulk single crystals, fine particles and nanoparticles can be synthesized using the process. It consists of a single-step with low-energy-consumption, and can be developed to be multi-energy processing: microwave-hydrothermal, mechanochemical–hydrothermal, or electrochemical–hydrothermal [26].

Ethylenediamine is a good solvent which has a low dielectric constant or relative permittivity (12.9 at 20 °C) [27]. Hence, CdS with an elongated structure is easily synthesized, a result of high monomer concentration [19]. By comparison, in water (dielectric constant at 20 °C = 80.1) [28], spherical nanoparticles are synthesized [19]. In ethylenediamine, S powder was slowly reduced to $S^{2-}$ ions [19]. The preferential growth of CdS continuously proceeded when its concentration was sufficiently high [19]. Growth of CdS nanocrystallites in ethylenediamine

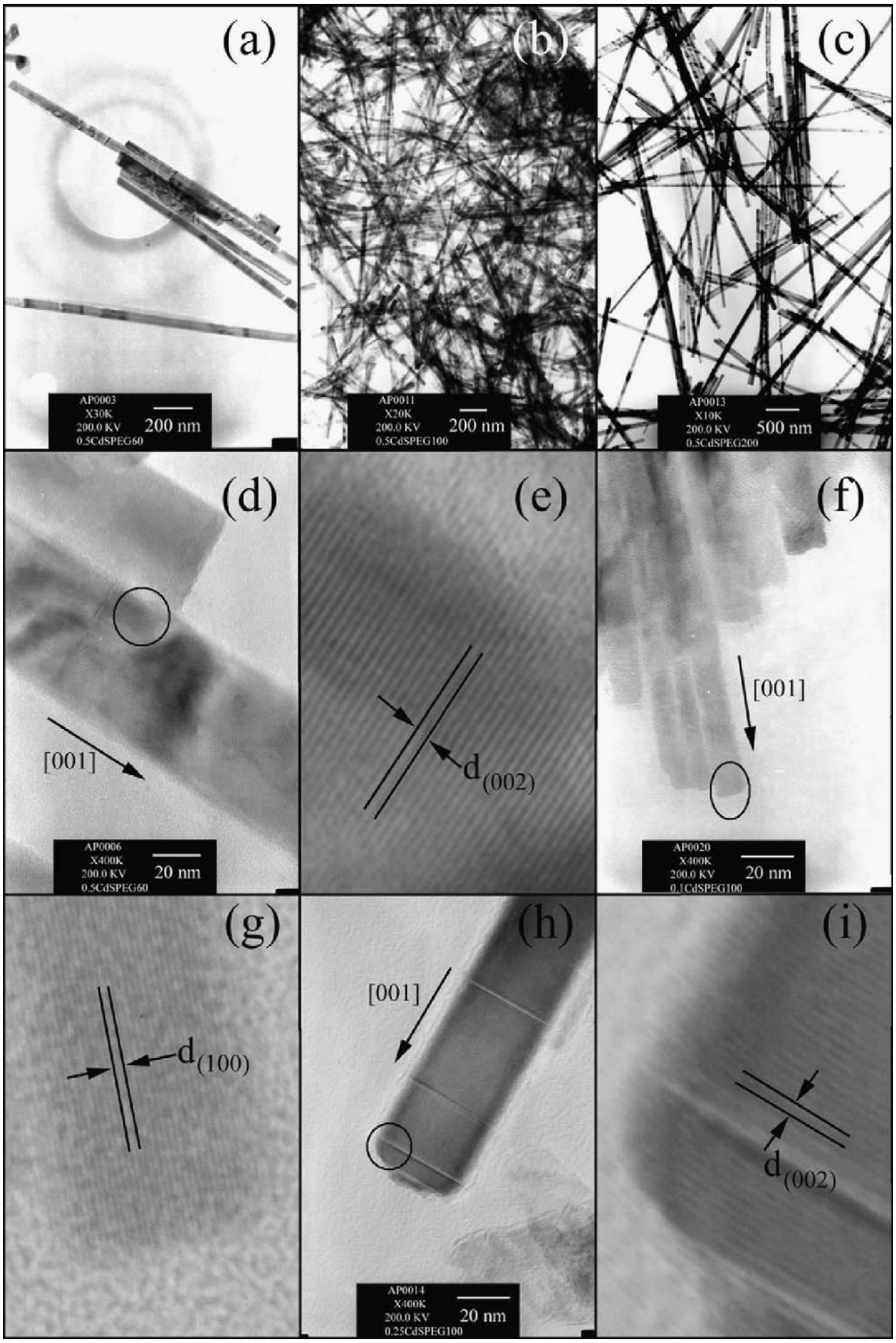

Fig. 3. TEM and HRTEM images of CdS synthesized in the solutions of (a–c) 0.50 g PEG with the molecular weights of 6000, 10,000 and 20,000, (d, e) 0.50 g PEG with the molecular weight of 6000, (f, g) 0.10 g and (h, i) 0.25 g PEG with the molecular weight of 10,000, respectively.

favored the [0 0 1] direction [19]. To form CdS nanowires with a high aspect ratio, PEG was used in ethylenediamine to model the growth of CdS nanostructures with well-defined morphologies. $Cd^{2+}$ ions reacted with ethylenediamine (en), a strongly bidentate ligand, to form $[Cd(en)_2]^{2+}$ complex ions [3,7,19,20]:

$$Cd^{2+} + 2en \rightarrow Cd(en)_2{}^{2+}$$

At the same time, S powder was reduced by ethylenediamine to form $S^{2-}$ ions [19,20]:

$$S_n + 2NH_2CH_2CH_2NH_2 \rightarrow [NH_2CH_2CH_2NH\text{-}S_{n-1}\text{-}NHCH_2CH_2NH_2] + H_2S$$

$$H_2S \rightarrow 2H^+ + S^{2-}$$

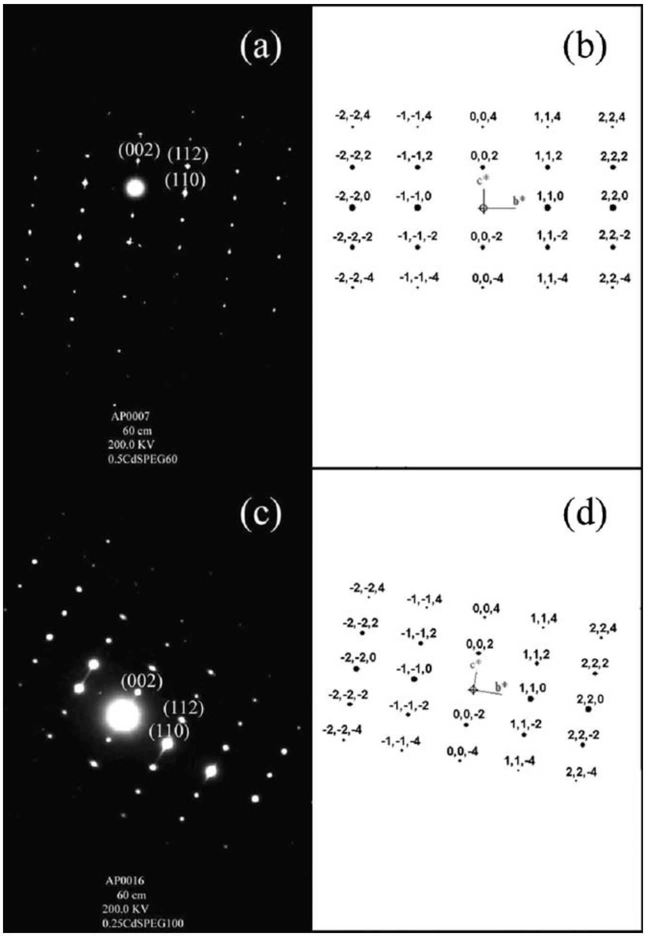

Fig. 4. SAED and simulated patterns of CdS synthesized in the solutions containing (a, b) 0.50 g PEG with the molecular weight of 6000, and (c, d) 0.25 g PEG with the molecular weight of 10,000.

$[Cd(en)_2]^{2+}$ further reacted with $S^{2-}$ ions in a home-made stainless steel autoclave at 200 °C for 72 h. To show that en was the reducing agent which supplied electrons to S powder, en with and without adding S powder was characterized using an ultraviolet–visible (UV–vis) spectrophotometer by Gaorong et al. [19]. A characteristic peak of pure en was detected at 244 nm. When S powder was added to en, a sharp peak of S-en solution was detected at 618 nm; the intensity of the peak also increased with an increase in S concentration. The sharp peak could be ascribed to the production of $S^{2-}$ ions in en by the charge-transfer process [29].

CdS was synthesized by releasing the volatile ethylenediamine molecules from the complex ions [14,19,20]:

$$Cd(en)_2{}^{2+} + S^{2-} \rightarrow CdS + 2(en)$$

Once CdS nuclei formed, they were not fully developed (nascent). Initially, PEG adsorbed onto the side walls of the nuclei, which caused a termination of lateral growth. At this stage, PEG has a stronger interaction with the side walls of the nanowires than with their ends. Growth of the side walls was inhibited by heavy capping of PEG. The tips remained active and the growth proceeded in the axial direction. As shown by TEM and HRTEM, growth in the *x*- and *y*-directions was limited. The nuclei grew in the [0 0 1] direction via the diffusion process. Hence, CdS nanowires with large aspect ratios were synthesized. They grew in the same direction as found by other researchers [7,13,14,19]. Some wires were in straight lines but some were bent, depending on the internal stress developed. In each condition, nanowires of different lengths were synthesized. This indicated that they nucleated at different times. Their growth rates were probably different as well. The present research shows that PEG played an important role in the one-dimensional growth of CdS nanowires. Both the molecular weight and the amount of PEG had a strong influence on the axial growth of the nanowires.

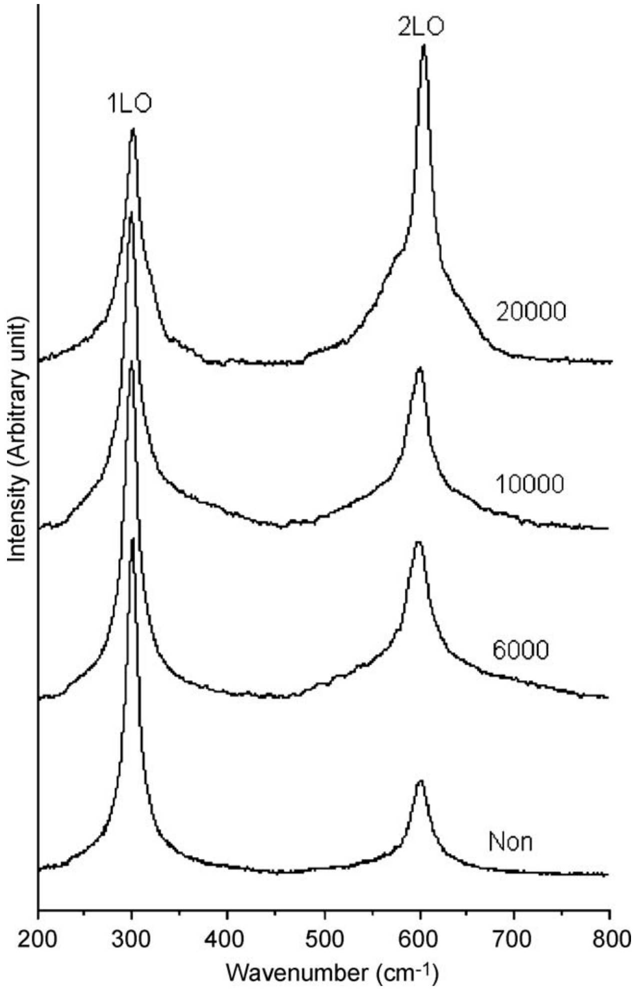

Fig. 5. Raman spectra of CdS synthesized in PEG-free solution and the solutions containing 0.50 g PEG with different molecular weights.

### 3.7. Photoluminescence

The photoluminescent (PL) property is influenced by some parameters, such as structure, composition and morphology [6]. PL spectra (Fig. 6) of the products were characterized using 210 nm excitation wavelength ($\lambda_{ex}$). Distinct PL emissions were detected at 518 nm, which are very close to the findings in a previous report [13]. Some energy was lost during the characterization, and the emission of longer

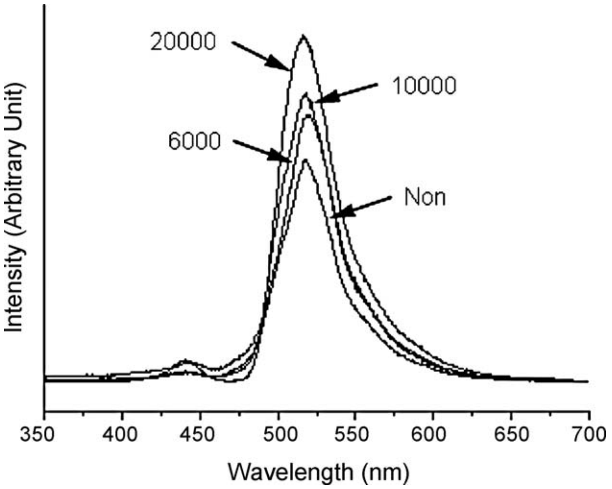

Fig. 6. PL spectra of CdS synthesized in PEG-free solution and the solutions containing 0.50 g PEG with different molecular weights.

wavelengths than $\lambda_{ex}$ was detected. In PEG-free solution, the PL spectrum was emitted from the nanoparticles without templating. In the solutions of 0.50 g PEG, stronger intensities were emitted from a number of nanowires templated by PEG. The intensities increased with the increase in the molecular weight of PEG. The emission intensity was strongest for the longest nanowires, which were synthesized in the solution containing 0.50 g PEG with a molecular weight of 20,000. The present results thus show that PEG with different molecular weights has an influence on the PL emissions of the products.

## 4. Conclusion

CdS nanowires were successfully synthesized by 200 °C solvothermal reactions in ethylenediamine containing different amounts and molecular weights of PEG. The hcp phase of the products was detected using XRD and SAED. The interpreted SAED patterns were in accordance with those obtained by the simulation. SEM, TEM and HRTEM revealed the presence of nanowires composed of atoms in a lattice array. A mechanism was proposed in accordance with the analytical results. Two main peaks of Raman spectra were detected at 300 and 601 $\mathrm{cm}^{-1}$, which were, respectively, specified as the fundamental and overtone modes. The distinct PL emission peaks were at 518 nm, although the products were synthesized under different conditions.

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