PREPARATION AND OPTICAL PROPETRTIES OF	CHẾ TẠO VÀ NGHIÊN CỨU CÁC TÍNH CHẤT

CdSe/CdS CORE/SHELL NANOSTRUCTURES

ABSTRACT

The CdSe/CdS core/shell nanostructures were prepared by chemical method. The absorption, photoluminescence and Raman spectra of CdSe cores, CdSe/CdS core/shell nanostructures have been comparatively studied. The CdSe nanocrystals with the narrow size distribution were obtained. The photoluminescence full width at half maximum is less than 20 nm. The effects of the reaction temperature and shell thickness on the optical characteristics of CdSe/CdS core/shell nanostructures have been investigated. The highest luminescence efficiency of CdSe/CdS core/shell nanostructures was obtained for the CdS shell thickness of 2 monolayers.

INTRODUCTION

Colloidal semiconductor nanocrystals are of great interest for both fundamental studies and technical applications such as light-emitting devices, lasers, and fluorescent labels [1]. Besides the development of synthesis techniques to prepare samples with narrow size distributions, surface effects are also known to influence the optical properties of these

QUANG CỦA CẤU TRÚC NANO LÕI/VỎ CdSe/CdS

TÓM TẮT checked

Chúng tôi tiến hành chế tạo các cấu trúc nano lõi/vỏ CdSe/CdS bằng phương pháp hóa học. Sau đó nghiên cứu phổ hấp thụ, phổ quang phát quang và phổ Raman của các lõi CdSe, các cấu trúc nano lõi/vỏ CdSe/CdS. Chúng tôi đã thu được các tinh thể nano CdSe có phân bố kích thước hẹp. Độ rộng tại nửa cực đại của phổ quang phát quang nhỏ hơn 20 nm. Ảnh hưởng của nhiệt độ phản ứng và độ dày vỏ đến các tính chất quang của các cấu trúc nano lõi/vỏ CdSe/CdS cũng được nghiên cứu. Hiệu suất phát quang của cấu trúc nano lõi/vỏ đạt giá trị cao nhất khi độ dày vỏ CdS bằng 2 đơn lớp.

GIỚI THIỆU
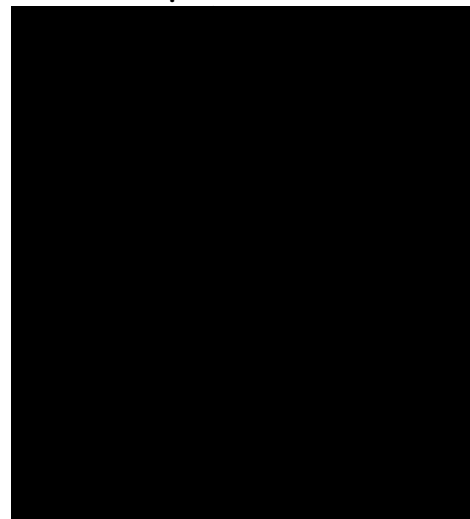
nanometre particles. In order to suppress surface effects, inorganic passivation has been utilized where the nanocrystals have been covered with a high-band-gap material. This is a well solution to enhance the luminescence efficiency and colloidal stability of the particles [2]. For the visible spectral range CdSe nanocrystals are considered as the most promising emitting material because their emission color can be precisely adjusted from blue to red. Several wide band gap semiconductors (CdS, ZnS) were employed as the shell material. The ZnS shell has wide band gap (3.8 eV) in comparison with CdSe core (1.75 eV). So it can provide the best passivation of CdSe core. However, the large mismatch ($\square$ 12 %) between CdSe and ZnS lattice parameters induces the strain at the interface between the core and shell, and this interfacial strain leads to formation of misfit dislocations relaxing the nanocrystal structure [3]. In the case of CdSe/CdS core/shell nanostructures, the lattice mismatch between the core and shell material is relatively small ($\square$ 3.9 %), so it can provide the better stability by decreasing interfacial strain.

In this paper we present the preparation of colloidal CdSe/CdS core/shell nanostructures and their optical properties. The noncoordinating solvent used in this study was octadecene (ODE), which is a liquid at room temperature and boils at about 320 oC. Oleic acid (OA), a natural surfactant, was chosen as the ligand for stabilizing the nanocrystals. Cadmi oxide (CdO) and elemental sulfur (S), two naturally occurring minerals, were chosen as the precursors for the growth of CdSe core and CdS shell.

EXPERIMENTAL

Chemicals: Cadmi oxide, oleic acid, sulfur, selenium (Se), octadecene, tri-n-octylphosphine (TOP).

Preparation: CdSe/CdS core/shell nanostructures were prepared by two main steps:

Step A: Preparation of CdSe core. A mixture of CdO, OA and ODE was stirred and heated to 190-200 oC. At this temperature, a solution of TOPSe in ODE was rapidly injected into this hot solution to grow CdSe core. The reported experimental results unambiguously revealed that the initial Cd:Se ratio of the precursors is a determining

factor for the emission properties of the nanocrystals [4]. In our experiments, the Cd:Se ratio in the stock solution was about 2:1.

Step B: Preparation of CdS shell. A quantity of ODE was loaded into a reaction flash and heated to high temperature. Subsequently, the CdSe nanocrystals in toluene were added, then the Cd^{2+} precursor solution (CdO dissolved with OA in ODE) and the S^{2-} precursor solution (S powder dissolved in ODE) were injected into CdSe solution. In this work, the precursor solutions were slowly injected to keep a low monomer concentration to suppress the homogenous nucleation of CdS. The preparation of CdSe core and CdS shell layer was performed under nitrogen gas flow. The reaction mixture obtained after each step was allowed to cool to room temperature, and a centrifugation procedure was used to purify the nanocrystals from unreacted precursors and side products. After centrifugation, the nanocrystals were dispersed in toluene for further processing.

The CdSe core size was estimated from the first exciton peak position of the absorption spectrum. The particle
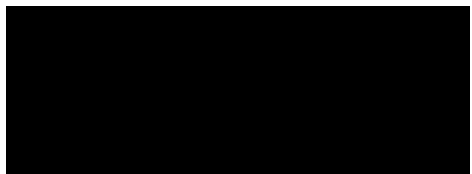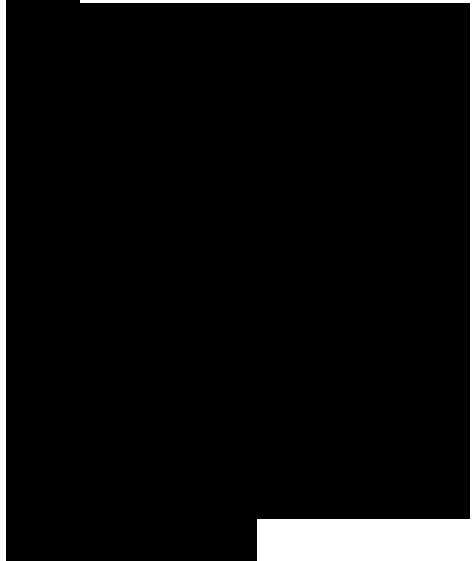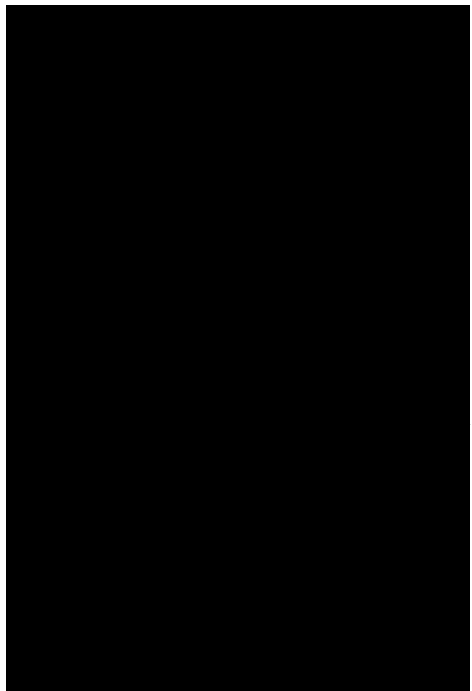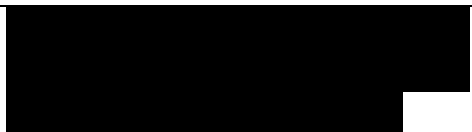
concentration of the purified CdSe solution in toluene, as stock solution for core/shell growth, was determined using Beer's law with the reported extinction coefficient of CdSe nanocrystals [5].

The quantity of precursors added into the growth solution for each CdS shell monolayer (ML) was based on the size of the nanocrystal templates, the concentration of the nanocrystals in the solution, and the lattice constants of the crystal system [6].

Measurements: The optical absorption spectra were recorded by using Jasco V670 UV-Vis-NIR spectrometer. The photoluminescence (PL) and Raman scattering (RS) spectra were measured by using LABRAM-1B spectrometer (Jobin Yvon) with 488 nm excitation line of Ar+ ion laser. All the optical measurements were performed at room temperature.

RESULTS AND DISCUSSION
The temporal evolution of the size and photoluminescence full width at half maximum (PL FWHM) in CdSe nanocrystals growth experiment is shown in Figure. 1. Over the reaction time there are two distinct kinetic regimes: During the first 20 min, the average size of CdSe nanocrystals increases

relatively rapidly (Figure 1a). Simultaneously, their PL FWHM strongly decreases, exhibiting the focusing of size distribution (Figure 1b). Subsequently, the CdSe nanocrystals grow more slowly and their size distribution broadens.

Fig. 1: Evolution of the size (a) and PL FWHM (b) during the growth of CdSe nanocrystals

The above picture can be explained as follows: At any given monomer concentration, there exists a critical size, which is at equilibrium. Nanocrystals smaller than the critical size are dissolved, while larger ones grow at rates dependent strongly on size. Focusing of the size distribution occurs when the nanocrystals present in solution are all slightly larger than the critical size. Under these conditions, the smaller nanocrystals in the distribution grow faster than the larger ones. When the monomer concentration is depleted due to growth, the critical size becomes larger than the average size present, and the distribution broadens because some smaller nanocrystals are shrinking and eventually disappear, while larger ones are still growing [7].

Figure 2 shows the absorption and PL spectrum of CdSe nanocrystals obtained after 20 min of reaction time. Their PL FWHM is 19 nm, so monodisperse CdSe nanocrystals can be obtained in the optimal preparation condition.

Fig. 2: The absorption and PL spectrum of CdSe nanocrystalsobtained after 20 min of reaction time

For preparing a qualitative CdS shell on CdSe core surface the reaction temperature was investigated. Fig. 3 shows the PL spectra of CdSe nanocrystals before and after the coating of CdS shell prepared at 220, 240 and 260 oC during the identical reaction time. All spectra were normalized in the intensity. As the reaction temperature increases, the intensity of the surface emission band decreases due to the increased passivation of the CdSe core surface by CdS shell layer. Comparing the surface emission intensities of the obtained CdSe/CdS core/shell nanostructures, it is found that a higher reaction temperature was necessary for the formation of CdS shell layer. In our experiments the CdS shell layers were prepared at 250- 260 oC.

Fig. 3: PL spectra of CdSe
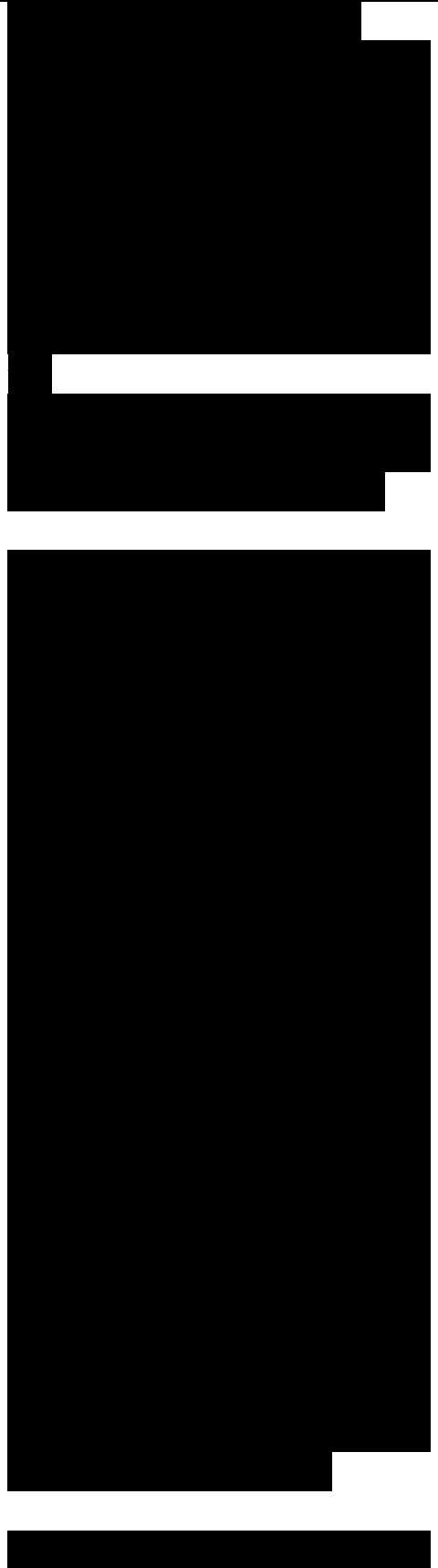
nanocrystals before (a) and after the coating of 3 ML CdS shell at 220 (b), 240 (c) and 260 oC (d)

To understand the effect of CdS passivation on the optical properties of CdSe/CdS core/shell nanostructures, we divided the CdSe core solution into multiple fractions and added varying amounts of Cd and S precursors to each fraction at identical reaction temperatures and addition times. The result was a series of samples with similar CdSe cores but with various CdS shell thicknesses. Figure 4a shows the progression of the PL spectra for these samples covered by CdS shell with the various thicknesses. As the thickness of the CdS shell increases, there is a red- shift in the PL, reflecting an increased leakage of the exciton into the shell. Figure 4b charts the evolution of the emission area for the CdSe/CdS nanostructures as a function of the CdS shell thickness. We saw a dramatic increase in the followed by a steady decline after 2 MLs of CdS. The emission area increases with the addition of CdS, approaching a maximum value at approximately 2 MLs coverage. At higher coverage the emission area begins to decrease steadily.
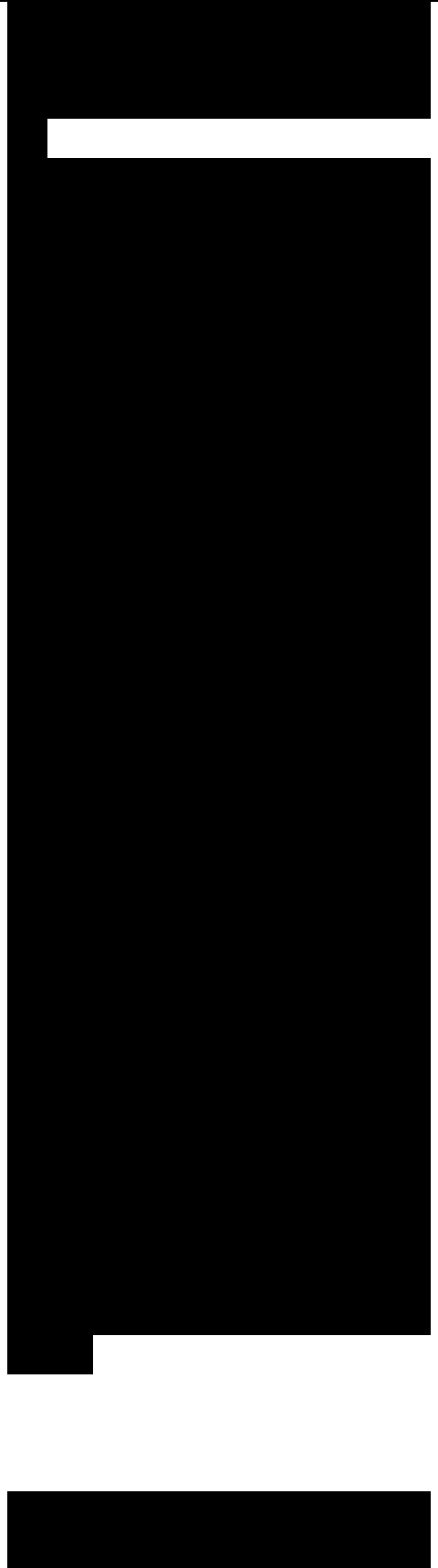
This was explained as follows: The first, emission area rises progressively because of the increasing passivation of the core surface, then decreases, presumably as a result of the higher concentration of structural defects created within the thicker deposited shell [8].

Shell thickness (ML)   Fig 4: The progression of the PL spectra of CdSe nanocrystals covered by CdS shell with the various thicknessess (a) and the dependence of PL emission area on the CdS shell thickness (b)

Figure 5 present the RS spectra of CdSe core and CdSe/CdS core/shell nanostructure. Strong scattering due to the longitudinal optical (LO) phonon mode of CdSe core was observed (Figure 5a). The LOCdSe peak is shifted to lower frequency side ($\sim$ 206 cm-1) in comparison with that of bulk CdSe crystal (213 cm-1) and has the asymmetric shape due to the quantum confinement of phonons and the contribution of the surface optical (SO) phonon mode.

The RS spectrum of the CdSe/CdS core/shell nanostructure is characterized by two strong LO modes (Figure 5b). The position of LOCdS peak at $\sim$ 292 cm-1 indicates the presence of CdS shell around CdSe core. The
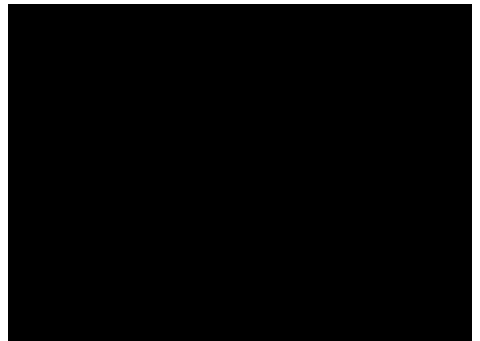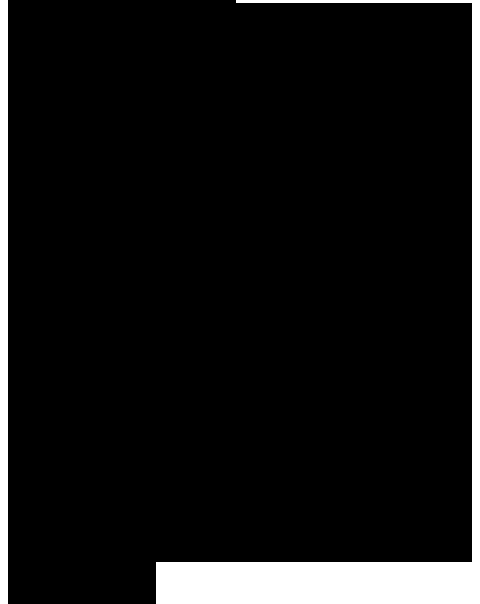
LOCdSe peak is shifted to higher frequency side in comparison with that of CdSe core and becomes narrower. In addition, the low frequency shoulder of LOCdSe peak increases in the intensity. It is possible that the S-atoms in CdS shell diffuse into the CdSe core, and similarly, the Se-atoms in CdSe core diffuse into the CdS shell during the growth of CdS shell layer at high temperature. This leads to form the CdS_xSe_{1-x} alloy layer between CdSe core and CdS shell. In this case, the low frequency shoulder of LOCdSe peak is the combination of SOCdSe, LOCdSe-like and SOCdSe-like vibrational mode, and therefore, the low frequency shoulder of LOCdSe peak increases in the intensity.

In order to determine the size of CdSe core, the experimental RS spectrum was fitted by applying the phonon confinement model of Campbell and Fauchet [9] for LOCdSe mode and using Lorentz function for SOCdSe mode. The best fitting result is shown by the solid line in Figure 5a. LOCdSe and SOCdSe phonon mode are shown by dashed and dotted line, respectively. The obtained diameter of CdSe core is 5.8 nm in good agree with the value of 5.9 nm determined from its
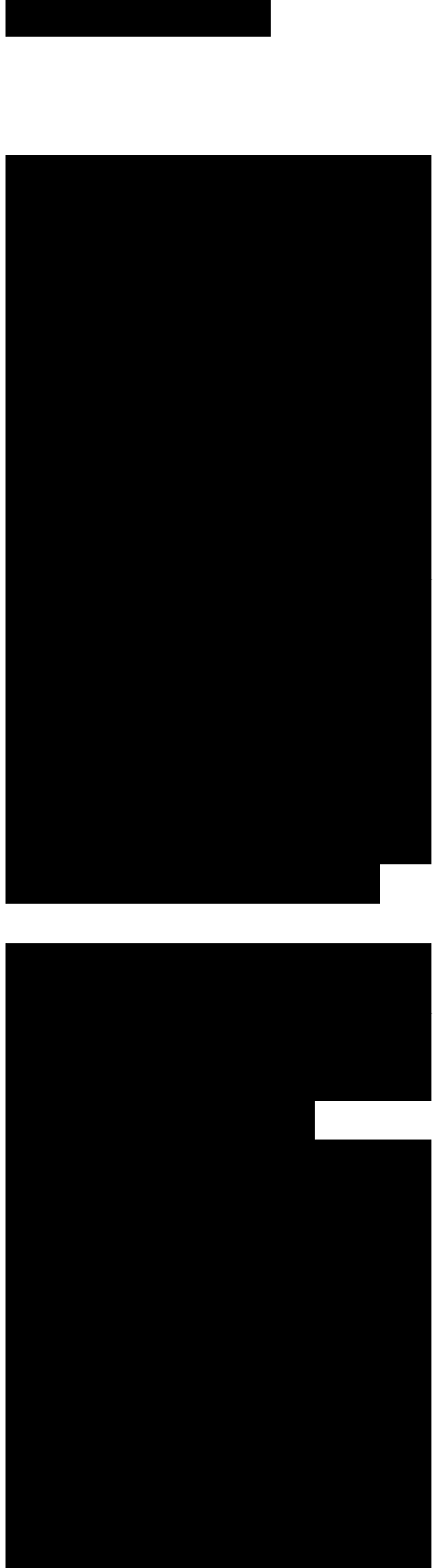
absorption spectrum.

Fig. 5: RS spectra of CdSe core (a) and CdSe/CdS core/shell (2 MLs) structure (b)

CONCLUSION

The colloidal CdSe nanocrystals and CdSe/CdS core/shell nanostructures were prepared by chemical method using octadecene, a noncoordinating solvent. The evolution of the size and size distribution of CdSe nanocrystals during the growth, the effect of reaction temperature and CdS shell thickness on the optical characteristics of CdSe/CdS nanostructures were investigated. The monodisperse CdSe nanocrystals with PL FWHM of 19 nm were obtained in the optimal preparation condition. The highest PL emission intensity of CdSe/CdS core/shell nanostructures was obtained for the CdS shell thickness of 2 MLs. The average size of the CdSe nanocrystals were determined from the RS spectra by applying the phonon confinement model of Campbell and Fauchet is in good agree with the value determined from absorption spectra.