Effect of Phosphine-Free Selenium Precursor Reactivity on The Optical and Vibrational properties of Colloidal CdSe Nanocrystals

L A Thi1,6, N T T Lieu2, N M Hoa3, N Tran4, N T Binh5, V X Quang1, N X Nghia1,6*

1Institute of Research and Development, Duy Tan University, 3 Quang Trung, Da Nang, Vietnam
2Posts & Telecommunications Institute of Technology, km10 Nguyen Trai, Hanoi, Vietnam
3Hue College of Medicine and Pharmacy, 6 Ngo Quyen, Hue, Vietnam
4Department of Physics and Oxide Research Center, Hankuk University of Foreign Studies, Yongin, Gyeonggi 449-791, South Korea
5Graduate University of Science and Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi
6Institute of Physics, Vietnam Academy of Science and Technology, 10 Dao Tan, Hanoi, Vietnam

nghianx.ims@gmail.com

Abstract. Phosphine-free selenium precursor solutions have been prepared by heating at temperatures ranging from 160 °C to 240 °C and studied by means of infrared absorption spectroscopy. The colloidal CdSe nanocrystals (NCs) synthesized from all those solutions by the wet chemical method. The influence of heating temperature on the chemical reactivity of selenium precursor and its role on the optical and vibrational properties of CdSe NCs are discussed in details. Their morphology, particle size, structural, optical and vibrational properties were investigated using transmission electron microscopy, X-ray diffraction, UV-Vis, fluorescence and Raman spectroscopy, respectively.

1. Introduction

Colloidal nanocrystals (NCs) of groups II-VI have attracted wide interest in many fields of physical, chemical, biochemical,... [1]. Many of these applications rely on the fluorescence emission of the quantum dots (QDs), and by proper surface engineering, quantum yields approaching unity are now being achieved with type II-VI NCs based on CdSe. By regulating the particle size, the Photoluminescence (PL) emission peaks of CdSe NCs could be tuned spanning most of the visible spectrum [2,3]. CdSe NCs have been providing an ideal stage to explore the nucleation and growth mechanisms of NCs satisfying more complicated application, various structured NCs such as alloys [4], core/shell [5], doping [6] or heterostructure [7].

The first synthesis of high-quality CdSe NCs involved high-temperature synthesis using dimethyl cadmium and phosphine based selenium precursors [8,9]. However, for their application as active materials in photovoltaics or sensors, the presence of more ligand, surface-bound organic species may
be a disadvantage to device performance. Moreover, trialkylphosphines are toxic, expensive, and oxidize easily. It is interesting to investigate the development of stable selenium precursors in the absence of strongly bound phosphine [1,5].

Jacek Jasieniak and co-workers reported the first phosphine-free synthesis of CdSe, based on the dissolution of selenium (Se) in 1-octadecene (1-ODE) after prolonged periods of heating at high temperatures [11]. Subsequently, other research groups have employed similar approaches to synthesize phosphine-free NCs. Solvents such as olive oil and oleylamine (OLA) have also been implemented [10]. Using OLA is another candidate with a high boiling point which forms a Se-OLA precursor complex, but it contains an amine group which effects to characterizations and structure of the NCs [3]. So the OLA and ODE were chosen as solvents with either the double bond and amine or the double bond only functionality for complex formation. In addition to, a long time heating protocols aimed at facilitating the dissolution of Se, additives including NaBH₄ and alkylthiols have been introduced. The disadvantage of the latter approaches is the introduction of additional elements (Na, B, and Se) which could appear as impurities in the final product [12]. It also affects to the characterizations of NCs. Recent studies have demonstrated that the synthesis of QDs can be carried out by employing insolubilized Se or SeO₂ powder with good yields [12]. To now, the use of a stable phosphine-free solution prepared by the dissolution of elemental Se in ODE (Se-ODE) has been explored as a viable selenium precursor for CdSe, ZnSe NCs synthesis [6,13]. All research groups have been developed the Se–ODE solution approach in various forms and investigated the high quality of binary NCs growth as Se precursor. However, the mechanism of formation and nature of the Se precursors in these solvents remain to be fully elucidated.

Herein, we report a detailed study of the phosphine-free selenium precursor solutions system. We establish that the efficacy of Se-ODE is highly dependent on preparation temperature. Further, we have investigated the role of chemical reactivity of them for the characterizations of CdSe NCs. The obtained results will helpful to available choice the suitable Se precursor for fine control the homogeneously and gradient alloyed semiconductor NCs.

2. Experimental

2.1. Phosphine-free selenium precursor solutions

For a typical preparation of Se-ODE solution (0.1 M), 3 mmol of Se powder (99.99%) was transferred to a three-necked round-bottom flask, and 20 mL of ODE (99.99%) was added. This mixture have heated at temperatures ranging from 160 °C to 240 °C and stirred for 30 minutes (min) under nitrogen.

2.2. Synthesis of CdSe QDs

A mixture of oxide cadmium (CdO, 99.99%) (0.6 mmol), 10 mL of ODE and 1.2 mmol of oleic acid (OA-99.99%) was loaded into a three-neck flask and heated up to 250 °C, set under nitrogen gas until the mixture turned clear. Further, the Se precursor was quickly injected into the cadmium solution which was being stirred at 280 °C. The color of this mixture turned from yellow to red depending on the size of the CdSe nanocrystals formed. They were allowed to grow for different times to 60 min. The QDs were purified by dissolving in isopropanol, toluene and centrifuged to remove all residual products.

2.3. Characterization

Transmission electron microscopy (TEM) images were collected using a JoelJEM1010 operating at 80 kV. Absorption spectra were recorded using a Varian-Cary-5000 Ultraviolet-visible (UV–Vis) spectrophotometer. PL spectra were measured by a JobinYvonFlurolog FL3-22 fluorescence spectrophotometer with the wavelength of the exciting radiation of 400 nm. Fourier transforms infrared (FTIR) spectra were taken with a Nicolet IS 10 FTIR Spectrometer. Raman spectra (Ra) were recorded by an XploRA spectrometer (HoribaJobin-Yvon) with a laser wavelength of 532 nm. X-ray powder diffraction (XRD) was conducted on a Siemens D5005 X-ray diffractometer using Cu-Kα1 radiation with a wavelength of 0.15406 nm. For Ra and XRD measurements, the samples were deposited on glass slides. All of these measurements were performed at room temperature.
3. Results and Discussion

3.1. Characterization of Se-ODE Precursor

The dissolution time of Se in ODE was strongly dependent on the temperature. It was found to decrease when the temperature increases. Such as, it took 30 hours (h) at 160 °C, 6 h at 180 °C, 3 h at 220 °C, 1 h at 220 °C and 45 min at 240 °C. Those times were taken to be the point at which observing Se dissolved completely in an ODE. The color of the Se-ODE solution changes after heats at the different temperature. The strongest coloration observed changing yellowish to orange-yellow color when the temperature heating increases from 160 °C to 200 °C. However, at a higher temperature (from 220 °C to 240 °C), it became increasingly colorless. The changing of color due to the formation of solvated Se in ODE when heat elemental Se in an ODE. In order to investigate the ODE–Se complex and predict the reaction mechanism of them, we analyzed the FTIR spectra (shown in Fig.1(a)).

![Figure 1. (a) Normalized FTIR spectra of ODE non-heating (I), ODE heating 180 °C (II), Se-ODE 180 °C (III), Se-ODE 240 °C (IV) for 30 min; (b) The main features of the various spectral responses are identical to those highlighted in Fig.1 (a)](image)

We have been collected of ODE non-heating, ODE heating at 180 °C, Se-ODE heating at 180 °C and 240 °C for 30 min to measure. Fig.1(a) shows that for ODE non-heating the feature IR peaks of the vinyl group out of plane C–H bend located at $v = 908.2$ (cm$^{-1}$), $v = 991.3$ (cm$^{-1}$), the –C=C– stretch is located at 1642 cm$^{-1}$ and C–H stretch located at 3077.6 (cm$^{-1}$) [14].

After heating ODE at 180 °C, the Se-ODE solution at 180 °C and 240 °C, the emergence of a band at $v = 964.4$ cm$^{-1}$ appear and intensity is increased correlated higher temperature while it has disappeared in ODE’s FTIR spectra non-heating and heating at 180 °C (see arrow Fig.1(b)). Thus, the kinetics of colorimetric changes of Se-ODE mixtures heated at a different temperature to confirm a reaction between Se and ODE that forms a poly-sulfur-alkyl complex.

3.2. The influence of Selenium Precursors on the characterization of CdSe Nanocrystals

3.2.1. Morphologies and structures

For this investigation, the CdSe NCs synthesized using Se-ODE precursors heated at three temperatures of 160 °C, 180 °C, and 240 °C. A series of CdSe NCs samples prepared at the growth temperature of 280 °C. Their name is denoted A160, A180, and A240 NCs.

The series TEM images of them with growth time of 15 min of NCs are shown in Fig.2a, b, c. The insets show the size distribution histograms of Fig. 2a, b, c, respectively. The shape and size of the CdSe QDs depend on the varied Se-ODE precursor. A160 and A180 NCs are spherical shapes with an average diameter about 11 ± 0.6 nm and about 5 ± 0.5 nm, respectively. Whereas, A240 is shown the
cubic and triangles shapes with an average diameter about 10 ± 0.5 nm. A160 presents less chemical reactivity of Se precursor led to the low stabilizer, higher precursor concentration promotes the formation of larger nuclei and lower quality QDs (Fig.2a). While a higher chemical reactivity of Se precursor was found in A180 sample because the growth of QDs is faster and homogeneous. The A180 NCs particle size could be close to monodisperse (narrow size distributions) (see Fig. 2b). However, with A240 sample, we predicted possible too strong or less chemical reactivity of Se precursor so the growth of NCs is inhomogeneous (see Fig. 3c). Here, the less chemical reactivity Se precursor is possible some Se loss can occur.

Figure 2. TEM images of (a) A160, (b) A180 (c) A240 NCs, the inset shows size distribution histogram of NCs (d) The XRD patterns of them.

To further characterization of the structures of CdSe NCs, their crystallographic properties were determined using powder XRD. The XRD patterns obtained from CdSe NCs with growth time of 30 min prepared using varied Se-ODE precursors are shown in Fig. 2d. According to the XRD pattern, three obvious diffraction peaks located near 2θ ≈ 25.41°, 42.1° and 49.1° corresponded to the (111), (220), and (311) planes of zinc blende phase CdSe. The broadening of the full width at half maximum (FWHM) in XRD patterns of A160 is observed (see Fig.3d.). It due to the interior defects produced in the lower quality QDs.

3.2.2. Optical properties
The time evolution absorption (Abs) and PL spectra of NCs are shown in Fig. 3a, b, c. It shows that in all reactions a significant red shift of the band-edge transition peak was observed after injection of the Se precursor.
Figure 3. The temporal evolution of absorption spectra and PL spectra of CdSe nanocrystals using different Se precursors (a) A160, (b) A180, and (c) A240 NCs and (d) The PL peak position of A160, A180 growth at 280 °C

The Abs peaks of NCs shift from 2.16 eV to 2.04 eV for A160 and from 2.11 eV to 1.94 eV for A180 (Fig. 3d). However, the optical properties of A240 NCs are presented badly quality after injected the Se-ODE precursors see in Fig. 3c. This is the reason that the Se-ODE prepared at high temperature is probably too strong chemical activity and ability Se loss had occurred [15]. Ability Se loss had occurred led to low of the reaction yield. We can see that these different kinds of Se precursors have been used to collect information on the reactivity of CdSe NCs and get optimized conditions to synthesize different sizes of high-quality CdSe QDs.

In general, the reaction speed was relatively slow with A160 and faster with A180. It has been presented by the evolution of the concentration of NCs and their PL’s FWHM which shown in Fig. 4. These results indicate that the high quality of NCs is prepared with Se precursor heated at a higher temperature.

Figure 4. (a) Concentration NCs and (b) FWHM of the PL as functions of time for the A160 (circle) and A180 (triangle) NCs grew at 280 °C

This is due to a possible mechanism for the monomer formation in reactions. The number of NCs formed and their final size depends on both the rate of monomer generation and on the takeover of nucleation by growth. With the same reaction conditions for A160 and A180 NCs, the rate of nucleation and growth for A160 NCs is slow because of the monomer concentration is rich, so leads to the formation of larger particles size and NCs concentration is lower. For A180 NCs, these rates and the amount of precipitate formed of NCs are stronger, leads to the higher of NCs concentration (Fig.4a). Hence, the chemical reactivity of Se Precursor heating at 180 °C is higher than 160 °C. It might also affect the size distribution of NCs and led to change PL’s FWHM (Fig.4b). It turned
broader when the reaction lasted longer. For A160 NCs was changed strongly between 26 and 34 nm in the whole reaction while 23 nm and 27 nm for A180 NCs. According to the relation between the FWHM and the real nanocrystal size, the small FWHM of the NCs reveals that the sizes of them could be close to monodisperse (narrow size distributions). This means the chemicals reactivity of Se precursors plays an important role in forming the CdSe NCs. Adding different active Se-ODE into reaction solution changes the diffusion rates of the monomer and therefore controls nanocrystal growth so that the various size distributions can be achieved.

3.2.3. Vibrational properties
The room-temperature Raman spectra of CdSe NCs are shown in Fig. 5a. These two components can be assigned to surface optical (SO) and longitudinal optical (LO) phonons in agreement with previous observations for NCs [16].

![Raman spectra and fitting](image)

**Figure 5.** (a) Raman spectra and (b) Fitting of the main Raman band for A160, A180, and A240NCs

To evaluate the LO and the SO phonons, the elemental Raman bands are fitted by a sum of several Lorentzian peaks as shown in Fig. 5b. The peak parameters of A160, A180 and A240 NCs are shown in Table 1. The results show that the 1LO frequency increases from A160 to A180 and then decreases with A240. Whereas, the 1SO frequency decrease from A160 to A240. Herein, we also observed the phonon overtones up to the third order of LO phonons (see Fig. 5b). On the other hand, the FWHM of 1LO is decreased from A160 to A240. It is reasonable that can be related to the internal strain and phonon confinement in NCs.

| CdSe  | 1SO (cm⁻¹) | 1LO (cm⁻¹) | 2SO (cm⁻¹) | 2LO (cm⁻¹) | 3LO (cm⁻¹) | FWHM 1LO |
|-------|------------|------------|------------|------------|------------|----------|
| A160  | 197.39     | 203.0      | 379.25     | 407.39     | 621.10     | 17.6     |
| A180  | 195.72     | 203.58     | 381.95     | 409.55     | 616.19     | 10.1     |
| A240  | 172.99     | 200.37     | 379.59     | 406.53     | 613.7      | 9.3      |

4. Conclusions
In summary, the different heating of selenium powder dissolved in 1-octadecene has been made. The chemical reactivity of the Se-ODE is found to be highly dependent on heating temperature. The dissolution of the elemental selenium within 1-ODE proceeds through the fragmentation of the selenium chains to selenium bridges between alkene solubilizing molecules.

We evaluated the results of the influence of chemical reactivity of Se precursor on the characterization of colloidal CdSe NCs. It’s high-quality NCs for A180 with fairly narrow size distributions.
We observe multiple Raman spectra by characteristic phonons up to the third order. The first order optical phonon peak that has allowed to be well-deconvoluted into two components assigned to SO and LO phonon modes. The band shifts and significantly broadens with respect varial Se precursor due to were found to result from a subtle balance between phonon confinement effects and lattice contraction due to internal strain. Moreover, this finding highlights that this easily prepared, cheap, and stable Se-ODE precursor is a highly viable selenium source for the synthesis of semiconductor nanocrystals.

References
[1] Dolai S, Dutta P, Muhoberac B B, Irving C D and Sardar R 2015 Mechanistic study of the formation of bright white light-emitting ultrasmall CdSe nanocrystals: Role of phosphine free selenium precursors Chem. Mater.27 1057–70
[2] Yu W W, Qu L, Guo W and Peng X 2003 Experimental determination of the extinction coefficient of CdTe, CdSe, and CdS nanocrystals Chem. Mater.15 2854–60
[3] Zimdars J and Bredol M 2015 Reduction of Selenium for the Phosphine-Free Synthesis of Metal Selenide Nanoparticles † New J. Chem.40 1137–42
[4] Aldakov D, Lefrançois A and Reiss P 2013 Ternary and quaternary metal chalcogenide nanocrystals: synthesis, properties, and applications J. Mater. Chem. C1 3756
[5] Shen H, Wang H, Tang Z, Niu J Z, Lou S, Du Z and Li L S 2009 High-quality synthesis of monodisperse zinc-blende CdSe and CdSe/ZnS nanocrystals with a phosphine-free method CrystEngComm11 1733
[6] Shen H, Wang H, Li X, Niu J Z, Wang H, Chen X and Li L S 2009 Phosphine-free synthesis of high-quality ZnSe, ZnSe/ZnS, and Cu-, Mn-doped ZnSe nanocrystals Dalt. Trans. 10534
[7] Manthiram K, Beberwyck B J, Talapin D V. and Alivisatos A P 2013 Seeded Synthesis of CdSe/CdS Rod and Tetrapod Nanocrystals J. Vis. Exp. e50731
[8] Wang F, Richards V N, Shields S P and Buhro W E 2014 Kinetics and mechanisms of aggregative nanocrystal growth Chem. Mater.26 5–21
[9] Flamee S, Cirillo M, Abe S, De Nolf K, Gomes R, Aubert T and Hens Z 2013 Fast, high yield, and high solid loading synthesis of metal selenide nanocrystals Chem. Mater.25 2476–83
[10] Sapra S, Rogach A L and Feldmann J 2006 Phosphine-free synthesis of monodisperse CdSe nanocrystals in olive oil J. Mater. Chem.16 3391
[11] Jasieniak J, Bullen C, Van Embden J and Mulvaney P 2005 Phosphine-free synthesis of CdSe nanocrystals J. Phys. Chem. B109 20665–8
[12] Pu C, Zhou J, Lai R, Niu Y, Nan W and Peng X 2013 Highly reactive, flexible yet green Se precursor for metal selenide nanocrystals: Se-octadecene suspension (Se-SUS) Nano Res.6 652–70
[13] Wang L, Sun X, Liu W and Yu X 2010 Phosphine-free synthesis of high-quality zinc-blende CdSe nanocrystals in air Colloids Surfaces A Physicochem. Eng. Asp.355 232–7
[14] Banski M, Afzaal M, Malik M A, Podhorodecki A, Misiewicz J and O’Brien P 2015 Special Role for Zinc Stearate and Octadecene in the Synthesis of Luminescent ZnSe Nanocrystals Chem. Mater.27 3797–800
[15] Bullen C, Van Embden J, Jasieniak J, Cosgriff J E, Mulder R J, Rizzardo E, Gu M and Raston C L 2010 High activity phosphine-free selenium precursor solution for semiconductor nanocrystal growth Chem. Mater.22 4135–43
[16] Pejova B 2013 Phonon confinement and related effects in three-dimensional assemblies of cubic cadmium selenide quantum dots synthesized by conventional chemical and sonochemical routes J. Phys. Chem. C117 19689–700