Influence of Ligand Exchange on the Structural and Optoelectronic Properties of CdSe Nanocrystals

Nguyen Tam Nguyen Truong and Chinho Park*

Abstract—We report the influence of changing surface ligands of synthesized CdSe nanocrystals on its structural, optical and electrical properties. TOPO-capped CdSe nanocrystals of 2 to 7 nm sizes have been synthesized by hot injection method, and the surface capping molecule, TOPO was subsequently replaced by tributyl amine. It was found that the exchange of surface ligands significantly altered the physical properties of nanocrystals. The shifting toward the shorter wavelength (higher energy) in the visible range of optical absorption band edge was observed by UV-VIS spectroscopy, and a blue-shift of photoluminescence peaks was observed with luminescent quenching. A slight reduction in nanocrystal’s size during the ligand exchange procedure was confirmed by transmission electron microscopy, indicating the change in quantum confinement effect. The surface ligand exchange was also found to cause the increase in the nanocrystal’s surface energy, resulting in the improvement of charge carrier separation.

Key words—Ligand, nanocrystals, blue shift, band edge, photoluminescence quenching.

I. INTRODUCTION

The colloidal semiconducting nanocrystals have attracted great attention in the last decade for their wide use in diverse research and industrial applications, including lasers [1], [2], light emitting diodes [3], [4] and solar cells [5]. The CdSe nanocrystal is a one of them whose band gap (Eg= 1.74 eV) lies in the visible spectrum and thus have been considered as an n-type material in the simple, low-cost, high performance bulk hetero-junction (BHJ) solar cells [6]. The properties of CdSe nanocrystals were studied by many research groups; the effect of thermal annealing on the structural and optical properties of CdSe nanocrystals was reported [7], indicating that after annealing in air or N2-atmosphere at 250 °C and 350 °C, the crystallinity and surface passivation characteristics of the CdSe nanocrystals were enhanced. Annealing induced phase transitions were observed, which resulted in the significant change of nanocrystal’s electrical and optical properties. A quantitative study of nanocrystals has been reported in the context of the effect of particle size and surface ligands on the photo-degradation of CdSe nanocrystals [8], which indicated that the emission properties and lifetime values of CdSe nanocrystals be dependent on the oxidation potential of surface ligand and crystallite size. The effect of atomic ratios of Cd:Se in CdSe nanoparticles on optical edge shifts and photoluminescence properties was investigated [9], and it was shown that the blue-shift of the optical absorption edge concurrent with the CdSe nanoparticle’s size reduction agree well with the quantum confinement effect. However, the roles of various different surface capping ligands of the nanocrystals in modifying the optical, chemical and electrical properties of nanocrystals remain mostly unexplored. In this study, we consider the influence of ligand exchange after nanocrystal synthesis on its materials properties. The structural, optoelectronic, and chemical properties of nanocrystals before and after the ligand exchange procedure were characterized systematically and the mechanisms investigated.

II. EXPERIMENTAL

The CdSe nanocrystals were synthesized by using a slightly modified hot injection method [10], and the surface ligand, TOPO (trioctyl phosphine oxide) naturally formed on CdSe nanoparticles during the synthesis was exchanged with tributyl amine by a liquid-liquid extraction process controlled at room temperature for 24 hrs. The tributyl amine capped CdSe nanocrystals were dispersed in a liquid solution and then centrifuged for three times to yield high-purity tributyl amine capped CdSe nanocrystals. Drying of nanocrystals was made in a vacuum oven with a temperature at around 60 °C. The size of nanocrystals was estimated by high-resolution transmission electron microscope (HR-TEM, H-7600), and the optical properties and chemical composition of CdSe nanocrystals were measured by photoluminescence (PL) spectroscopy and X-ray photoelectron spectroscopy (XPS), respectively.

III. RESULTS AND DISCUSSION

![Graph showing intensity versus wavelength for two different peaks (A and B) at 597 nm and 588 nm respectively.]}
Figure 1. Absorption spectra of CdSe nanocrystals capped with (A) TOPO and (B) tributyl amine.

Figure 2. Photoluminescence spectra of CdSe nanocrystals capped with (A) TOPO and (B) tributyl amine.

Figures 1 and 2 show the UV-Vis and PL spectra of CdSe nanocrystals capped with TOPO and tributyl amine ligands, respectively. The CdSe nanocrystals were dispersed in chlorobenzene solvent prior to the spectroscopy measurements. We observed that the absorption edge of UV-Vis spectra was shifted to a shorter wavelength from 597 nm to 588 nm, and the emission peak of PL spectra shifted towards higher energy from 1.93 eV to 1.96 eV. The shifting of absorption edge and emission peak toward shorter wavelength is often called “blue-shift,” and this could be caused by the quantum confinement effect due to the reduction in the nanocrystal’s size [11, 12]. Surface defect related emission property change could also occur in the nanocrystalline semiconducting materials. Since the smaller size nanocrystals have a larger surface to volume ratio compared to that of the larger size crystals and most of the photo-generated charge carriers undergo recombination at the surface vacancies, it could make the smaller size nanocrystals to luminesce much stronger. However, the quenched PL spectra were observed from the nanocrystals of this study, contradicting the report from a literature [11].

The size and structural property of CdSe nanocrystals were measured by HR-TEM, and the results are shown in Figure 3. It was observed that both TOPO-capped and tributyl amine-capped CdSe nanocrystals are highly crystalline with cubic phase. From the quantitative analysis of TEM images (inserted figures), the average nanocrystal sizes were found to be 5 to 6 nm and 3 to 4 nm for TOPO-capped and tributyl amine-capped nanocrystals, respectively. As expected from the optical measurement results, slight reduction in nanocrystal’s size during the ligand exchange procedure was confirmed by the transmission electron microscopy. The decrease in the nanocrystal’s size during the ligand exchange process is explained by the possible loss of Cd and Se atoms present on the nanoparticle surface [13] which makes the nanocrystals shrink in size. The removal of surface atoms is facilitated by the relatively high defect density on the surface as well as the high surface energy. The reduction in nanocrystal’s size subsequently causes the blue-shifts of absorption edge and photoluminescence peaks. It is further speculated that the PL quenching observed from the samples of this study indicates the removal of surface defects and subsequent passivation of the surface by electron donating amine ligands.

Figure 3. Transmission electron microscopic images of CdSe nanocrystals capped with (a) TOPO and (b) tributyl amine.

Figure 4. The XPS survey spectra of CdSe nanocrystals: (a) TOPO-capped CdSe, (b) tributyl amine-capped CdSe.

The effect of ligand exchange on the chemical bonding characteristics of CdSe nanocrystals was investigated by X-ray photoelectron spectroscopy (XPS). Figure 4 shows the XPS survey spectra of TOPO-capped and tributyl amine-capped nanocrystals. The general survey spectrum mainly reveals the Cd and Se peaks from nanocrystals, even though the C and O peaks were also observed, indicating the presence of surface ligands. The survey spectra from different surface ligands were identical in the number of peaks and their positions which are close to the bulk values [14]. High resolution XPS spectra were taken for the samples of TOPO-capped CdSe and tributyl amine-capped one, and the corresponding Cd 3d, Se 3d and O 1s spectra are shown in Figure 5 (I-III), respectively.

As shown in Figure 5 (I) (curve a), the presence of Cd 3d_{5/2} peak at 402.34 eV indicated that the Cd exists either in metallic form (unreacted Cd) or in CdSe form [15]. Figure 5 (I) (curve b) shows the Cd 3d_{5/2} peak at 402.85 eV after ligands...
were changed from TOPO to tributyl amine, shifting 0.51 eV toward higher binding energy. The intensity of the Cd 3d levels decreases while the full width at maximum (FWHM) remains the same, which indicates that this was caused not by the surface oxidation but by forming stronger bonding in the CdSe nanocrystals.

Figure 5. The XPS spectra of CdSe nanocrystals from (a) TOPO-capped CdSe and (b) tributyl amine-capped CdSe: (I) XPS spectra corresponding to the Cd 3d region; (II) XPS spectra corresponding to the Se 3d region; (III) XPS spectra corresponding to the O 1s region.

Similarly, Figure 5 (II) shows the XPS spectra from Se 3d. In the case of TOPO-capped CdSe nanocrystals (curve a), the Se 3d peak position was observed at 50.92 eV, while it was observed at 51.24 eV for the samples of tributyl amine-capped ones, shifting 0.32 eV toward higher binding energy. The presence of Se 3d at 50.92 eV and 51.24 eV, and the none existence of the peak at 60 eV further confirms the CdSe only phase [16, 17]. Figure 5 (III) shows the XPS spectra from O 1s region, and the O 1s peak was observed at 528.16 eV for TOPO-capped nanocrystals (curve a), whereas for tributyl amine-capped CdSe samples (curve b) the O 1s peak shifted toward higher binding energy (by 0.75 eV). The presence of C 1s at ~282 eV was also identified [18]. The XPS studies also confirmed the absence of cadmium oxide, hydroxide, and selenium oxide, indicating the high purity of CdSe nanocrystals synthesized in this study.

IV. CONCLUSIONS

Highly crystalline and pure CdSe nanocrystals were successfully synthesized in this study, and the influence of exchanging the surface ligands on the synthesized CdSe nanocrystals on its structural, optical and electrical properties was characterized in detail. After the ligand exchange, the nanocrystal's size was slightly reduced, resulting in higher surface energy, and subsequently causing the blue-shift of absorption edge and photoluminescence peaks. The photoluminescence quenching was also observed due to the removal of surface defects and enhancement of surface passivation during the ligand exchange. The improvement of charge carrier separation at the surface is expected to occur.

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VI. REFERENCES


*Corresponding Author: Chinho Park (chpark@ynu.ac.kr)

Nguyen Tam Nguyen Truong received his B. Sc degree from University of Pedagogy (HCM), Vietnam in 2005 and M. Sc degree from Yeungnam University, Republic of Korea in 2007. He is currently a Ph. D. student in the School of Chemical Engineering at Yeungnam University. His research interests are in inorganic and organic photovoltaic devices. He is a student member of Korean Institute of Chemical Engineers (KIChe).

Chinho Park received his B. S. degree from Hanyang University, Republic of Korea in 1981, M. S. degree from Seoul National University, Republic of Korea in 1983, and Ph. D. degree from the University of Florida, U.S.A. in 1992. He is currently a professor in the School of Chemical Engineering at Yeungnam University. His area of research includes the fabrication of thin film photovoltaic cells and light emitting diodes using both inorganic and organic materials as well as their composites. He is a lifetime member of Korean Institute of Chemical Engineers (KIChe), Korean Association of Crystal Growth and Korean Society of Engineering Education. He is currently serving as a secretary general of KIChe and the director of the Materials Division of KIChe. He is also serving as a director of the Institute of Solar Energy Research at Yeungnam University.