Research Article

Pinned Luminescence Emission and Absorbance Band from Ultrasmall Ball-Milled Cd$_{0.3}$Zn$_{0.7}$Se Nanocrystals

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We report the pinned absorbance and emission spectra of Cd$_{0.3}$Zn$_{0.7}$Se nanocrystals synthesized via mechanical alloying. The first emission peaks of Cd$_{0.3}$Zn$_{0.7}$Se nanocrystals milled for 5 and 10 h are observed at 3.36 eV, while the absorbance spectra of those milled for 10 and 20 h are observed at 4.47 eV. The emission peaks of nanocrystals milled for 5, 10, and 20 h have broad emissions centered at 2.90, 2.88, and 2.92 eV, respectively. Transmission electron microscopy histogram shows that each nanocrystal size distribution has a single population maxima of <2 nm. In addition, the center of each size distribution shifts toward the ultrasmall particles upon continuous milling. Particle sizes (d) of 0.73 nm are calculated from the first excitonic peaks of the pinned absorbance bands through the semiempirical sizing equation. The continuous reduction in particle sizes increases the surface-to-volume ratios of the nanocrystals. This increase eventually results in an increase in the surface states that translate into low photoluminescence intensity of pinned emission.

1. Introduction

A semiconductor nanocrystal with dimension of <2 nm is typically synthesized via a chemical route [1–3]. Mechanochemical synthesis route is relatively new compared with chemical method and is a nonequilibrium method that employs forced chemical mixing to produce nanostructure materials [4–6]. Nanometer-sized semiconductor crystallites have been fabricated through this method [7–9].

Small semiconductor nanocrystals have a high surface-to-volume ratio, and one-third to one-half of their atoms are located on the surfaces [8], which are dominated by defects, such as dangling bonds. This unique feature induces additional electronic states coupled with intrinsic states in the band gap [9].

Ultrasmall nanocrystals have excellent linear and nonlinear optical properties that are preferred for several technological applications. For example, they can be used for efficient solid-state lighting, particularly white light-emitting diodes, because of their broad emission through the entire UV spectrum [10]. They are also used in fluorescent biological labeling [11] and lasing applications [12]. Engineers utilize their nonlinear optical properties to fabricate optical switches for telecommunication industries [13].

Decrease in nanocrystal diameter results in the blue-shifting of the band-edge emission and band-edge absorption through the quantum confinement effects [14–18]. However, optical band gap insensitivity occurs when the particle sizes are less than 2 nm. The nanocrystals exhibit new features, such as a fixed absorption peak at the short wavelength of the absorption spectrum, when their sizes decrease further to values less 2 nm [17]. The first emission feature might also become pinned and appear as a broad emission [18].

The origin and mechanism of the pinned emission and fixed excitonic absorption spectra remain controversial. Thus, understanding the origin of the pinned emission is

of technological importance. Meanwhile, the quantum yield of ultrasmall CdSe is only approximately 9% [19]. Lee et al. argued that the fixed conduction band in particles below 1 nm may be attributed to the shifting of an s-state in the bottom of the conduction band to high energy through the quantum confinement effect; meanwhile, hybridized 5p/5s states are unaffected by size [20]. However, the possibility that the surface state is the root cause of the pinned conduction band cannot be discounted. Similarly, Puzder et al. suggested that surface states are responsible for the pinning of the conduction band [21]. Recently, Dukes et al. concluded that the pinned emission is due to a surface state introduced by a phosphoric acid ligand bound to the nanocrystal surface [18]. By contrast, Zanella et al. merely associated the fixed peaks in the absorption spectra with the discontinuous growth of groups II–VI semiconductor nanocrystals [22].

The following similarities were noted among these theories: (i) most of the conclusions are based on chemical-wet methods for binary systems and (ii) the pinned emission/absorbance features are attributed to the effects of the surface states.

Mechanochemical synthesis is a simple method that produces extremely small nanoparticles. In this method, the influence of the surface ligand, particularly that ascribed to the root cause of the surface state by Dukes et al. [18], is completely eliminated.

The aim of this work is to uncover the root cause/effect of pinning in $Cd_{0.3}Zn_{0.7}Se$ nanocrystals synthesized via mechanochemical route.

As far as we know, this study is the first to observe the pinned emission/absorption peaks from nanocrystals synthesized via mechanochemical route. Accordingly, we observe the pinning of the first emission/absorption peaks in nearly all the milled samples.

2. Experimental

The experimental procedure is similar to our previous report [23]. Elemental Cd, Zn, and Se powders with 99.9% purity were separately mixed with nominal composition of $x = 0.7$ sealed with Argon gas in stainless-steel grinding jar containing 3 mm diameter steel balls. The powders were mechanically treated successively with PM100 (Retsch) with ball-to-powder ratio of 10 : 1 for 5 h, 10 h, and up to 20 h. The smallest nanoparticles were extracted by an appropriate size-selection technique [23]. The extracted nanoparticles were deposited on a clean quartz substrate through drop casting to form a homogenous and thin film layer or dissolved in organic solvent and then placed in a quartz cuvette for optical characterization.

Photoluminescence (PL) measurement was performed with a Perkin-Elmer LS-55 luminescence spectrophotometer. The optical spectra were recorded in a UV-vis absorption spectrophotometer (UV-1650PC SHIMADZU JAPAN). Particle size characterization was conducted with the aid of a LEO 912AB transmission electron microscope.

3. Results and Discussion

3.1. Particle Size Analysis.
Image J [24] was used to determine the nanoparticle size distribution. Histograms are calculated

from the transmission electron microscopy (TEM) images of each sample, as shown in Figures 1(a)–1(c). The milled powder has a wide size distribution, and the distribution centers of the samples milled for 5, 10, and 20 h are located at around 3.5, 2.66, and 2.00 nm, respectively. The distribution centers tend to shift toward the small particles upon continuous milling. The relative population of small particles is considerably higher than that of the large particles. The milled powder contains particles with sizes ranging from 1 nm to 10 nm, as shown in Figures 2(a)–2(c). The nanoparticles of the samples milled for 5, 10, and 20 h have mean diameters of 4.0, 3.4, and 2.2 nm, respectively. The TEM images show agglomerates consisting of small particles (approximately 6 nm in size). Average crystallite sizes of 4.9 nm to 13.4 nm were reported by de Lima et al. and Baltazar-Rodrigues et al. in milled ZnSe nanostructures [25, 26]. The agglomeration rate increases with milling time despite the reduction in particle size. In the histograms, we observe long tailing, which implies high level of agglomeration in the nanoparticles. During mechanical attrition, severe plastic deformation crushes the powder into fine particles, which subsequently agglomerate into fairly large aggregates before a steady state is attained. The absence of a stabilizing agent could be a contributing factor for the observed agglomeration.

At high spin rates, mechanical milling provides an enormous amount of rotational energy during the interaction between the balls and grinding jar. This energy ultimately improves the fracture and deformation properties of the nanoparticles. The energy transferred to the powder has a linear dependence on spin rate [27].

3.2. UV-Vis Absorbance Spectroscopy.
Figure 3 provides the room-temperature absorption spectra of the $Cd_{0.3}Zn_{0.7}Se$ nanocrystals. The first excitonic peaks of the samples milled for 5, 10, and 20 h correspond to ≈3.69 eV (335.98 nm), 4.47 eV (277.35 nm), and 4.47 eV (277.35 nm), respectively. The absorption spectra of the samples milled for 10 and 20 h remain fixed with continuous milling despite the reduction in their particle sizes. These spectra show a blue shift with respect to the sample milled for 5 h. We associate the blue shift to the formation of smaller particles. The energy position of the peaks is relatively lower than the values in the CdSe clusters reported in [28]. The band gap absorption increases by 2.3 eV compared with the bulk ($Cd_{0.2}Zn_{0.8}Se = 2.42$ eV) [29] at the end of the milling process. The empirical sizing equation reported by Yu et al. [30] is used to further confirm the particle size. The particle size is determined to be 0.73 nm from the first excitonic peaks of the absorbance spectra.

3.3. PL Spectroscopy.
The room-temperature PL spectra of the samples milled at various times are shown in Figures 4(a)–4(c). A multi-Gaussian line shape (A–D) is used to fit all the emissions. The fitting parameters are displayed in Table 1. After milling for 5 h, an excitonic emission appears at 3.36 eV (369 nm, A), accompanied by three strong peaks centered at 2.90 eV (429 nm, C) with shoulders at 3.02 eV (411 nm, B) and 2.73 eV (453 nm, D). Upon continuous milling for 10 h, the excitonic emission A and shoulder B remain fixed, whereas peaks C and D show a red shift.. The intensity of peak A
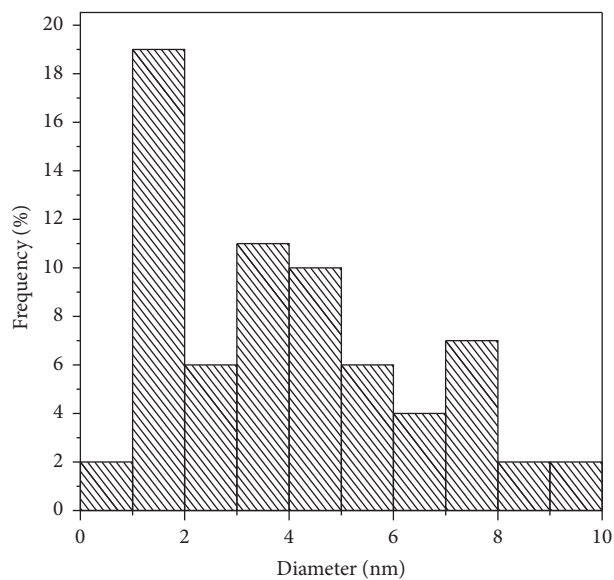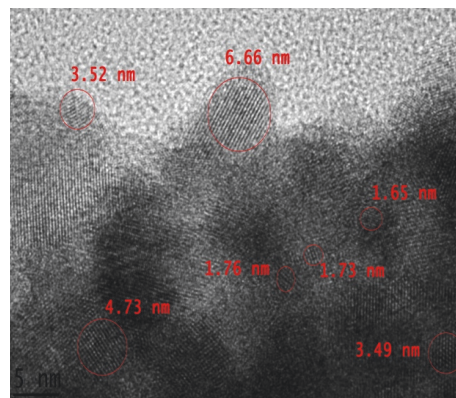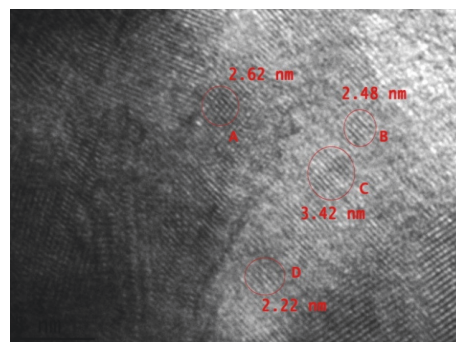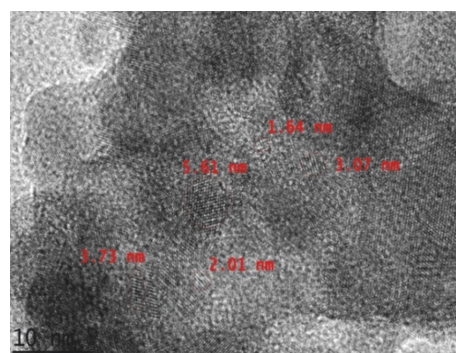
(a)
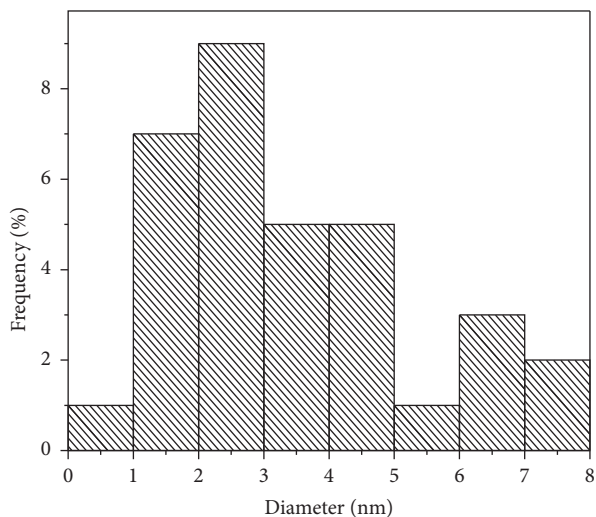
(b)
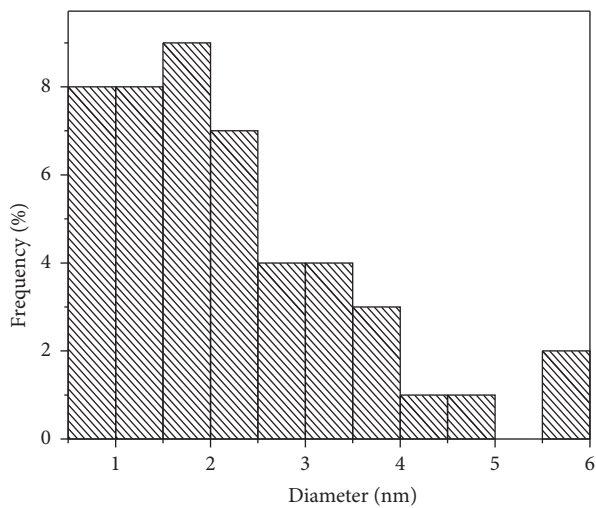
(c)

Figure 1: Histograms for the particle size distributions of the samples milled for 5, 10, and 20 h.

(a)

(b)

(c)

Figure 2: HRTEM images for 5, 10, and 20 h milled samples.

decreases by a factor of three, whereas those of peaks B–D increase with milling time. Similarly, the full width at half maximum (FWHM) of peak A decreases after 20 h.

The first emission peak appears to be a band-edge emission. Thus, it is expected to shift toward a high-energy portion of the spectrum when the milling time increases from 5 h to 20 h. However, as shown in Table 1, the first emission peaks are fixed in the samples milled for 5 and 10 h. Notably, the intensity of the band-edge emission depends on particle size and surface-to-volume ratio of the nanocrystals. Particularly, the surface-to-volume ratio increases with continuous milling because of the decreases in the particle
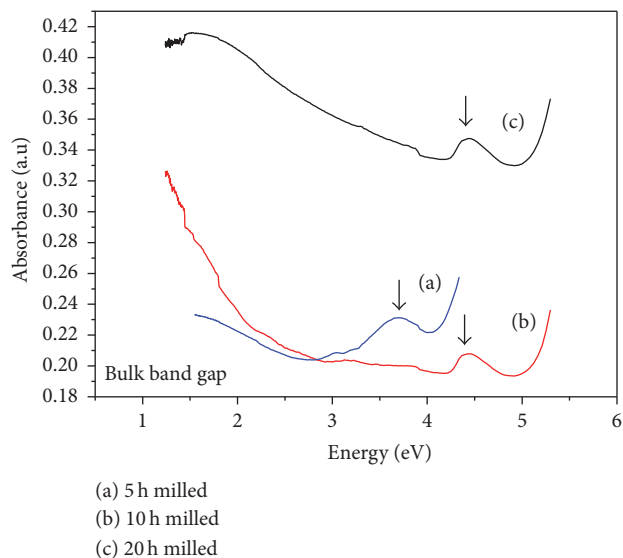
(a) 5 h milled
(b) 10 h milled
(c) 20 h milled

FIGURE 3: Optical spectra of the samples milled for 5, 10, and 20 h. Arrows show the positions of the first excitonic peaks.

sizes. This effect subsequently increases the traps for radiative transitions, thereby causing reduction in the intensity of the first emission peak of 20 h milled sample. The surface-trapping process rate decreases as the particle size increases, thereby lowering the surface-to-bulk ratio [31]. In other words, a large surface-to-volume ratio increases the decay rate.

4. Conclusions

We report an observed pinning of the first emission and excitonic features in ultrasmall nanocrystals synthesized via mechanochemical method in a ternary compound of $Cd_{0.3}Zn_{0.7}Se$ nanocrystals. We attribute the origin of the pinning of the emission and absorption features to the surface defects. Our argument is based on observed reduced PL intensity of the first emission feature with continuous milling. Decrease in particle size is essentially accomplished with increase in surface-to-volume ratio and surface states. The pinning due to surface states does not necessarily have to originate from any ligand binding on the surface of the nanocrystal, as suggested by Dakes et al. Future experiment should focus on methods that can reduce the influence of surface states on ultrasmall nanocrystals.

Conflicts of Interest

The authors declare that they have no conflicts of interest.
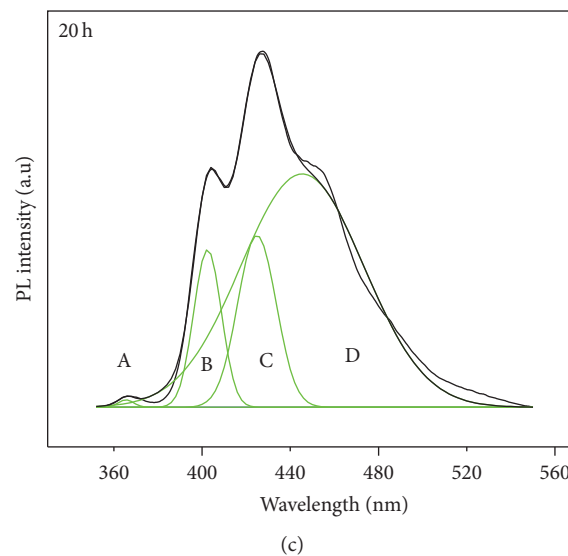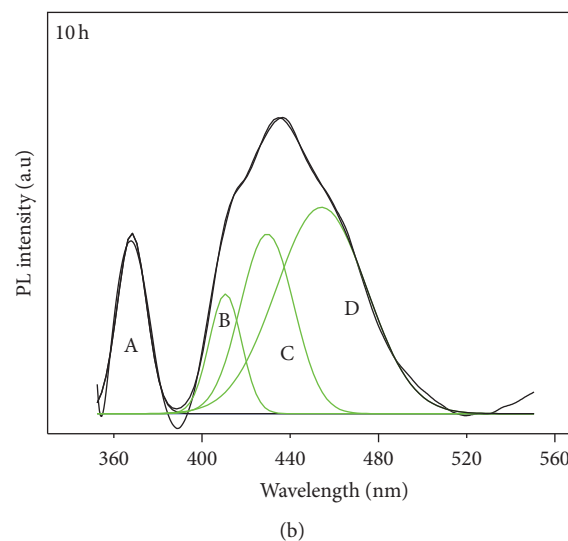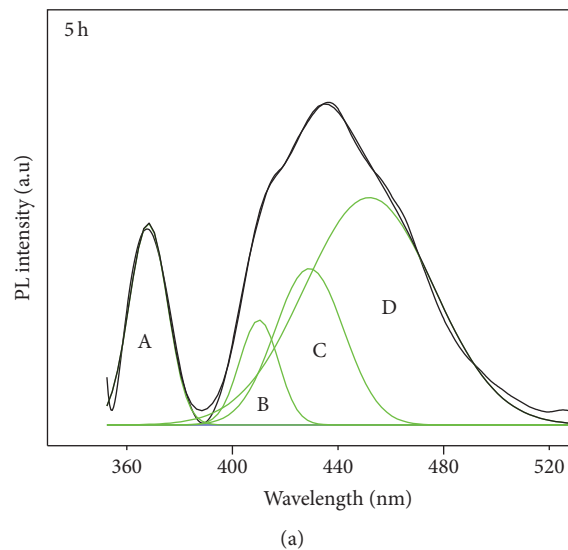
Acknowledgments

(a)

(b)

(c)

FIGURE 4: Room-temperature PL of powders milled for (a) 5, (b) 10, and (c) 20 h.

TABLE 1: Fitting parameters for milled CdZnSe powders.

Peak number	Peak assignment	Center maximum (nm) and (eV)	Maximum height	FWHM
5 h milled				
Peak 1	A	369 (3.36)	48	17.02
Peak 2	B	411 (3.02)	25	17.34
Peak 3	C	429 (2.90)	38	30.78
Peak 4	D	453 (2.73)	55	57.54
10 h milled				
Peak 1	A	369 (3.36)	45	15.60
Peak 2	B	411 (3.02)	30	17.30
Peak 3	C	431 (2.88)	45	28.52
Peak 4	D	455 (2.72)	51	48.32
20 h milled				
Peak 1	A	366 (3.39)	14	8.25
Peak 2	B	402 (3.08)	298	14.74
Peak 3	C	424 (2.92)	324	20.59
Peak 4	D	446 (2.78)	441	65.54

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