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Effect of lateral size and thickness on the electronic structure and optical properties of quasi two-dimensional CdSe and CdS nanoplatelets

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The effect of lateral size and vertical thickness of CdSe and CdS nanoplatelets (NPLs) on their electronic structure and optical properties are investigated using an effective-mass envelope function theory based on the 8-band $\mathbf{k} \cdot \mathbf{p}$ model with valence force field considerations. Volumetrically larger NPLs have lower photon emission energy due to limited quantum confinement, but a greater transition matrix element (TME) due to larger electron-hole wavefunction overlap. The optical gain characteristics depend on several factors such as TME, Fermi factor, carrier density, NPL dimensions, material composition, and dephasing rate. There is a red shift in the peak position, more so with an increase in thickness than lateral size. For an increasing carrier density, the gain spectrum undergoes a slight blue shift due to band filling effect. For a fixed carrier density, the Fermi factor is higher for volumetrically larger NPLs and so is the difference between the quasi-Fermi level separation and the effective bandgap. The transparency injection carrier density (and thus input current density threshold) is dimension dependent and falls for volumetrically larger NPLs, as they can attain the requisite exciton count for transparency with a relatively lower density. Between CdSe and CdS, CdSe has lower emission energy due to smaller bandgap, but a higher TME due to lower effective mass. CdS, however, has a higher *so* hole contribution due to a lower spin-orbit splitting energy. Both CdSe and CdS NPLs are suitable candidates for short-wavelength LEDs and lasers in the visible spectrum, but CdSe is expected to exhibit better optical performance.

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I. INTRODUCTION

Low-dimensional wide-bandgap II-VI semiconductor nanocrystals have received increasing research interest owing to their intriguing fundamental properties that can be leveraged for potential applications in optoelectronic and display devices.^{1–3} They form the active region of semiconductor lasers and light emitting diodes (LEDs) and result in significant performance improvement.³ Recent advances in nanofabrication technology have enabled us to colloiddally synthesize a new class of atomically flat quasi-2D semiconductor nanocrystal called nanoplatelets (NPLs).⁴ Other methods of ultra-thin epitaxial layer growth such as molecular beam epitaxy are generally more complicated, and suffer from process-induced defects deteriorating the crystal quality.¹ Colloidal synthesis, on the other hand, is one of the most cost-effective ways to prepare high quality single-crystal samples.⁵ An isolated ideal NPL has a vertical thickness much less than the lateral edge sizes as illustrated schematically and using a 3D atom-by-atom view of a typical NPL in Fig. 1. NPLs remarkably differ from quantum dots (QDs)—NPLs show strong 1D confinement due to their small thickness (typically few monolayers) compared to the Bohr radius,⁶ while QDs offer 3D confinement to the excitons. Solution processed NPLs also

FIG. 1. ((a) top) NPL schematic representation and ((b) bottom) 3D atom-by-atom view of a typical NPL.

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differ from vacuum-deposited epitaxial quantum wells (QWs) as they have an enhanced splitting between bright and dark excitons due to dielectric confinement⁷ and also exhibit giant oscillator strength.⁸ NPLs possess the wide bandgap tunability of QDs and the short exciton decay time of QWs bringing together advantageous features from two domains.⁹ They have superior optoelectronic properties over QDs, such as reduced Auger recombination and inhomogeneous broadening plus a narrow emission spectra. They are excellent candidates for pure color lasing as NPL lasers have been reported with emission threshold as low as $41 \mu\text{J}/\text{cm}^2$ and photoluminescence full width at half maximum (FWHM) as low as 2 nm .⁴ Recently, for the first time colloidal NPLs have demonstrated the continuous wave laser operation.¹⁰ Similar to QDs, NPLs can find application in photovoltaics,¹¹ photodetectors,¹² laser,¹³ solar cells,¹⁴ etc.

Optoelectronic properties of II-VI semiconductor NPLs are dictated by their electronic bandstructure and band mixing probabilities, which are strongly geometry dependent. Carriers have reduced freedom of movement in such low-dimensional structures, thus significantly modifying the density-of-states and wavefunction distributions.¹⁵ The resulting discrete energy spectrum narrows down the optical transition energy between these states. This characteristic accompanied by increased carrier confinement results in the optical transition matrix enhancement, leading to improved performances in optoelectronic devices.¹⁶ NPLs however have been reported to be characterized by their thickness alone,^{8,17} claiming that they emit at discrete wavelengths depending on atomic-layer thickness. The lateral sizes often vary

among these observations but are commonly neglected. In this work, we study the effect of vertical thickness and lateral size of NPLs in tandem for CdSe and CdS. The findings of this study can enable us to obtain a relatively more continuous tunable emission spectrum rather than discrete wavelength dependent only on thickness.

II. THEORETICAL FRAMEWORK

We have studied CdSe and CdS NPLs in the zincblende phase, assuming they are synthesized colloiddally.⁴ The 3D atom-by-atom model of a typical NPL is shown in Fig. 1(b). In a colloidal solution, they are surrounded by a ligand dielectric medium, which helps to stabilize them and enhances their optical properties by passivating the surface electronic states. For each NPL geometry, we use an effective mass envelope function theory approach based on the 8-band $\mathbf{k} \cdot \mathbf{p}$ method which simultaneously takes into account the nonparabolicity of the coupled conduction band (CB) and valence band (VB) including the orbit-splitting bands to solve its eigenenergy and obtain its electronic structure in the vicinity of the Γ -point of the Brillouin zone. The 8-band Hamiltonian is represented in the Bloch function basis of $|s\rangle \uparrow$, $|11\rangle \uparrow$, $|10\rangle \uparrow$, $|1-1\rangle \uparrow$, $|s\rangle \downarrow$, $|11\rangle \downarrow$, $|10\rangle \downarrow$, $|1-1\rangle \downarrow$ as¹⁸

$$H = \begin{pmatrix} H_{int} & 0 \\ 0 & H_{int} \end{pmatrix} + H_{so} + V_0, \quad (1)$$

where H_{int} is a Hamiltonian with all the k -independent, k -linear, and k -quadratic terms, expressed as

$$H_{int} = \begin{pmatrix} h_{11} & \frac{ip_0(k'_x + ik'_y)}{\sqrt{2}} & ip_0k'_z & \frac{ip_0(k'_x - ik'_y)}{\sqrt{2}} \\ \frac{-ip_0(k'_x + ik'_y)}{\sqrt{2}} & h_{22} & h_{23} & h_{24} \\ -ip_0k'_z & h_{23}^* & h_{33} & h_{34} \\ \frac{-ip_0(k'_x - ik'_y)}{\sqrt{2}} & h_{24}^* & h_{34}^* & h_{44} \end{pmatrix}, \quad (2)$$

where $p_0 = \hbar\sqrt{E_p/2m_e}$ and E_p is the matrix element of Kane's theory. k'_x , k'_y , k'_z are the modified wavevectors. Expressions for Hamiltonian elements (h_{ij}) are given.

$$\begin{pmatrix} k'_x \\ k'_y \\ k'_z \end{pmatrix} = \begin{pmatrix} k_x \\ k_y \\ k_z \end{pmatrix} (I_3 - \varepsilon), \quad (3a)$$

$$h_{11} = E_g - \frac{\hbar^2}{2m_0} \gamma_c (k_x^2 + k_y^2 + k_z^2) + a_c [tr(\varepsilon)], \quad (3b)$$

$$h_{22} = h_{44} = -\frac{\hbar^2}{2m_0} \left[\frac{L' + M'}{2} (k_x^2 + k_y^2) + M' k_z^2 \right] + a_v [tr(\varepsilon)] + \frac{b}{2} [tr(\varepsilon) - 2\varepsilon_{zz}], \quad (3c)$$

$$h_{33} = -\frac{\hbar^2}{2m_0} \left[M' (k_x^2 + k_y^2) + L' k_z^2 \right] + a_v [tr(\varepsilon)] + b [3\varepsilon_{zz} - tr(\varepsilon)], \quad (3d)$$

$$h_{23} = h_{34} = -\frac{\hbar^2}{2m_0} \left[\frac{N' (k_x - ik_y) k_z}{\sqrt{2}} \right] + \sqrt{6} d (\varepsilon_{xz} - i\varepsilon_{yz}), \quad (3e)$$

$$h_{24} = -\frac{\hbar^2}{2m_0} \left[\frac{L' - M'}{2} (k_x^2 - k_y^2) - iN' k_x k_y \right] + \frac{3b}{2} (\varepsilon_{xx} - \varepsilon_{yy}) - i\sqrt{12} d \varepsilon_{xy}, \quad (3f)$$

$$\gamma_c = \frac{m_0}{m_e^*} - \frac{E_p}{3} \left[\frac{3E_g + 2\Delta_{so}}{E_g (E_g + \Delta_{so})} \right], \quad (3g)$$

where E_g is the bulk bandgap, ε is the strain tensor matrix, and b and d are the shear deformation potentials while a_c and a_v are hydrostatic deformation potentials. We have used modified Luttinger parameters, $L' = L - E_p/E_g = (-\hbar^2/2m_0)(\gamma_1 + 4\gamma_2 + 1)$, $M' = M = (-\hbar^2/2m_0)(\gamma_1 - 2\gamma_2 + 1)$ and $N' = N - E_p/E_g = (-\hbar^2/2m_0)(6\gamma_3)$, derived from modified L-K effective mass parameters $\gamma_1, \gamma_2, \gamma_3$ as enlisted in Table I.

We assume that NPLs are periodically arranged in three dimensions, as is the case in typical colloidal solutions or films with the periodicity L_x, L_y, L_z . We expand the basis using plane waves as

$$\Phi_m = \{\Phi_m^j\} (j = 1, 2, \dots, 8), \quad (4a)$$

with

$$\Phi_m^j = \frac{1}{\sqrt{V}} \sum_{n_x, n_y, n_z} a_{m, n_x, n_y, n_z}^j \exp[i(k_{nx}x + k_{ny}y + k_{nz}z)], \quad (4b)$$

where $V = L_x L_y L_z$, $k_{nx} = 2\pi n_x/L_x$, $k_{ny} = 2\pi n_y/L_y$, $k_{nz} = 2\pi n_z/L_z$. n_x, n_y, n_z are the plane wave numbers set in the range ± 3 . j and m are the basis and energy subband indices, respectively.

The atomistic relaxation due to the interatomic interactions is estimated using the valence force field (VFF) model which is a microscopic theory accounting for bond-stretching (2-body interaction) and bond-bending (3-body interaction). The total VFF energy is given by²⁶

$$E = \frac{1}{2} \sum_{i(j)} \frac{3\alpha_{ij}}{8d_{0,ij}^2} \left(|\mathbf{r}_i - \mathbf{r}_j|^2 - d_{0,ij}^2 \right)^2 + \sum_{i(j,k)} \frac{3\beta_{jik}}{8d_{0,ij}d_{0,ik}} \times \left(|\mathbf{r}_i - \mathbf{r}_j| |\mathbf{r}_i - \mathbf{r}_k| - \cos \hat{\theta}_{ijk} \cdot d_{0,ij}d_{0,ik} \right)^2, \quad (5)$$

where i, j , and k index the atoms in the crystal lattice; $d_{0,ij}$ denotes the ideal bond length between atom_{*i*} and atom_{*j*} related to its lattice constant $a_{0,ij}$ as $d_{0,ij} = (\sqrt{3}/4)a_{0,ij}$.²⁷ $\mathbf{r}_i - \mathbf{r}_j$ is the displacement vector between atom_{*i*} and atom_{*j*}. $\hat{\theta}_{ijk}$ is the ideal bond angle between the three atoms (indexed i, j ,

and k), with atom_{*i*} at the vertex. For zincblende structure, $\hat{\theta}_{ijk} = \frac{1}{3}$, α_{ij} is the bond stretching force constant of the i - j bond, and β_{jik} is the bond bending force constant of the j - i - k bond angle, as tabulated in Table I.

The linear optical gain of the NPL active region based on the density-matrix equation is given by²⁸

$$\mathcal{G}(E) = \frac{2\pi e^2 \hbar}{cn_r \varepsilon_0 m_e^2 \Omega} \sum_{c,v} \frac{|\mathcal{P}_{cv}|^2 (f_c - f_v)}{E_{cv}} \times \mathcal{L}_{cv}(E - E_{cv}), \quad (6)$$

where symbols ($e, \hbar, c, n_r, \varepsilon_0, m_e, E$) have standard physical meanings, while Ω is the NPL volume in real space. The sum over spins is accounted by the prefactor 2. Discrete states in the CB and VB are represented by subscripts c and v . The probability of electron occupation in the energy levels E_c and E_v are given by the Fermi distribution functions f_c and f_v , respectively. When $f_c = 1$ (fully occupied upper level) and $f_v = 0$ (fully empty lower level), the gain is maximum. The gain is proportional to the Fermi factor $(f_c - f_v)$ coming from $f_c(1 - f_v) - f_v(1 - f_c)$: the first term accounting for stimulated emission and the second for band-to-band absorption.²⁹ The gain spectra also consider the transition energy broadening (dephasing) accounted by the term $\mathcal{L}_{cv}(E - E_{cv})$ in Eq. (6), as³⁰

$$\mathcal{L}_{cv}(E - E_{cv}) = \frac{\Gamma_{cv}/(2\pi)}{(E - E_{cv})^2 + (\Gamma_{cv}/2)^2}, \quad (7)$$

whose FWHM is Γ_{cv} and polarization dephasing or scattering rate is $\Gamma_{cv}/2\hbar$. The intraband relaxation time τ_s is related to Γ_{cv} by $\Gamma_{cv} = \hbar/\tau_s$. The term $|\mathcal{P}_{cv}|^2$ is the optical transition matrix element (TME)—a measure for the strength of stimulated electron transition between the hole-subband and electron-subband.³¹ It can be calculated as $\mathcal{P}_{cv,i} = \langle \Psi_{c,k} | \mathbf{e}_i \cdot \mathbf{p} | \Psi_{v,k} \rangle$, $i = x, y, z$ where $\mathbf{p}$ is the momentum operator, and $\Psi_{c,k}$ and $\Psi_{v,k}$ are the real electron and hole wavefunctions, respectively.³² Expressions for the $\mathcal{P}_{cv,i}$ along the x, y , and z directions are given below.

$$\mathcal{P}_{cv,x} = \frac{p_0}{\sqrt{2}} \sum_{n_x, n_y, n_z} \left[(a_{v,n_x, n_y, n_z}^2 + a_{v,n_x, n_y, n_z}^4) a_{c,n_x, n_y, n_z}^{1*} + (a_{v,n_x, n_y, n_z}^7 + a_{v,n_x, n_y, n_z}^9) a_{c,n_x, n_y, n_z}^{6*} + (a_{c,n_x, n_y, n_z}^{2*} + a_{c,n_x, n_y, n_z}^{4*}) a_{v,n_x, n_y, n_z}^1 + (a_{c,n_x, n_y, n_z}^{7*} + a_{c,n_x, n_y, n_z}^{9*}) a_{v,n_x, n_y, n_z}^6 \right], \quad (8a)$$

$$\mathcal{P}_{cv,y} = \frac{ip_0}{\sqrt{2}} \sum_{n_x, n_y, n_z} \left[(a_{v,n_x, n_y, n_z}^2 - a_{v,n_x, n_y, n_z}^4) a_{c,n_x, n_y, n_z}^{1*} + (a_{v,n_x, n_y, n_z}^7 - a_{v,n_x, n_y, n_z}^9) a_{c,n_x, n_y, n_z}^{6*} + (a_{c,n_x, n_y, n_z}^{2*} - a_{c,n_x, n_y, n_z}^{4*}) a_{v,n_x, n_y, n_z}^1 + (a_{c,n_x, n_y, n_z}^{7*} - a_{c,n_x, n_y, n_z}^{9*}) a_{v,n_x, n_y, n_z}^6 \right], \quad (8b)$$

$$\mathcal{P}_{cv,z} = p_0 \sum_{n_x, n_y, n_z} \left[a_{v,n_x, n_y, n_z}^3 a_{c,n_x, n_y, n_z}^{1*} + a_{v,n_x, n_y, n_z}^8 a_{c,n_x, n_y, n_z}^{6*} + a_{c,n_x, n_y, n_z}^{3*} a_{v,n_x, n_y, n_z}^1 + a_{c,n_x, n_y, n_z}^{8*} a_{v,n_x, n_y, n_z}^6 \right], \quad (8c)$$

TABLE I. Material parameters of CdSe and CdS.

Parameter	Symbol (unit)	CdSe value	CdS value
Lattice constant ¹⁹	a (Å)	6.052	5.832
Effective electron mass ¹⁹	m_e^* (m_e)	0.12	0.25
Kane matrix element ⁸	E_p (eV)	16.5	21.0
Bulk bandgap ^{19,20}	E_g (eV)	1.732	2.5
Spin-orbit splitting energy ^{21,22}	Δ_{so} (meV)	420	65
Refractive Index ^{20,23}	n_r	2.5	2.529
Luttinger parameters ²⁴	γ_1	3.265	2.721
(Eq. (3))	γ_2	1.162	0.841
	γ_3	1.443	1.152
Deformation potentials	a_c (meV)	-2832.4	-2778.1
	a_v (meV)	1148.7	1608.0
	b (meV)	-1047.6	1091.2
	d (meV)	-3100.0	-3500.0
VFF parameters ²⁵	d_{Cd-X} (Å)	2.6206	2.5253
(X = Se, S)	α_{Cd-X}	35.22	39.63
	$\beta_{Cd-X-Cd}/\beta_{X-Cd-X}$	3.14	3.68

where $p_0 = \langle S|p_x|X \rangle = \langle S|p_y|Y \rangle = \langle S|p_z|Z \rangle$. A higher average of $\mathcal{P}_{cv,x}$ and $\mathcal{P}_{cv,y}$ (TME in the x and y directions) leads to a higher transverse electric (TE) mode optical gain. On the other hand, a higher $\mathcal{P}_{cv,z}$ (TME in the z direction) leads to a higher transverse magnetic (TM) mode optical gain. The TE mode gain is polarized in the x - y plane, while the TM mode gain is polarized along the z direction. The gain spectrum is affected by temperature changes, but in this work we have performed all our simulations for 300 K (room temperature). The material parameters of CdSe and CdS used in this work are tabulated in Table I.

III. RESULTS AND DISCUSSIONS

A. Electronic bandstructure and properties

The thickness and lateral sizes of both CdSe and CdS NPLs are varied to investigate their influence on the electronic bandstructure. Here we have considered only square NPLs i.e., $l = w$ for convenience of understanding and studied NPLs having thickness varying from 4 to 8 monolayers (MLs) and lateral size from 20 nm to as low as 3 nm. The thickness in ML can be converted to nm by computing $\text{ML} \times (a/2)$ where a is the lattice constant of the material in nm. For example: 5 ML CdSe NPL is 1.513 nm thick, while 5 ML CdS NPL is 1.458 nm thick [data in Table I]. Fig. 2 shows the excitonic transition energy (and emission wavelength) between bottom of conduction band (E1) to top of valence band (H1) i.e., E1-H1, and the transition matrix element of E1-H1 for varying sizes and thicknesses of CdSe NPLs. The main plots show the variation as a function of the lateral size of NPLs, while the insets show it as a function of the thickness. With an increase in both size and thickness, there is a red shift in the transition energy (photon emission energy). This shift is gradual for laterally large NPLs, but we observe that for NPLs smaller than 7 nm (~ 4 times the NPL thickness) the emission energy drastically increases. In reality, such small nanocrystals behave more like quantum dots rather than NPLs.

The value of TME for E1-H1 transitions in CdSe NPLs, as shown in Fig. 2(b), increases with an increase in the size and thickness of NPLs. This is because of the highest extent

of electron and hole wavefunction overlap, as we shall subsequently see. We will show that the H1 (top most valence band level) corresponds to heavy hole (hh) in both CdSe and CdS which is s -like. Its overlap extent with E1 (also s -like) determines this TME value, which is expected to be higher for volumetrically larger NPLs.

Fig. 3 shows a comparison between how the E1-H1 emission energy and TME of CdSe and CdS NPLs of identical geometries are affected by their dimensions. CdSe has lower emission energy due to its smaller bandgap. Also, it is marginally more sensitive to size effect as its magnitude of red shift with increasing size is larger. CdSe also has a higher TME as its conduction electrons can strongly couple with the holes. This is because CdSe ($m_e^* = 0.13$) has a lower effective electron mass than CdS ($m_e^* = 0.25$) and thus a more concave dispersion curve relating from $m^* = \hbar^2 (\frac{\partial^2 E}{\partial k^2})^{-1}$. CdSe can serve as a better active region material than CdS. CdS, on the other hand having a wider bandgap, can be an efficient barrier to CdSe in nanoheterostructures.

Comparing Fig. 3(a) with Fig. 3(c), we have two important observations—(i) On doubling the lateral size from 10 nm to 20 nm, the emission energy red shifts by ~ 80 – 100 meV for CdS and CdSe NPLs of 5 ML and 6 ML. But on doubling the thickness from 4 ML to 8 ML, the emission energy red shifts by ~ 300 – 400 meV for CdS and CdSe NPLs of size 15 nm and 20 nm. While drawing this comparison, we have ignored NPLs of size < 7 nm because they are practically QDs. (ii) The difference in emission between 5 ML and 6 ML NPLs in Fig. 3(a) is much greater than that between NPLs of size 15 nm and 20 nm in Fig. 3(c). From these two observations, we see NPLs emissions are considered to be primarily thickness dependent, as it is the most significant geometrical parameter in NPL design. The E1-H1 TME pattern in Fig. 3(b) is consistent with Fig. 3(d) as it increases with an increase in the volume. The s -like electron and hole wavefunction has a larger volumetric overlap with increasing size and thickness. However, a change in thickness affects the TME more than a change in the size, disregarding intentionally NPLs smaller than 7 nm. The increase in E1-H1 TME is ~ 4 – 6 times larger on doubling the thickness from 4 ML to 8 ML as compared to doubling the size from 10 to 20 nm.

FIG. 2. ((a) left) E1-H1 excitonic transition energy (photon emission wavelength) vs. lateral size of NPL, and vs. thickness of NPL (inset); and ((b) right) E1-H1 transition matrix element vs. lateral size of NPL, and vs. thickness of NPL (inset) for CdSe NPLs.

FIG. 3. ((a) top left) and ((b) bottom left) E1-H1 transition energy/wavelength and TME for CdSe and CdS NPLs vs. lateral size; and ((c) top right) and ((d) bottom right) E1-H1 transition energy/wavelength and TME for CdSe and CdS NPLs vs. thickness. Left and right panels are a comparison between size and thickness effects.

This phenomenon can be understood by visualizing the *s*-like E1 and H1 wavefunctions that are like oblate ellipsoids³³ spread in all directions inside the NPL. Its semi-principal axes are determined by the NPL size and thickness. The wavefunction ellipsoid is spread largely in the *x-y* plane, but restricted along the *z* direction. Thus, the differential change on overlap integral for calculating TME would be larger on varying the thickness as compared to varying the lateral size.

Among all the NPL cases studied so far, Fig. 4 shows the electronic bandstructure and the probability in band mixing between conduction electrons and valence heavy holes, light holes, and split off holes for CdSe NPLs of size (a) 15 nm × 15 nm × 5 ML, (b) 20 nm × 20 nm × 5 ML, (c) 15 nm × 15 nm × 6 ML, and (d) 20 nm × 20 nm × 6 ML at 300 K.

This choice is suitable to comparatively study the effect of thickness and size in tandem. We can observe that increasing the thickness from 5 ML to 6 ML red shifts the emission energy by 900 meV, while increasing the lateral size from 15 nm to 20 nm red shifts by only 100 meV. The effective heavy hole (*hh*) mass is much more than the effective electron mass for both CdSe and CdS¹⁹; therefore, the *hh* dispersion curve is much flatter than the conduction dispersion curve. Hence, the first 10 hole levels span only ~10–12 meV, while the first 10 electron levels span ~400–500 meV. The first few hole levels are *hh* dominant, while the *lh* contribution increases later. The band-mixing probabilities depend on the varying extent of coupling between the CB electrons and VB *hh*, *lh*, and *so* holes, and it can be empirically determined for

FIG. 4. Electronic bandstructure and the probability in band mixing between conduction electrons and valence heavy holes, light holes, and split off holes for CdSe NPLs of size (a) 15 nm × 15 nm × 5 ML, (b) 20 nm × 20 nm × 5 ML, (c) 15 nm × 15 nm × 6 ML, and (d) 20 nm × 20 nm × 6 ML. E1-H1 transition energies are indicated.

FIG. 5. Spatial charge density distributions of the first 10 conduction (electron “E”) and valence (hole “H”) bands of CdSe NPL of size $15\text{ nm} \times 15\text{ nm} \times 5\text{ ML}$ at 300 K cut along the x - y plane at $z = 0$ [refer Fig. 1(b)]. hh stands for heavy hole, lh for light hole.

any NPL. But the observed band mixing probabilities for each level directly relates to the aggregate electron and hole wavefunction and associated charge densities.

The spatial charge densities of the first 10 electron and hole states (square of the wavefunction i.e., probability of finding them) for the $15\text{ nm} \times 15\text{ nm} \times 5\text{ ML}$ CdSe NPL at 300 K cut along the x - y plane at $z = 0$ [refer Fig. 1(b)] are shown in Fig. 5. This corresponds to the NPL of Fig. 4(a). The E1 and H1 states are s -like, E2 and H2 are p -like, E3 and H3 are formed by s - p -mixing, and E4 and H4 are d_{xy} -like. E5 and H6 are $d_{x^2-y^2}$ -like, while E6 and H5 are d_{z^2} -like. hh has higher probability in the hole states H1 to H8, while H9 and H10 are lh dominated [see Fig. 4(a)]. In the TE mode, E1-H1 (hh) transition has the highest strength ($\text{TME} = 0.45$), while the second highest transition strength is of the TM mode E1-H9 (lh) transition ($\text{TME} = 0.44$). Both H1 and H9 are s -like and have favorable spatial wavefunction overlap with E1. This is consistent with the notion that the primary peak of a typical CdSe NPL absorption spectra comes from hh , while the secondary peak comes from lh .¹⁷ Spatial charge density distributions for other cases of Fig. 4 can also be obtained which will directly relate to their corresponding band mixing probabilities.

Similar to the four cases of Fig. 4, we have shown the electronic bandstructure and the probability in band mixing for CdS NPLs in Fig. 6. Increasing the thickness from 5 ML to 6 ML red shifts the emission energy by 600 meV (as compared to 900 meV in CdSe, see Fig. 4), while increasing the lateral size from 15 nm to 20 nm red shifts by only 100 meV. Broadly, thickness has a greater impact in both cases, but more in CdSe than CdS. Comparing Figs. 4 and 6, we also see that the first 10 hole levels span ~ 10 – 12 meV in CdSe, but only ~ 6 – 8 meV in CdS. This is due to the heavier effective hole mass property of CdS compared to CdSe, making its dispersion curve even more flatter. The same follows for first 10 electron levels, which span ~ 300 – 400 meV in CdS compared to ~ 400 – 500 meV in CdSe. In the individual band mixing probabilities, CdS has a much higher contribution from split-off holes because its spin-orbit splitting energy is over six times smaller than that of CdSe.^{21,22}

The charge densities of the first ten E and H states of the $15\text{ nm} \times 15\text{ nm} \times 5\text{ ML}$ CdS NPL of Fig. 6(a) are shown in Fig. 7. E1 and H1 are s -like, E2 and H2 are p -like, E3 and H3 have s - p -mixing, E4 and H4 are d_{xy} -like, and E5 and H8 are $d_{x^2-y^2}$ -like. H5, H9, and H10 have varying ratios of hh , lh ,

FIG. 6. Electronic bandstructure and the probability in band mixing between conduction electrons and valence heavy holes, light holes, and split off holes for CdS NPLs of size (a) $15\text{ nm} \times 15\text{ nm} \times 5\text{ ML}$, (b) $15\text{ nm} \times 15\text{ nm} \times 6\text{ ML}$, (c) $20\text{ nm} \times 20\text{ nm} \times 5\text{ ML}$, and (d) $20\text{ nm} \times 20\text{ nm} \times 6\text{ ML}$. E1-H1 transition energies are indicated.

FIG. 7. Spatial charge density distributions of the first 10 conduction (electron “E”) and valence (hole “H”) bands of CdS NPL of size $15\text{ nm} \times 15\text{ nm} \times 5\text{ ML}$ at 300 K cut along the x - y plane at $z = 0$. *hh* stands for heavy hole, *lh* for light hole, and *so* for split-off hole.

and *so* holes. The dominant contributors are 44% *so* (H5), 43% *hh* (H9), and 34% *so* (H10), but others are quite close, so we assign them as *mix*. The E1-H1 transition in TE mode is the strongest ($\text{TME} = 0.43$), followed by TM mode E1-H5 (*lh/so*) transition. The spatial charge density of E and H levels directly relates to their corresponding band mixing probabilities, and they have a fundamental structure. For zincblende semiconductors, the first few H levels are *hh* dominated followed by *lh* and *so* hole. The strongest TE transition comes from E1-H1 both of which are *s*-like, and the second strongest from TM transition from E1- H_n , which is near-*s*-like and *n* is case specific. Besides these, the detailed spatial charge densities and band mixing probabilities need to be empirically determined by calculation for a given NPL.

1. Section highlights

- Both thickness and lateral size have profound impact on the emission energy and TME. Although a differential change in the thickness has a larger impact, the effect of lateral size is also quite significant.
- Due to a larger m_{hh}^* compared to m_e^* in both CdSe and CdS, the *hh* dispersion curve is flatter and hole states are more densely packed in the energy spectrum.
- The spatial charge density relating to the probability in band mixing strongly depends on lateral size and thickness. Material properties determine the *hh*, *lh*, and *so*-hole contributions and *s*-*p*-*d* mixing.

B. Optical gain and properties

We would like to investigate the effect of lateral size and thickness on the optical properties of NPLs. For this, we choose CdSe NPLs, which can be used to fabricate high quality red, yellow, green, and blue laser amplifiers¹³ and other photonic devices. Fig. 8 shows the optical gain spectrum of CdSe NPLs of varying size and thickness as a function of photon emission energy/wavelength. We have studied NPLs of sizes 7, 11, 15, 20 nm having thicknesses of 5 to 8 ML. Within each row, the thickness increases from left to right, while the size is fixed. And within each column, the size increases from top to down, while the thickness is fixed. This allows us to study the effect of both parameters simultaneously. For each NPL case, we have the gain for varying carrier density ranging from 1 to $2.5 \times 10^{19}\text{ cm}^{-3}$. A higher carrier density translates to a higher lasing threshold current density.

The optical gain spectrum depends on several factors such as the TME (depending on E and H wavefunction overlap), carrier density, Fermi factor, NPL dimensions, material, dephasing, and scattering rate among others [Eq. (6)]. Among the cases of Fig. 8, the dephasing rate does not change which is only material (CdSe) dependent. The emission peak position is enlisted for each NPL case in the figure, which relates to the E1-H1 transition results in Fig. 2(a). There is a red shift in the emission wavelength with an increase in both size and thickness. This is because as the volume increases, the quantum confinement reduces and the allowed energy levels come closer. Thus, the E1-H1 transitions occur at lower energy. Among NPLs with same thickness but different lateral sizes, the red shift extent falls with an increase in the size. For example: $\Delta\lambda_{11\text{ nm}-7\text{ nm}}$ is in the range 15–20 nm, while $\Delta\lambda_{15\text{ nm}-11\text{ nm}}$ in 5–6 nm and $\Delta\lambda_{20\text{ nm}-15\text{ nm}}$ around 4–5 nm for the cases studied in Fig. 8. Similarly, among NPLs with same lateral size but varying thicknesses, the red shift extent falls with an increase in the thickness. In our case, $\Delta\lambda_{6\text{ ML}-5\text{ ML}}$ is in the range 19–23 nm, while $\Delta\lambda_{7\text{ ML}-6\text{ ML}}$ in 13–15 nm and $\Delta\lambda_{8\text{ ML}-7\text{ ML}}$ around 8–9 nm. This also goes to show that, broadly, the red shift is more prominent for increasing thickness compared to increasing size. The data obtained also show that volumetrically smaller NPLs are more prone to undergo a peak shift compared to larger NPLs.

However, for any particular NPL case, there is slight blue shift in the emission peak with an increase in the carrier density. When more carriers are injected, they start to occupy electronic states further away from the CB-bottom and VB-top, and the gap between the LUMO and HOMO increases. Excitonic recombinations occurring from such transitions have the emission energy larger than the E1-H1 gap, resulting in a blue shift (also known as band filling effect). We can observe that this effect is more prominent in volumetrically larger NPLs compared to smaller. In larger NPLs, the allowed energy states due to quantum confinement are much closer. When more carriers are injected, there is a higher probability of *near*-E1-H1 transitions to occur. In smaller NPLs, the next higher transition after E1-H1 is much far away which also has a lower TME and therefore does not contribute much.

The maximum optical gain of CdSe NPLs studied in Fig. 8 is presented in Figs. 9(a) and 9(b) for carrier densities 2 and $2.5 \times 10^{19}\text{ cm}^{-3}$. This mainly depends on the TME, Fermi factor, and volume of the NPL. The TMEs of the

FIG. 8. Optical gain spectrum (cm^{-1}) of CdSe NPLs of varying lateral sizes (7, 11, 15, 20 nm) and thickness (5, 6, 7, 8 ML) for varying injection carrier density ($1.0, 1.5, 2.0, 2.5 \times 10^{19} \text{ cm}^{-3}$) at 300 K. Left to right is increasing thickness, while top to down is increasing size. Carrier densities and E1-H1 emission peak positions are indicated.

CdSe NPL cases studied were presented in Fig. 2(b). It was found to be higher for larger and thicker NPLs due to higher absolute E and H wavefunction overlap. The other important parameter is the Fermi factor as shown in Figs. 10(a) and

10(b) for the corresponding carrier densities. The Fermi factor also has a positive co-relation with size and thickness and increases with their increment. But the Fermi factor increases more rapidly for smaller NPLs compared to larger

FIG. 9. Maximum optical gain of CdSe NPLs at 300 K with carrier density ((a) top left) $2 \times 10^{19} \text{ cm}^{-3}$ and ((b) bottom left) $2.5 \times 10^{19} \text{ cm}^{-3}$; and differential optical gain of CdSe NPLs at 300 K with carrier density ((c) top right) $2 \times 10^{19} \text{ cm}^{-3}$ and ((d) bottom right) $2.5 \times 10^{19} \text{ cm}^{-3}$. Dimensions of NPLs are indicated.

FIG. 10. Fermi factor of CdSe NPLs at 300 K with carrier density ((a) *top left*) $2 \times 10^{19} \text{ cm}^{-3}$ and ((b) *bottom left*) $2.5 \times 10^{19} \text{ cm}^{-3}$; and ((c) *right*) transparency carrier density ($\times 10^{19} \text{ cm}^{-3}$) of CdSe NPLs at 300 K. Dimensions of NPLs are indicated.

NPLs as it approaches towards unity. Broadly, it is higher for a higher carrier density. With an increase in the carrier density, the difference between the quasi-Fermi level separation and the effective bandgap increases more rapidly for volumetrically larger NPLs compared to smaller. Finally, from Eq. (6), the gain (thus maximum gain) is inversely proportional to the NPL volume in real space. Combining the effects of these three parameters, we obtained the results as shown in Figs. 9(a) and 9(b). The 7 nm CdSe NPL is seen to have a higher maximum gain over the 11 nm NPL in some cases owing to its lower volume, which overcomes the counteractive effect of lower TME and Fermi factor. NPLs smaller than this practically have QD-like nanocrystal properties. In the case of $2.5 \times 10^{19} \text{ cm}^{-3}$, the maximum gain of 20 nm CdSe NPL dips after 6 ML thickness. We can see that, by this stage, the Fermi factor had almost reached saturation [Fig. 10(b)]. For even larger NPLs, such high density leads to carrier occupation of levels not contributing much to the *near*-E1-H1 transitions. The reduction of the maximum gain can therefore be attributed to the aforementioned phenomenon. Another interesting aspect of optical properties of semiconductors is the differential gain, which is a measure of the effectiveness of a laser to transform injected carriers to photon emission. A higher differential gain corresponds to a narrower spectral emission width and a greater speed of modulation.^{34,35} The differential gain for the corresponding cases of Figs. 9(a) and 9(b) is shown in Figs. 9(c) and 9(d). It is smaller for higher density, which is expected as we approach saturation. It is also found to be decreasing with increasing NPL thickness.

Finally, we study the transparency condition³⁶ for NPLs. It tells us which carrier density gives us zero gain—a density higher than that would yield a gain, while a lower density would result in absorption. NPLs with a smaller volume need a higher density to attain the number of excitons required for transparency, while volumetrically larger NPLs can attain the transparency condition exciton count with a

significantly lower density. This can be clearly understood from Fig. 10(c). The photon wavelength for transparency is same as the emission wavelength of the NPL at the onset of gain with a density just above the transparency density.

Similar studies on gain spectrum, maximum gain, and Fermi factor were conducted for CdS NPLs. But in Fig. 11, we have shown only the gain spectrum of CdS NPLs with lateral size 11 and 15 nm, and thickness varying from 5 to 8 ML. Broad observations concerning the effect of size and thickness concur with those observed for CdSe. However comparing the optical performance of CdSe and CdS NPLs, we have found that for geometrically identical NPLs with the same carrier density, CdS NPLs have a lower gain spectrum, maximum gain, and a lower Fermi factor. CdS needs higher carrier density than CdSe to obtain a near identical gain. The E1-H1 peak positions of the CdS NPL gain spectrum are marginally less affected by dimension change as can be understood by observing Figs. 8 and 11. For CdS NPLs, $\Delta\lambda_{6\text{ML}-5\text{ML}}$ is in the range 9–10 nm, while $\Delta\lambda_{7\text{ML}-6\text{ML}}$ in 4–5 nm and $\Delta\lambda_{8\text{ML}-7\text{ML}}$ around 2–3 nm, which is much lower than that of its CdSe counterpart. From Fig. 3, we have also seen that CdS has a lower TME. Also, the higher effective mass of CdS lowers its carrier mobility compared to CdSe. It also has a higher bandgap; thus, geometrically identical CdS NPLs have lower emission wavelength than CdSe NPLs.

1. Section highlights

- Increment in thickness and size causes red shift in peak position. Although thickness has a greater impact, but similar % variations in the lateral size also incurs comparable extent of red shift. Thus, lateral size is an important parameter in the study of optical properties of NPLs.
- The gain is dependent on several parameters including Fermi factor and TME among others. NPL volume (i.e.,

FIG. 11. Optical gain spectrum (cm^{-1}) of CdS NPLs of varying lateral sizes (11, 15 nm) and thickness (5, 6, 7, 8 ML) for varying injection carrier density (1.0 , 2.5 , 4.0 , $5.5 \times 10^{19} \text{ cm}^{-3}$) at 300 K. Left to right is increasing thickness, while top to down is increasing size. Carrier densities and E1-H1 emission peak positions are indicated.

both thickness and size) also plays an important role to determine the overall optical performance.

- The transparency carrier density requirement goes down with increasing thickness and size of NPL.

IV. SUMMARY AND CONCLUSION

A comprehensive study of the electronic bandstructure, band mixing probability, charge densities, optical transitions, and gain of quasi two-dimensional colloidal CdSe and CdS NPLs in the zincblende phase is performed as a function of vertical thickness and lateral size.

Section Highlights in Section III emphasizes on some key results. Variations in size, thickness, and material significantly affect the energy levels, optical gain, etc. There is a red shift in the gain peak position as we move from CdS to CdSe. For geometrically identical NPLs, CdSe has lower photon emission energy because of its lower bandgap. However, it has a higher TME due to its relatively lower effective electron mass. CdS has a much higher contribution from split-off holes because its spin-orbit splitting energy is over six times smaller.

For any given NPL, an increase in carrier density leads to the band filling effect. The peak gain increases due to an increase in the Fermi factor. But for a fixed carrier density, the Fermi factor is higher for volumetrically larger NPLs. Incidentally, volumetrically larger NPLs need smaller injection carrier density to surpass absorption and transparency and produce gain. Thus, the overall gain characteristics are determined by a sum effect of all these influencing factors.

On the whole, the choice of material and dimension of NPLs must be made while optimizing the performance for a desired application. The often neglected lateral size parameter of NPL was found to be of significant importance affecting the bandstructure and band mixing probabilities. It also contributes to the optical gain positions and magnitude. Therefore, it is recommended that both lateral size and thickness must be carefully considered for NPL device designs

and applications for a precise estimation of the performance characteristics.

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