Numerical study of exciton states of core-shell CdTe/CdS nanotetrapods by using COMSOL Multiphysics

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Colloidal quantum dots (QDs)

Five different QD solutions are shown excited with the same long-wavelength UV lamp; the size of the nanocrystal determines the color. (from HP of “invitrogen” )

Colloidal QDs are synthesized from precursor compounds dissolved in solutions. (Chemical processes)
Application of colloidal QD

- Infrared detector, sensor
- QD electroluminescence device
- Solar cell
- Luminescent marker

CdSe QDs are injected into a mouse, and fluoresce under UV-light. Mark the location of cancer tumour. (from National Geographic)

Colloidal QD light-emitting device pixels
P.O. Anikeeva, et al.
(Nano Lett., 9, 2532, 2009)
Shape control of colloidal QD

Spherical QD   nanorod   nanotetrapod


Proposed model of a CdTe tetrapod

CdTe/CdS core-shell tetrapods

- With continuously grown CdS shell on CdTe tetrapod, features of type II heterostructures were observed in experiment, e.g. featureless absorption tail @ $t=1.2$ nm
- Study the influence of CdS shell on the exciton state, consequently the optical properties of core-shell tetrapod

Cross-section of one branch

CdTe(ZB) Core
CdTe(WZ) Arm
CdS shell $t$

$t=$CdS shell thickness

Theoretical model

(1) **Single particle Schrodinger equation** (Effective-mass approximation)
Solved with finite element method by using **COMSOL software**

\[ \Psi_i(r_i) = \varphi_i(r_i)u_i(r_i) \quad i = \text{e or h} \]

\[ \varphi_i \] is the envelope function and \( u_i \) is the atomic wave function

\[ H_i(r_i)\varphi_i(r_i) = \left\{ -\frac{\hbar^2 \Delta_i}{2m_i^*} + V_i(r_i) \right\} \varphi_i(r_i) = E_i\varphi_i(r_i) \]

Consider the lowest 20 electron and 20 hole states, whose wave functions only have \[ \text{A1} \] or \[ \text{T2} \] symmetry

(2) **Two-body Schrodinger equation**
Solved with configuration interaction method

\[ \Psi(r_e, r_h) = \sum_{i,j} a_{i,j} \varphi_e^{(i)}(r_e)\varphi_h^{(j)}(r_h), \]

\[ \left( H_e + H_h - \frac{e^2}{4\pi\varepsilon_0\varepsilon |r_e - r_h|} \right) \Psi(r_e, r_h) = E_X\Psi(r_e, r_h) \]

Same method as: **K. Sakoda et al., Opt. Mat. Express 1, 379 (2011).**
Lowest electron state(e1) and highest hole state(h1) wave function distribution

t=0 (nm)  t=0.1  t=0.2  t=0.3  t=0.6  t=0.9  t=1.2
Single-particle state e1&h1 overlap integral

Overlap integral

Shell thickness (nm)

e-h NOT totally separated

type II heterostructure NOT apparent
Shell thickness dependence of exciton energy with A1 and T2 symmetry

[Graph showing exciton energy (eV) vs. shell thickness (nm) with different symmetries A1, T2-1, T2-2, T2-3.]
Analytical calculation (1)

Constructed electron wave function, combination of 4 independent wave function on each branch

\[ \psi_{A1} = \frac{1}{2} (\phi_1 + \phi_2 + \phi_3 + \phi_4), \]
\[ \psi_{T2}^{(1)} = \frac{1}{2} (\phi_1 + \phi_2 - \phi_3 - \phi_4), \]
\[ \psi_{T2}^{(2)} = \frac{1}{2} (\phi_1 - \phi_2 + \phi_3 - \phi_4), \]
\[ \psi_{T2}^{(3)} = \frac{1}{2} (\phi_1 - \phi_2 - \phi_3 + \phi_4), \]

Two-body matrix element

\[ \langle k\ell|H_2|ij\rangle = \langle kj|H_2|il\rangle - 2\langle jk|H_2|il\rangle, \]

In which matrix element

\[ \langle kj|H_2|il\rangle = - \int dr_1dr_2 \psi_h^{(j)*}(r_2)\psi_e^{(k)*}(r_1) \]

\[ \times \frac{e^2}{\epsilon_0\epsilon|r_1 - r_2|} \psi_e^{(i)}(r_1)\psi_h^{(l)}(r_2) \]

@ \textbf{t=1.2 nm}, the order of lowest 4 exciton states NOT change.

Safe to choose only lowest 4 pair states for analytical calculation. (e1h1, e2h1, e3h1, e4h1)
Analytical calculation (2)

Diagonal matrix element

(A) Coulomb integral
same value for 4 diagonal elements

(B) exchange interaction integral (e1h1)

\[-2\langle j i | H_2 | i j \rangle = 2 \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{e_0^2}{2\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \]
\[\times [\phi_1(r_1) + \phi_2(r_1) + \phi_3(r_1) + \phi_4(r_1)] \varphi_{h1}(r_1)\]
\[\times [\phi_1(r_2) + \phi_2(r_2) + \phi_3(r_2) + \phi_4(r_2)] \varphi_{h1}(r_2)\]

Off-diagonal matrix element

(A) direct Coulomb integral
All off-diagonal elements for direct Coulomb integral are zero

(B) exchange interaction integral
All off-diagonal elements for exchange interaction integral are zero

Conclusion of analytical calculation:
The symmetry of lowest exciton state (t=1.2 nm) is T2
Symmetry break in core-shell tetrapod

For the imperfect cs-tetrapod, oscillator strength of the lowest-energy exciton state is NOT zero

Modification: one Arm with thicker shell

Modification: one thicker arm
Conclusion

- The electronic states of core-shell tetrapod with various shell thickness are calculated. Lowest 20 electron and hole wave functions have A1 or T2 symmetry.
- At \( t=1.2 \) nm, the carriers separation is not serious, core-shell tetrapod is not apparent type II heterostructure.
- Exciton states were investigated as a function of \( t \). For large \( t \), the lowest exciton state has T2 symmetry, which implies nonluminescence in emission spectrum.
- Core-shell tetrapod with broken symmetry shows non-zero oscillator strength for lowest exciton state.

Thank you for your attention!