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

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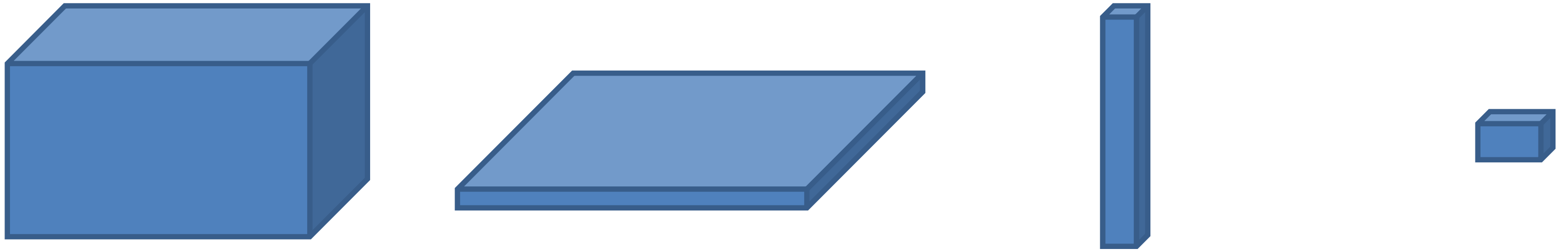
Colloidal quantum dots (QDs)



3D
(Bulk)

2D
(Quantum Well)

1D
(Quantum Wire)

0D
(Quantum Dot)

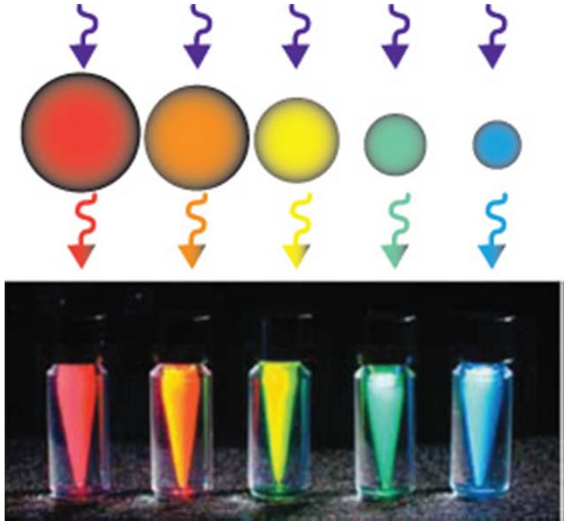
Colloidal QDs

are synthesized from

precursor compounds

dissolved in solutions.

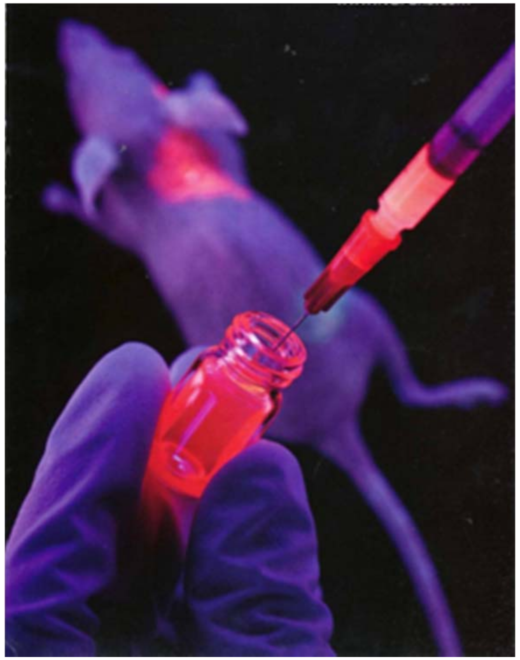
(Chemical processes)



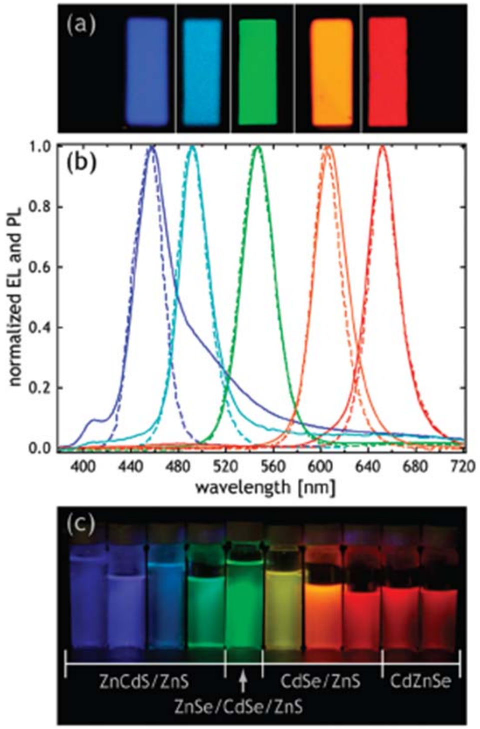
Five different QD solutions are shown excited with the same long-wavelength UV lamp; the size of the nanocrystal determines the color.
(from HP of “invitrogen”)

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)

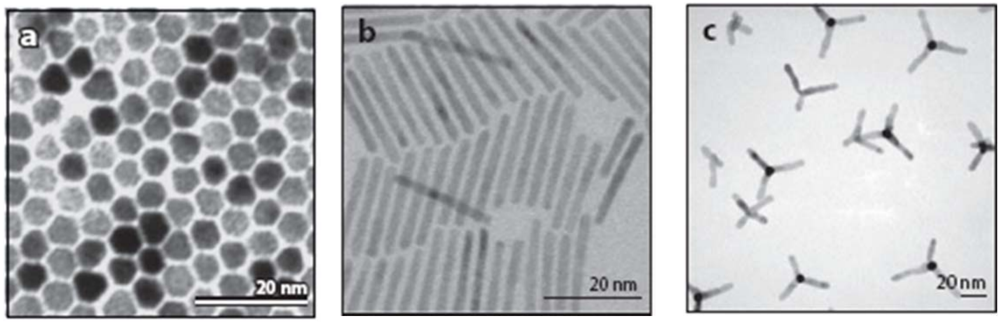
Shape control of colloidal QD

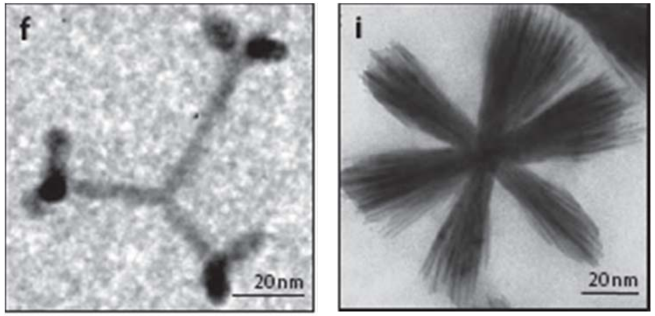
Colloidal QD

Spherical QD

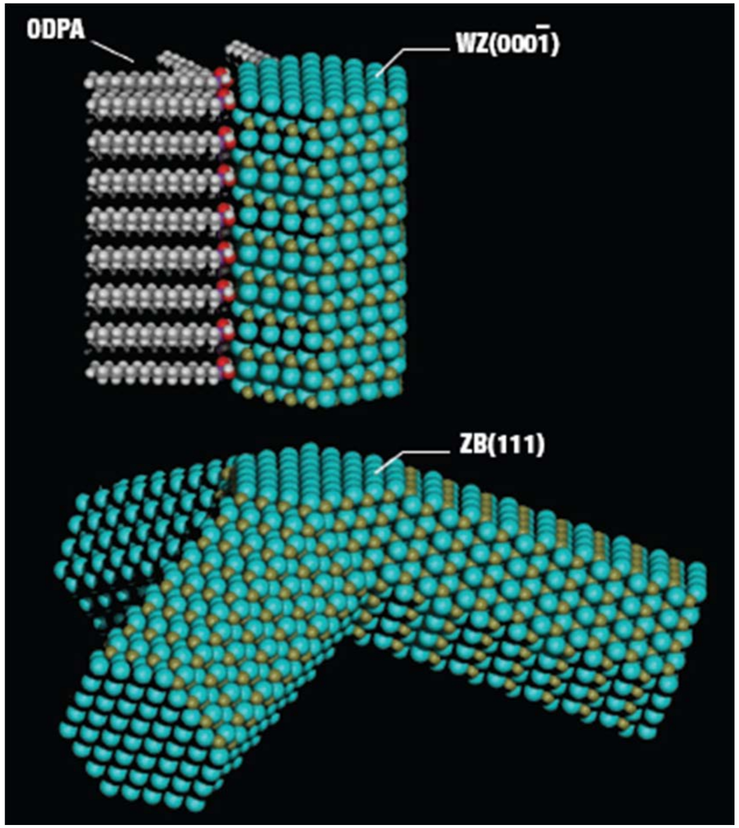
nanorod

nanotetrapod





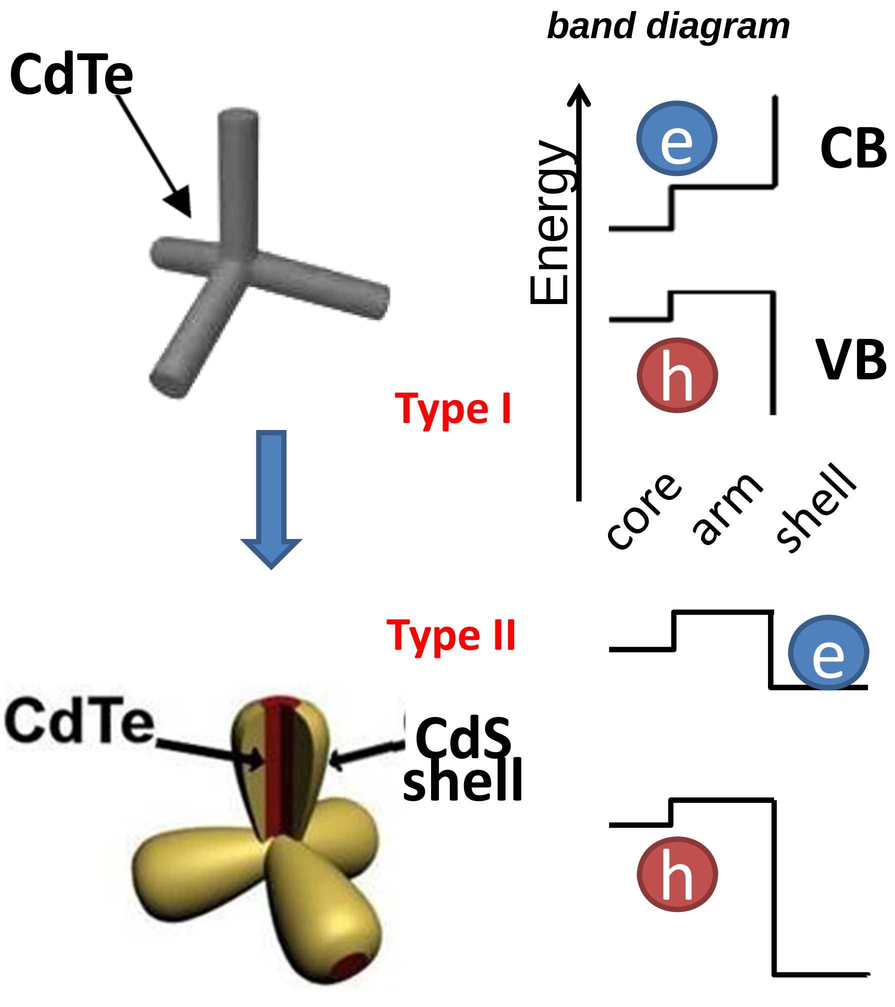
L. Choi, et al.,
Annu. Rev. Phys. Chem.
61, 369, 2010



Proposed model of a CdTe tetrapod

L. Manna, et al.
Nature materials, vol.2, 382 (2003)

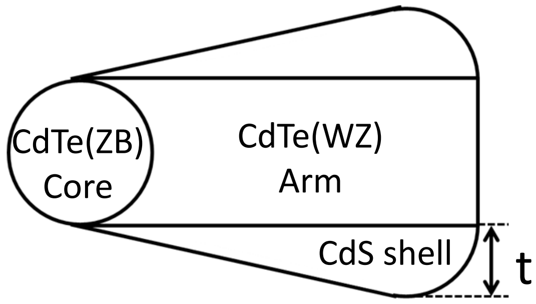
CdTe/CdS core-shell tetrapods



R. B. Vasiliev, et al. Mendeleev Commun. 19, 128 (2009)

- 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



t=CdS shell thickness

Theoretical model

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

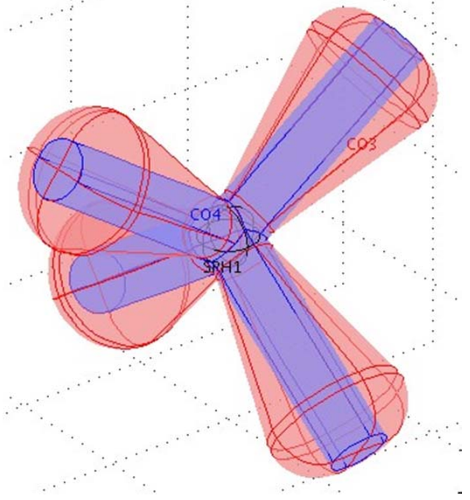
nice tool for modeling QD with complicated geometry

$\Psi_i(r_i) = \varphi_i(r_i) u_i(r_i)$ i= e or h

φ_i is the envelope function and u_i is the atomic wave function

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

Consider the lowest 20 electron and 20 hole states, whose wave functions only have **A1** or **T2** symmetry



3D model of CdTe/CdS core-shell tetrapod

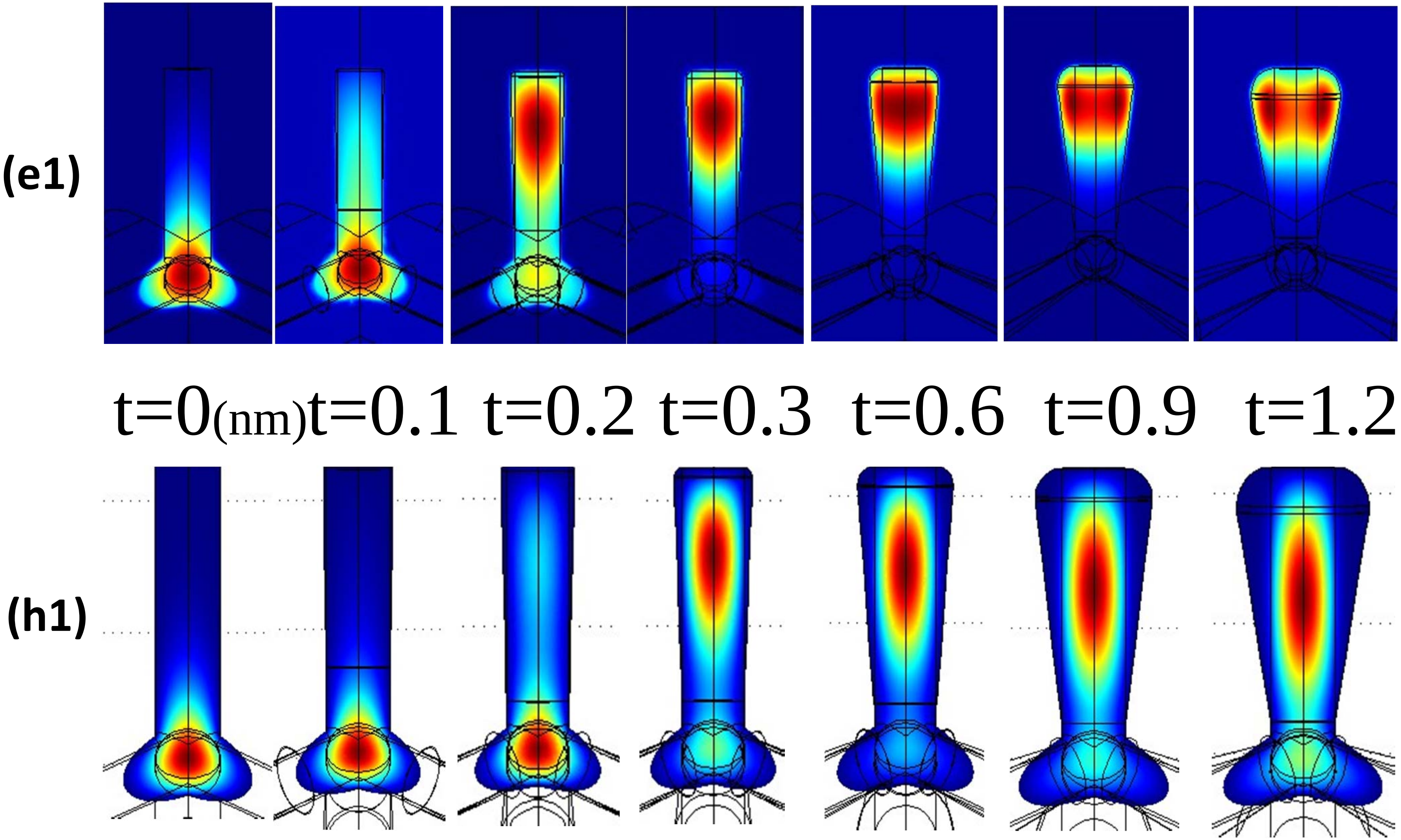
(2)**Two-body Schrodinger equation**
Solved with configuration interaction method

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

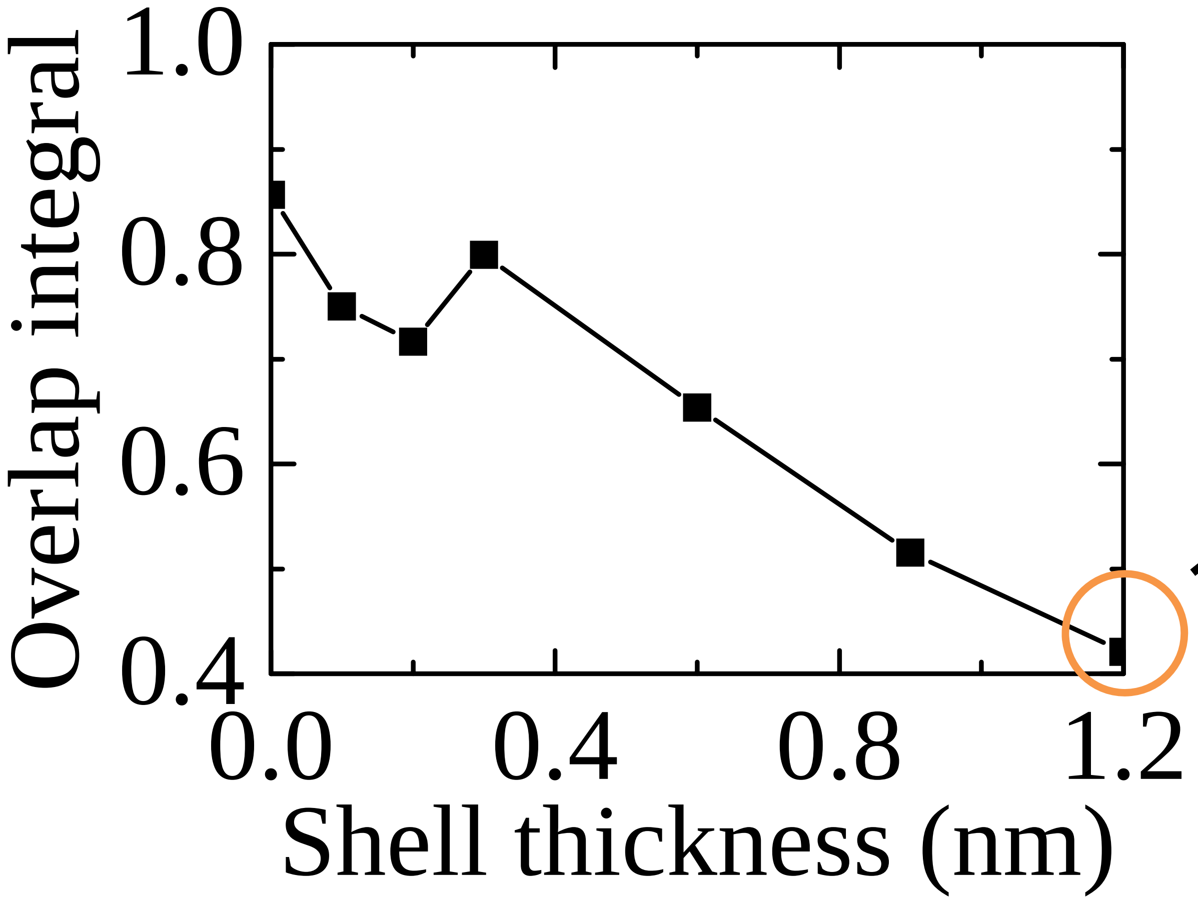
$$\left(H_e + H_h - \frac{e_0^2}{4\pi\epsilon_0\epsilon\,|r_e - r_h|}\right)\Psi(r_e, r_h) = E_X\Psi(r_e, r_h)$$

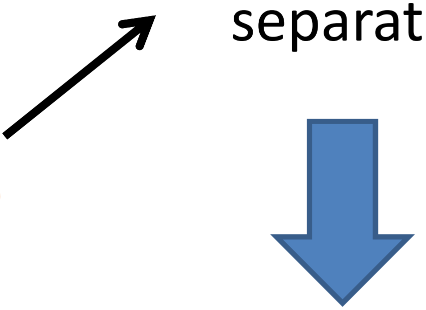
Same method as: **K. Sakoda et al., Opt. Mat. Express <u>1</u>, 379 (2011).**

Lowest electron state(e1) and highest hole state(h1) wave function distribution



Single-particle state e1&h1 overlap integral

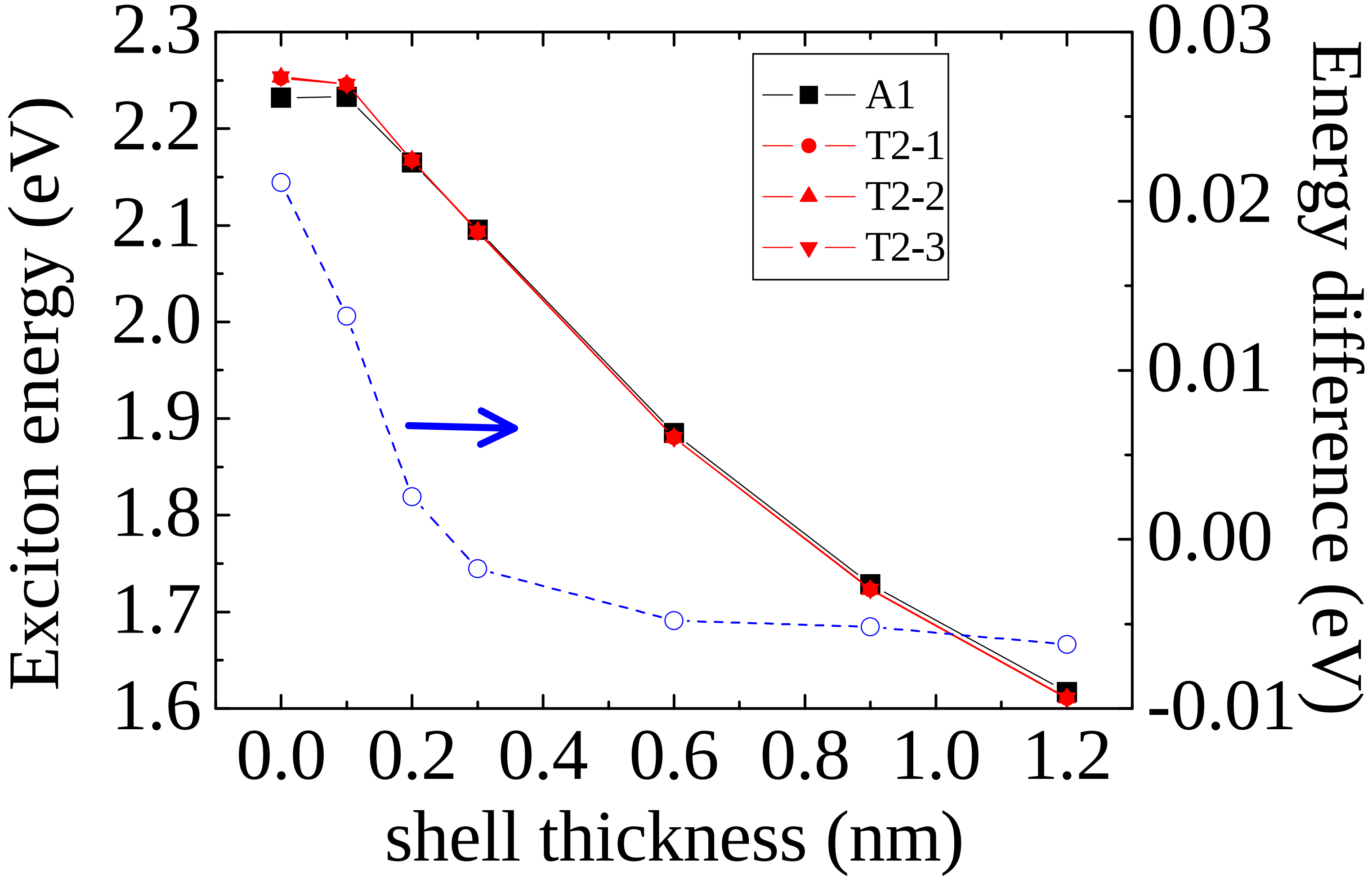




e-h NOT totally separated

type II heterostructure NOT apparent

Shell thickness dependence of exciton energy with A1 and T2 symmetry



Analytical calculation (1)

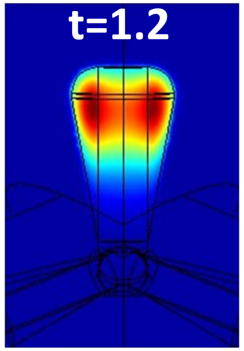
Constructed electron wave function, combination of 4 independent wave function on each branch

$$\varphi_{A1} = \frac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4), \quad (1)$$

$$\varphi_{T2}^{(1)} = \frac{1}{2}(\phi_1 + \phi_2 - \phi_3 - \phi_4), \quad (2)$$

$$\varphi_{T2}^{(2)} = \frac{1}{2}(\phi_1 - \phi_2 + \phi_3 - \phi_4), \quad (3)$$

$$\varphi_{T2}^{(3)} = \frac{1}{2}(\phi_1 - \phi_2 - \phi_3 + \phi_4), \quad (4)$$

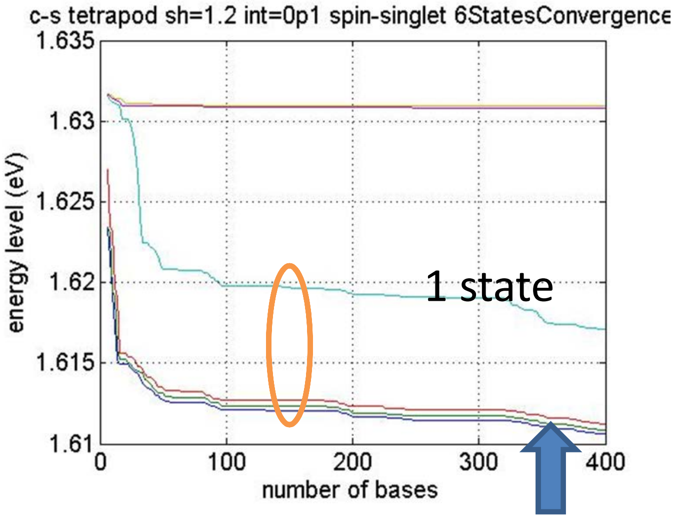


two-body matrix element

$$\langle kl(s)|H_2|ij(s)\rangle = \underbrace{\langle kj|H_2|il\rangle}_{\text{direct Coulomb}} - 2\underbrace{\langle jk|H_2|il\rangle}_{\text{exchange interaction}}, \quad (5)$$

In which matrix element

$$\langle kj|H_2|il\rangle = -\int\int dr_1 dr_2 \varphi_h^{(j)*}(r_2)\varphi_e^{(k)*}(r_1) * \frac{e_0^2}{\epsilon_0\epsilon|r_1 - r_2|}\varphi_e^{(i)}(r_1)\varphi_h^{(l)}(r_2) \quad (6)$$



3 degenerated states

@ **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)

$$-2\langle ji|H_2|ij\rangle = 2\int\int dr_1 dr_2 \frac{e_0^2}{\epsilon_0\epsilon|r_1-r_2|}\frac{1}{4}$$

$$*\left[\phi_1(r_1)+\phi_2(r_1)+\phi_3(r_1)+\phi_4(r_1)\right]\varphi_{h1}(r_1)$$

$$*\left[\phi_1(r_2)+\phi_2(r_2)+\phi_3(r_2)+\phi_4(r_2)\right]\varphi_{h1}(r_2)$$

exchange interaction integral (e2h1, e3h1, e4h1)

$$-2\langle ji|H_2|ij\rangle = 2\int\int dr_1 dr_2 \frac{e_0^2}{\epsilon_0\epsilon|r_1-r_2|}\frac{1}{4}$$

$$*\left[\phi_1(r_1)+\phi_2(r_1)-\phi_3(r_1)-\phi_4(r_1)\right]\varphi_{h1}(r_1)$$

$$*\left[\phi_1(r_2)+\phi_2(r_2)-\phi_3(r_2)-\phi_4(r_2)\right]\varphi_{h1}(r_2)$$

diagonal element of e1h1(A1) is larger than other three(T2)

Off-diagonal matrix element

(A)direct Coulomb integral

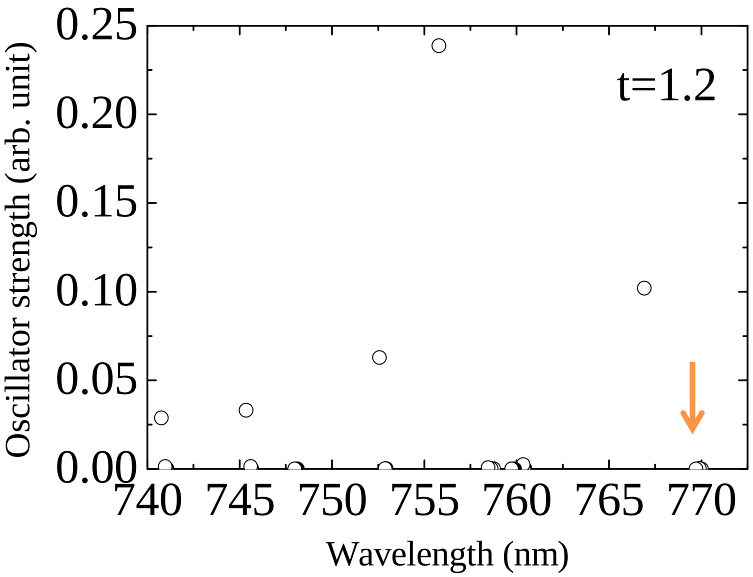
All off-diagonal elements for direct Coulomb integral are zero

(B) exchange interaction integral

All off-diagonal elements for exchange interaction integral are zero

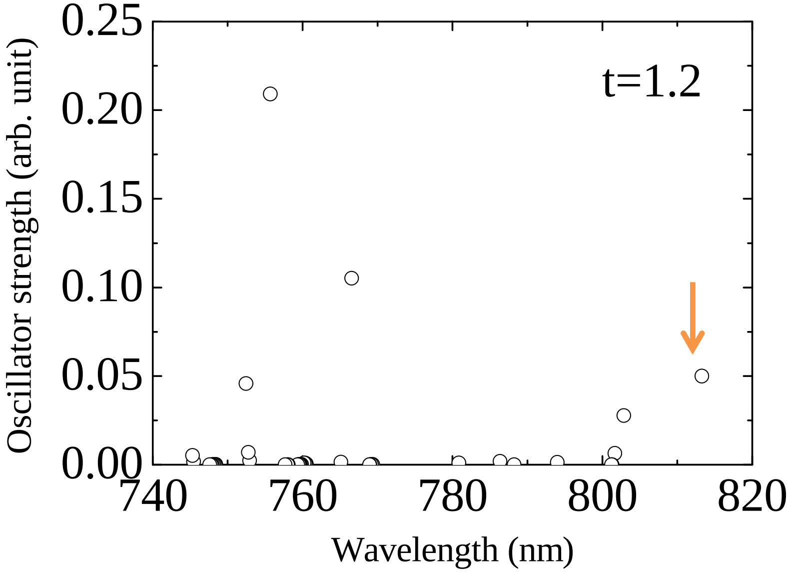
Conclusion of analytical calculation:
The symmetry of lowest exciton state (t=1.2 nm) is T2

Symmetry break in core-shell tetrapod

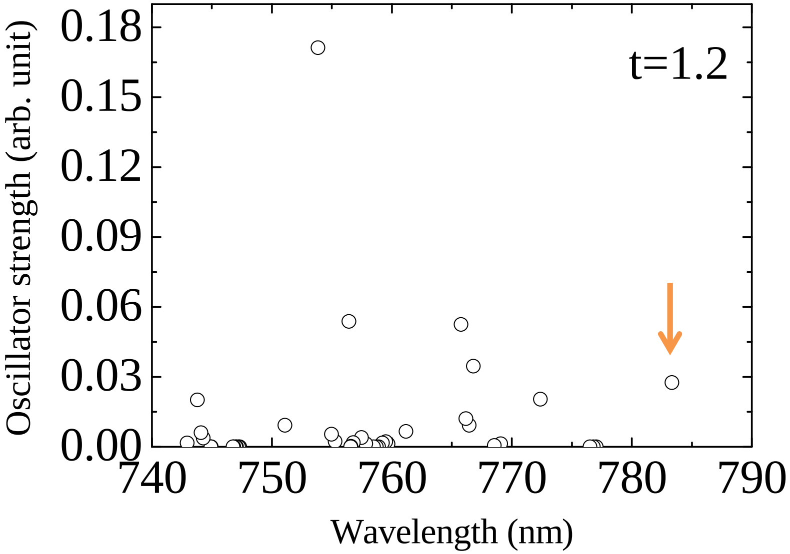


For the imperfect cs-tetrapod, oscillator strength of the lowest-energy exciton state is NOT zero

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 implys nonluminescence in emission spectrum.
- Core-shell tetrapod with broken symmetry shows non-zero oscillator strength for lowest exciton state.

Thank you for your attention!