Photo and Dark Conductivity in Ordered Array of Nanocrystals

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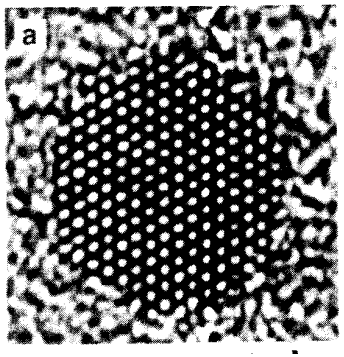
[*] Andrew Shabaev, Alexander L. Efros, and Alexei L. Efros, Nano Lett. **13**, 5454 (2013)

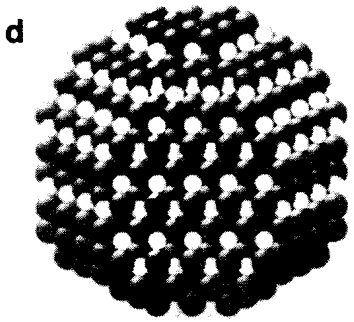
Semiconductor Nanocrystals

Arrays of Nanocrystals are most heavily studied nano-scale semiconductors ! [A. Ekimov (1981) in semiconductor doped glasses and L. Brus (1983) in colloidal solutions, First theory of growth and optical properties :Al. L Efros and A. L. Efros (1982]

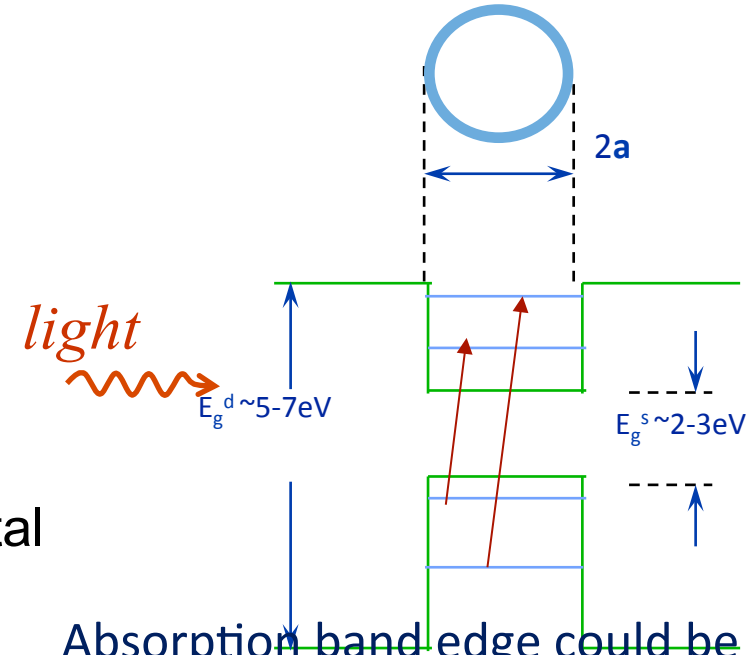
In May 26 of 2014 a special in Paris with the title "30 years of quantum dots" .

Nanocrystals:





TEM image of a bare CdSe nanocrystal



Absorption band edge could be shifted up to ~1 eV

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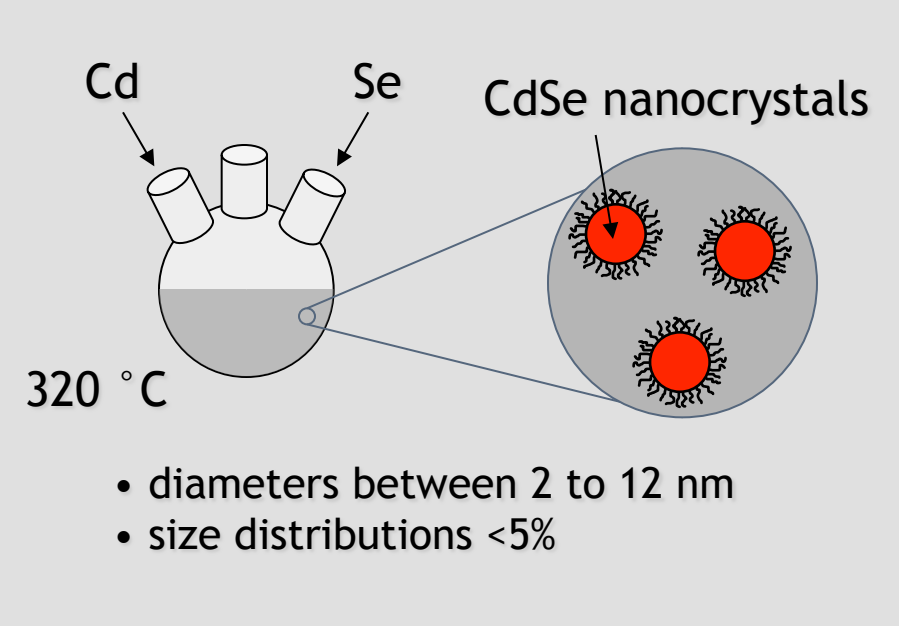
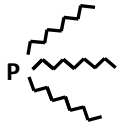
Colloidal Semiconductor Quantum Dots (Nanocrystals):

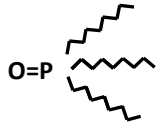


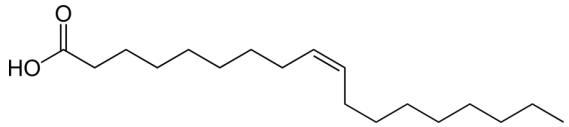
Murray, Norris, Bawendi; JACS **115**, 8706 (1993).

Liquid-phase synthesis:

- Crystallites of semiconductor
- Coated with surfactants:
  trioctylphosphine (TOP)
  trioctylphosphine oxide (TOPO)

TOP: 

TOPO: 

oleic acid: 

CdSe is the most heavily studied colloidal semiconductor nanocrystal

Size-Dependent Optical Properties

Fluorescence

CdSe nanocrystals

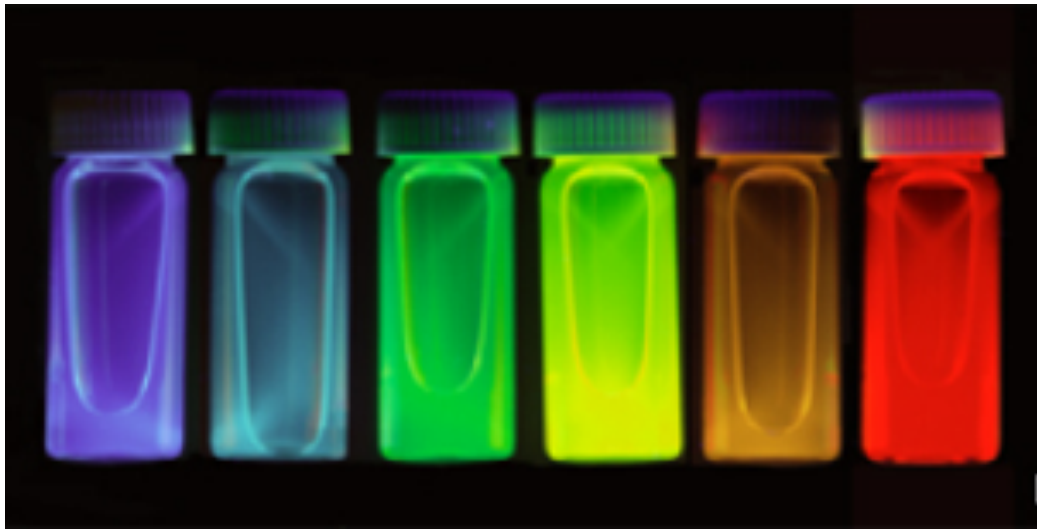


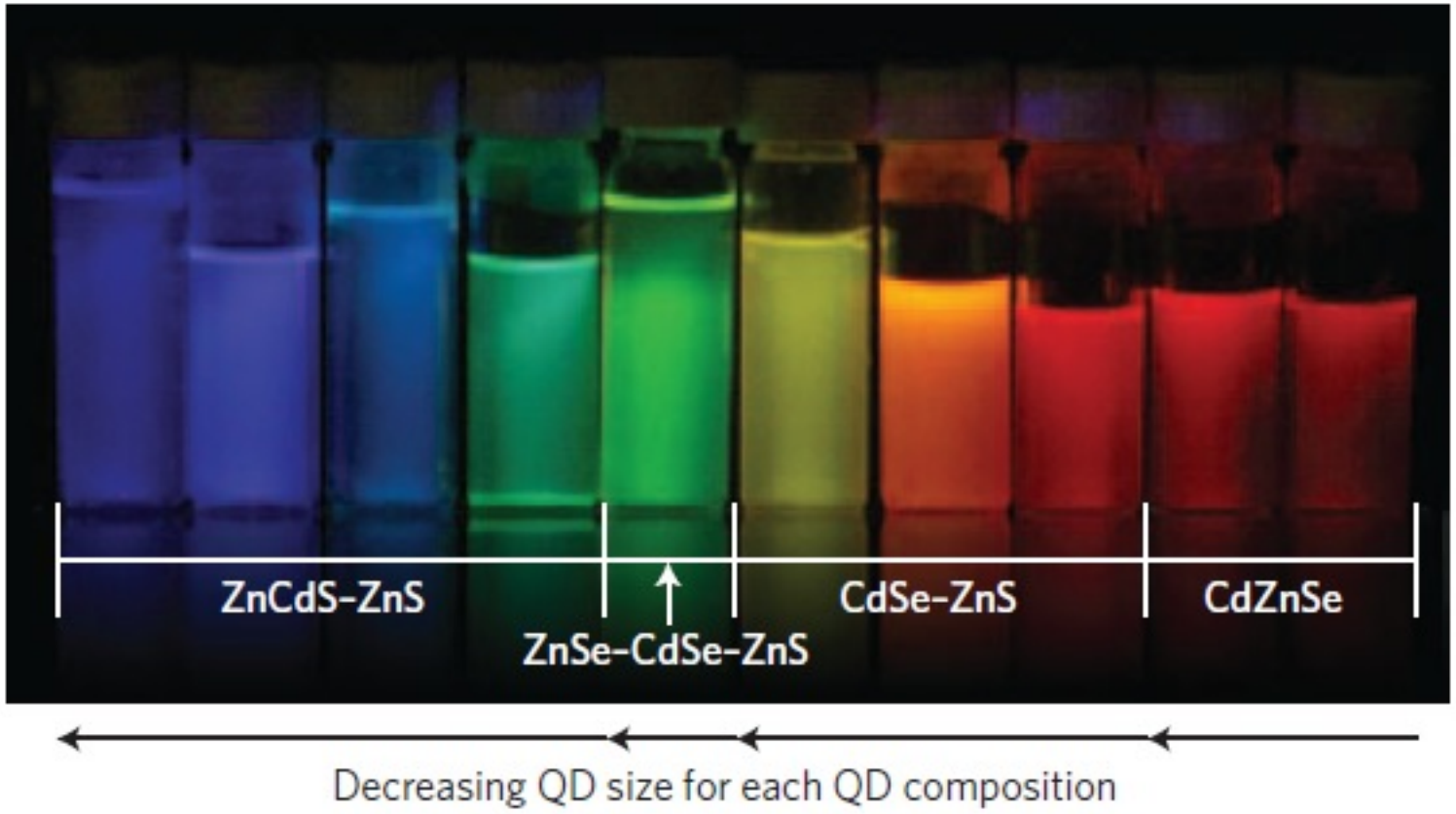
photo by Felice Frankel; samples by Bawendi Group (MIT)

decreasing size ←

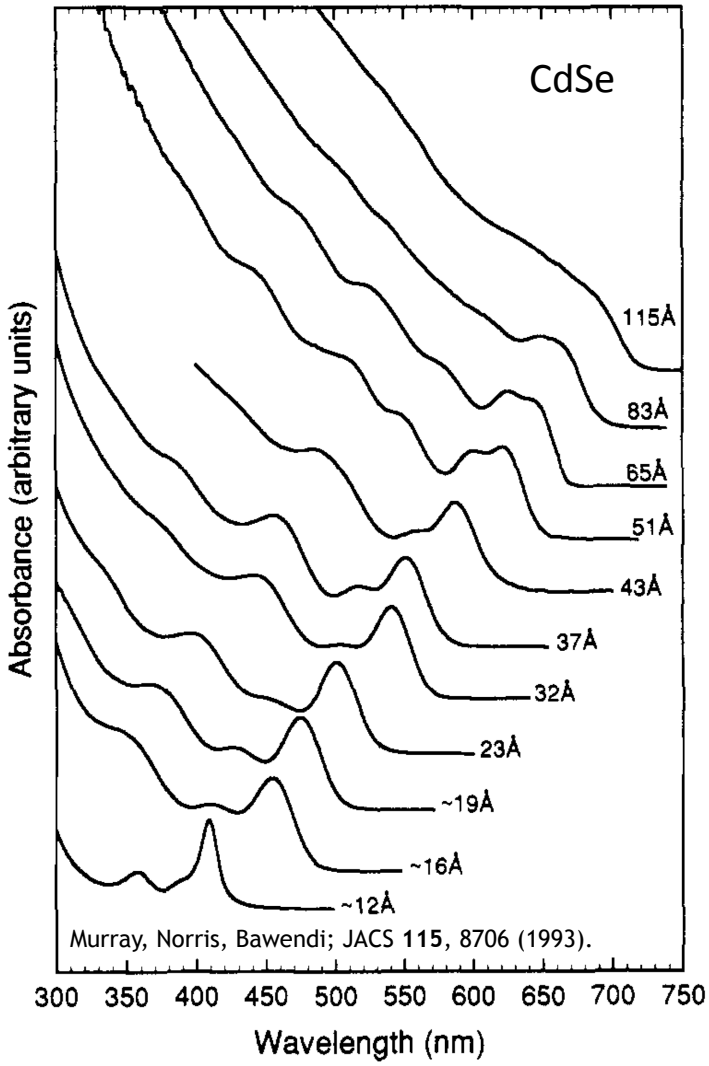
Tunable Fluorescence

Yasuhiro Shirasaki[1] et al.

Nature Photonics 2013

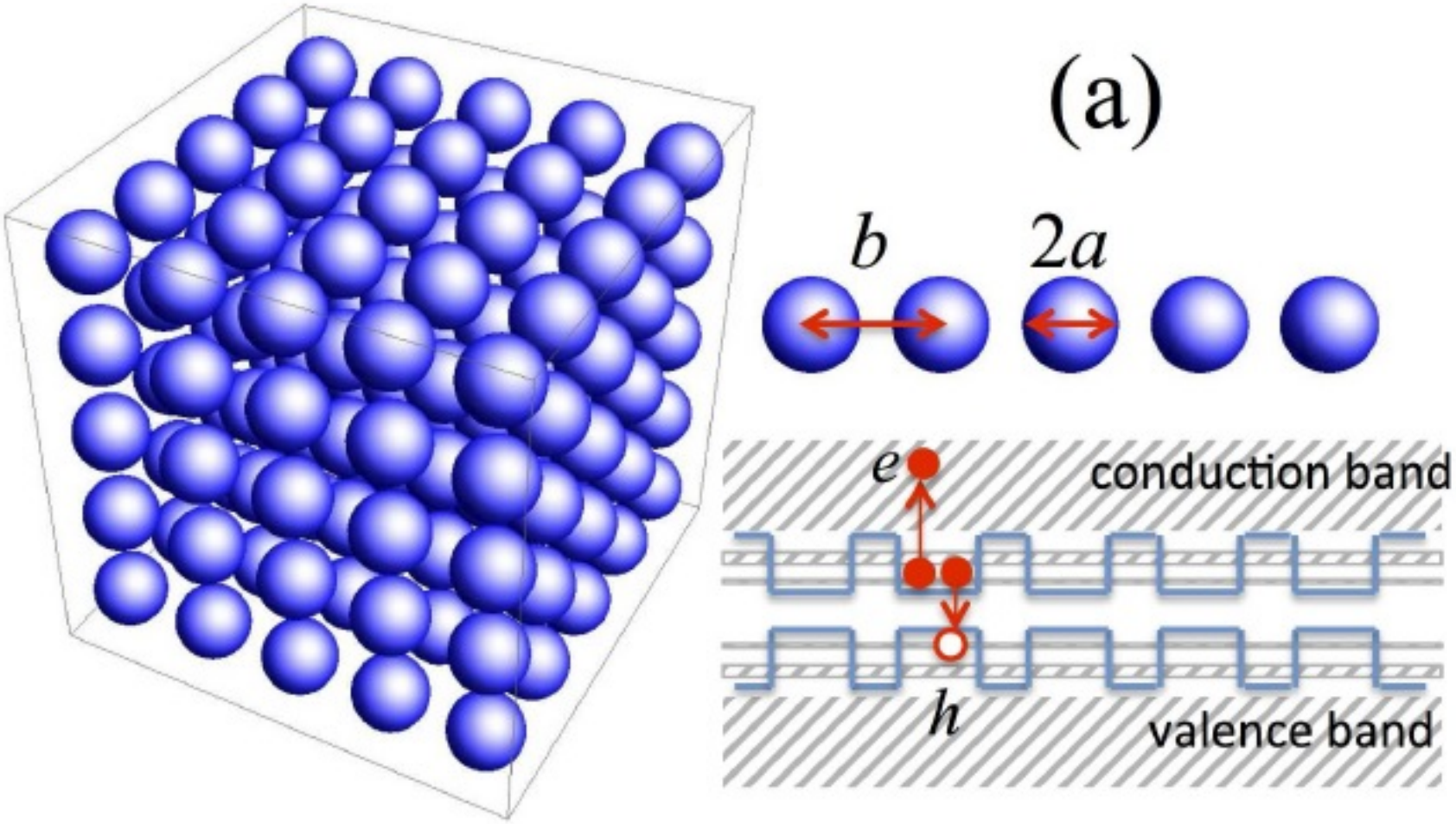


Also Tunable Absorbance



Tune Color of Material With Size

- Tailor absorption and fluorescence
- Can use different semiconductors
- Applications:
  - biological imaging
  - solid-state lighting
  - solar cells



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Motivations

1. Electron mobility in nanocrystal solids has risen by more than five orders of magnitude to 27 cm^2 /Vs with the T-dependence of a metallic type

*Ji-Hyuk Choi et. al. Nano Lett. 2012, **12**, 2631−2638*

2. Photoconductivity in nanocrystal solids exceeds dark conductivity by 2-3 orders of magnitude at relatively weak excitation generating much less than one electron-hole pair per nanocrystal.

*Jong-Soo Lee. et. al. Nature Nanotechnology, 2011, **6**, 348 .*

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Low Mobility of "Localized States" *vs* High Mobility of "Nearly Free States"

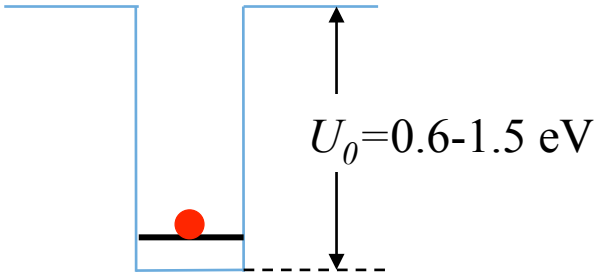
Photocurrent indicates a large change of the mobility stimulated by the light.

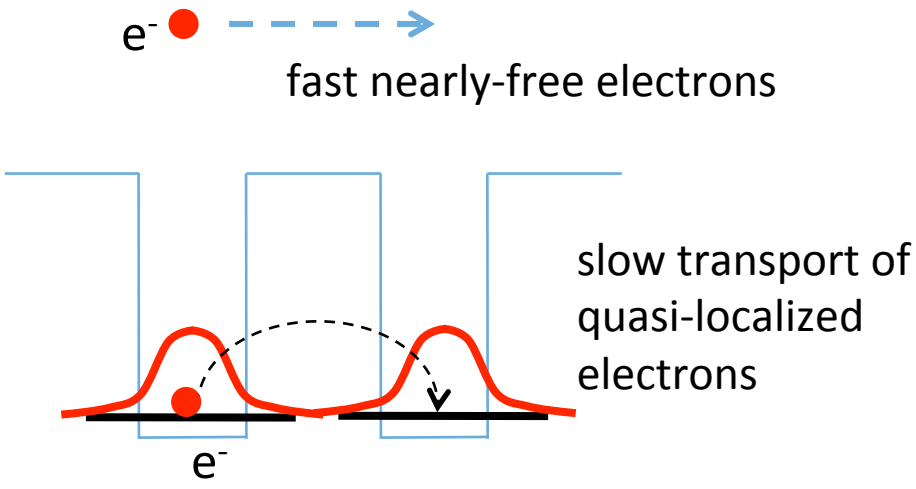
$$j = e(n_d\mu_d + n_p\mu_p)E$$

where n_d and μ_d are the concentration and mobility of resident carriers, n_p and μ_p are the concentration and mobility of carriers created by light.

If $\mu_p >> \mu_d$ significant increase of the current can be observed even at concentration of photoexcited carriers $n_p << n_d$.

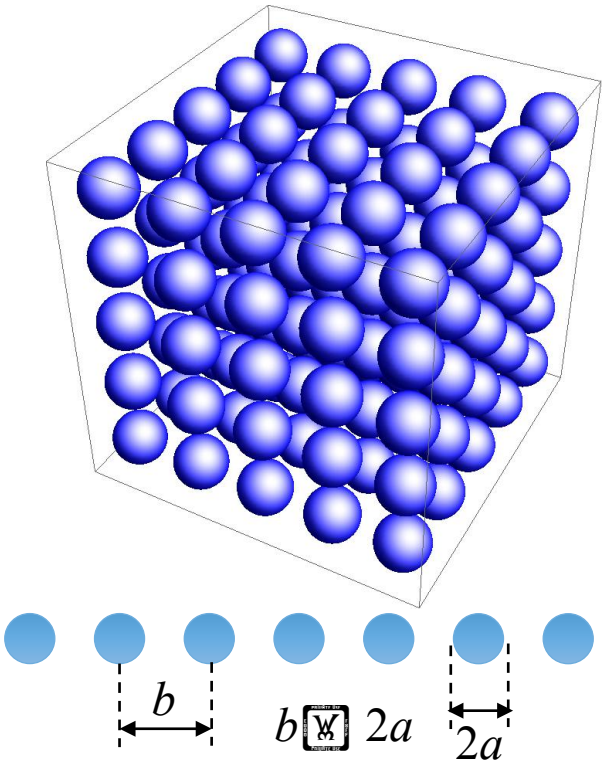
Nanocrystals embedded in glass matrix or polymer show well defined ionization threshold:





Electrons in a Periodic Array of Nanocrystals

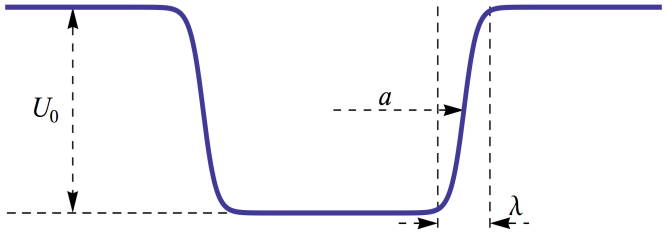
Electron transport in quasi-ideal three dimensional periodic array of *a* radius nanocrystals, which has a cubic lattice with period *b*.



Each NC is a three dimensional potential well for electrons, which has a form of the Woods-Saxon potential:

$$U(r) = -\frac{U_0}{1 + e^{(r-a)/\lambda}}$$

where U_0 is the depth of the potential, which is equal to the NC ionizations threshold, and parameter $\lambda \ll a$ is due to a NC atomic structure, $\lambda \sim (0.2\text{-}0.5)a_0$, where a_0 is the lattice constant of a semiconductor.



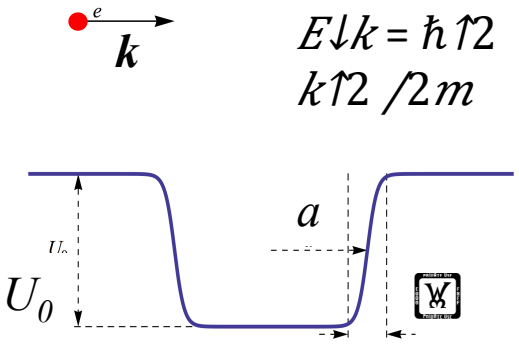
The periodic potential acting on electrons:

$$V(\boldsymbol{r}) = \sum_s U(|\boldsymbol{r} - \boldsymbol{R}_s|) = \frac{1}{N}\sum_{\boldsymbol{k}_s \neq 0} U_{\boldsymbol{k}_s} e^{i(\boldsymbol{k}_s \cdot \boldsymbol{r})}$$

where $\boldsymbol{k}_s = (\pi/b)(s_x\boldsymbol{x} + s_y\boldsymbol{y} + s_z\boldsymbol{z})$ are the reciprocal vectors of a cubic lattice and

$$U_{\boldsymbol{q}} = \frac{1}{8b^3}\int U(r)\, e^{i\boldsymbol{q}\cdot\boldsymbol{r}} d^3r \ .$$

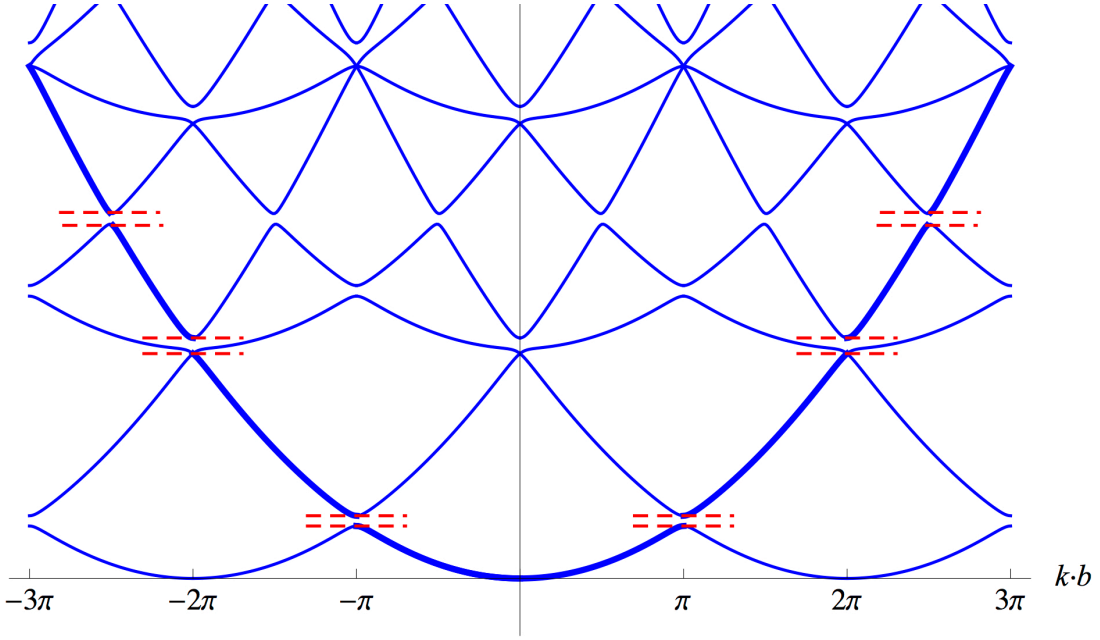
Nearly Free Electrons in a Periodic Array of Nanocrystals



$E\downarrow k = \hbar\uparrow 2$
$k\uparrow 2 \,/2m$

the origin of these parabolas is any reciprocal vector $\boldsymbol{k}_s$

The electron dispersion changes near intersection points forming energy gaps: $E_g(\boldsymbol{k}_s) = 2\,|U_{\boldsymbol{k}_s}|$



The band width E of a Brillouin zone can be found using $\frac{4\pi}{3}\left[(k+\Delta k)^3 - k^3\right] = \frac{\pi^3}{b^3}$

$$\Delta E(\boldsymbol{k}) = \frac{\hbar^2 k \Delta k}{m} = \frac{\pi^2\hbar^2}{4mkb^3}$$

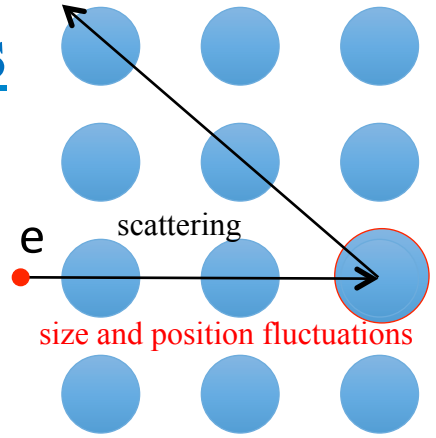
decreases with energy !!!

The nearly-free electron approximation is applicable if the gaps are smaller than the band width.

The ratio: $\dfrac{E_g(k_s)}{\Delta E(k_s)} \approx \dfrac{U_0 m}{\hbar^2}\dfrac{\pi\lambda a}{\sinh \pi k_s \lambda} \approx 0.05$

Near free approximation is valid.

Nearly Free Electron Transport Properties

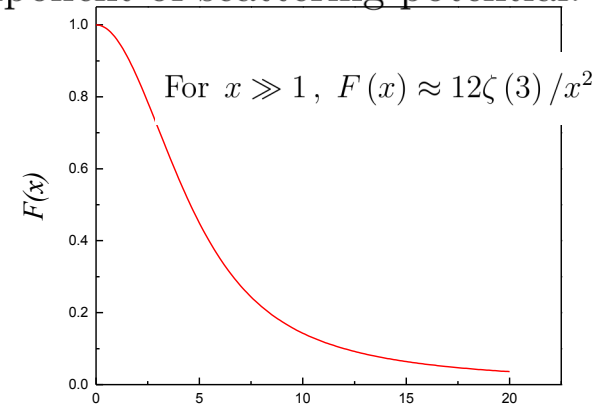


Scattering due to structural defects of the super-crystal: small fluctuations of the radii and positions of NCs. The transport time is

$$\frac{1}{\tau_k} = \frac{2\pi}{\hbar}\left(\frac{b}{\pi}\right)^3 \int (1-\cos\theta)\left|U_{\boldsymbol{q}}^{(d)}\right|^2 \delta\left(\frac{\hbar^2 k^2}{2m} - \frac{\hbar^2(\boldsymbol{k}+\boldsymbol{q})^2}{2m}\right) d^3q \ ,$$

where θ is the scattering angle and $U_{\boldsymbol{q}}^{(d)}$ is the Fourier component of scattering potential.

Scattering rate: $$\frac{1}{\tau_k} \approx 8\pi\chi^2 \frac{U_0^2 a^4}{b^3}\frac{m}{\hbar^3 k} \cdot F(4\pi k\lambda) \ ,$$



where $\chi^2 = \dfrac{\langle \xi_a^2 \rangle + \langle \boldsymbol{\xi}_r^2 \rangle}{a^2}$, $\langle \xi_a^2 \rangle$ and $\langle \boldsymbol{\xi}_r^2 \rangle$ are the mean squared fluctuation of the NC radius and NC position displacement.

For electrons created by Auger ionization processes, the energy is so high that $\tau_k \sim$ 1.2 ps, and the length of flight during the relaxation time ~ 1 μm

Calculating the photoconductivity and mobility of excited electrons requires the energy distribution function of hot electrons. Assuming majority of photoexcited carriers has photoexcitation energy, $E_p \sim$ 2eV, using

$$\mu_p = e\tau_k/m \ \text{ we obtain } \ \mu_p \approx 2100 \ \text{cm}^2/(\text{V}\cdot\text{s})$$

THE LOWEST ENERGY BAND AND DARK TRANSPORT

Relevant Homogeneous Material Parameters of NCs

1.Effective mass at the bottom of the band m*(0).

2. m*(E) .

Additional Parameters of the NC:

3 Ionization Threshold U_0 0.5-1.6Ev

Radius of NC a

$$m^*(E_0)$$

First one should find the energy of the lowest level in a framework of the Kane model

$$E_0 = \mathrm{h}^2 k^2 / 2m^*(E_0)$$

In CdSe NCs: $m/m↑*(E↓0) = α↓c + E↓p/3\,(2/E↓g + E↓0 + 1/E↓g + Δ + E↓0)$ where α_c=0.16, E_p=17.5 eV, E_g=1.84 eV, and Δ=0.42 eV. (Kane model)

In PbSe NCs: $m/m↑*(E↓0) = α↓c + E↓p/E↓g + E↓0$ where α_c=3.9, E_p=2.64 eV, and E_g=0.28 eV, (Dimmock & Wright)

Lowest Energy Band Basis Functions

In the tight-binding approximation the basis functions are the wave functions of electrons in the ground state of single NCs:

$$\varphi(r) = \sqrt{\frac{2}{ar^2}} A \begin{cases} \sin(k_0 r)\,, & r < a \\ \sin(k_0 a)\exp[-\kappa(r-a)]\,, & r \geq a \end{cases}$$

where $k_0 = \sqrt{2m^* E_0}/\hbar$, $\kappa = \sqrt{2m(U_0 - E_0)}/\hbar$, m^* and m are the effective masses of an electron in the NC and the barrier, and E_0 is the ground state energy of NC, which is determined by the smallest solution of the following equation:

$$1 - k_0 a \cot(k_0 a) = (m^*/m)(1 + \kappa a)$$

In small NC, nonparapolicity of the conduction band should be taken into account via energy dependence of the electron effective mass, $m^*(E)$.

The normalization constant A is given by

$$A = \left[1 + \sin^2(k_0 a)/(a\kappa) - \sin(2k_0 a)/(2k_0 a)\right]^{-1/2}.$$

Lowest Energy Band

In the tight binding approximation the wavefunctions of the electron free motion can be represented as the Bloch sum $\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_l \tilde{\varphi}(\boldsymbol{r} - \boldsymbol{R}_l) \exp(i\boldsymbol{k}\boldsymbol{R}_l)$

In the limit $\kappa a \gg 1$ the band energy spectrum is

$$E_{\boldsymbol{k}} = E_0 + \Delta E_0 + 2t\left(\cos k_x b + \cos k_y b + \cos k_z b\right)$$

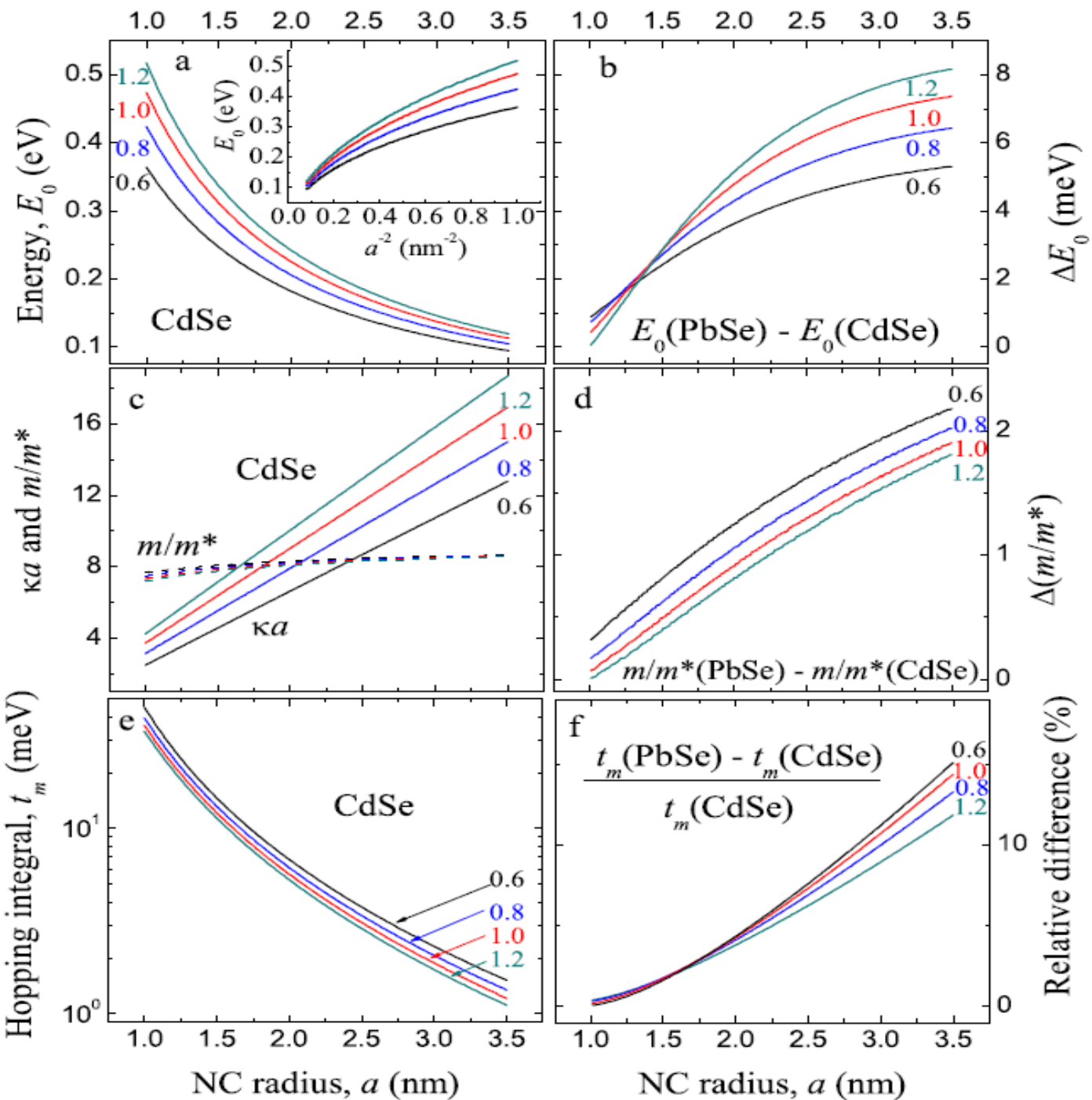
$$\Delta E_0 = -3\beta U_0 \qquad t = -\gamma U_0$$

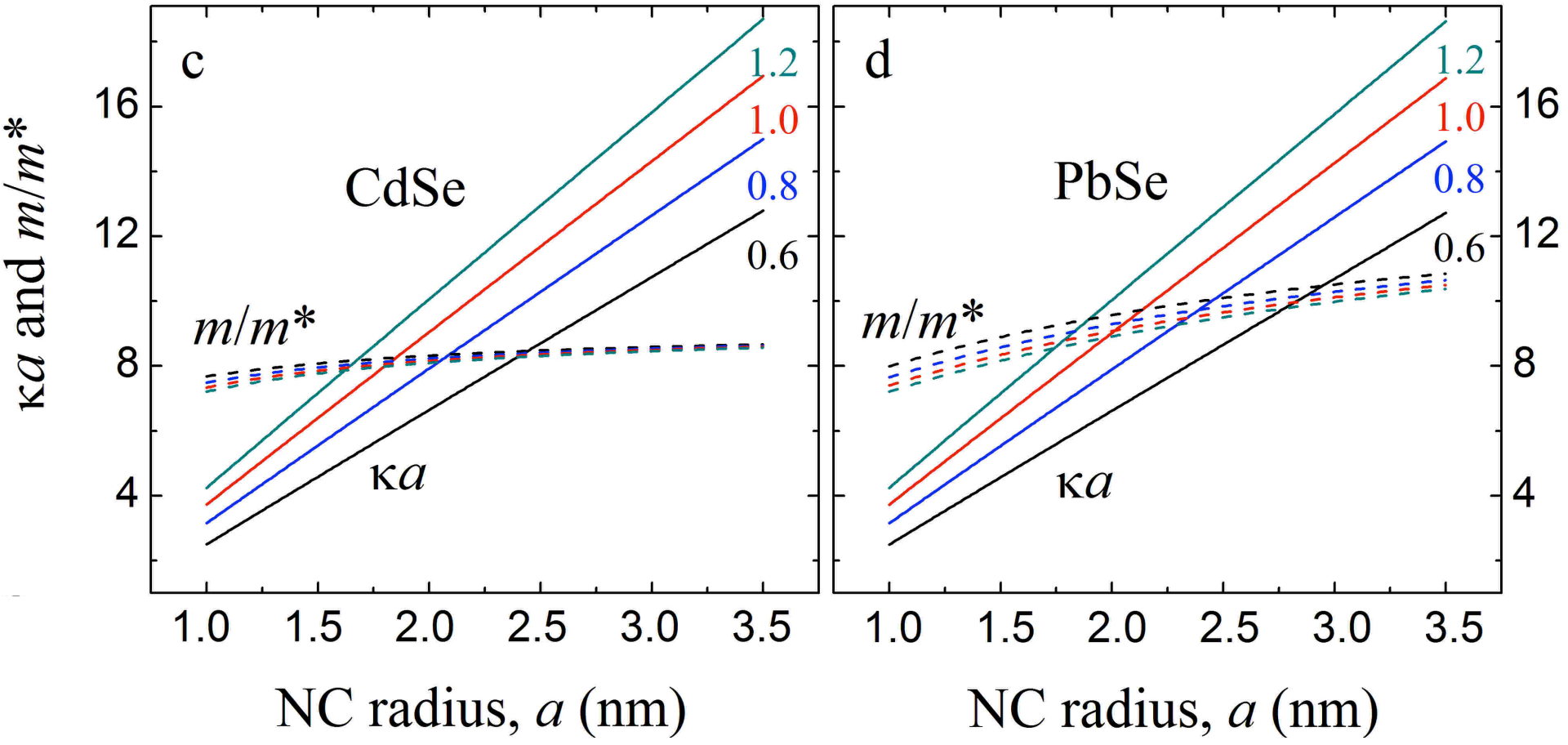
$$\gamma = \gamma_m (2a/b)\exp[\kappa(2a-b)]\,, \beta = \gamma \frac{a}{b-a}\frac{m^*}{m+m^*}\exp[\kappa(2a-b)]$$

$$\gamma_m(a) = [A\sin(k_0 a)/\kappa a]^2 (1 + m^*/m)/2$$

$$\gamma_m \approx \frac{1}{2\kappa^2 a^2} \begin{cases} \left(\frac{\pi}{\kappa a}\right)^2 \frac{m}{m^*}\left(\frac{m}{m^*}+1\right), & \text{when } \frac{m}{m^*} \ll \kappa a \text{ (case I)} \\ \frac{3}{2}, & \text{when } \frac{m}{m^*} \gg \kappa a \text{ (case II)} \end{cases} . \quad (17)$$

One can see from Eq. (17) that in the case I corresponding to large a the overlap $\gamma_m \sim (\kappa a)^{-4}$ is very small. The energy of the lowest level is $E_0 \approx \hbar^2\pi^2/\left(2m_0^* a^2\right)$, where m_0^* is the effective mass at the bottom of the energy band of the NC material. This asymptote for the energy E_0 is clearly seen in the inset of Fig. 2a,b. In the case II, corresponding to small a, the overlap is significantly larger. The asymptotic expression for the energy of the level is $E_0 \approx (3\hbar^2/2ma^2)(\kappa a)$. It is important to note that E_0 and κa, which enters the tunneling exponent, are both independent of the effective mass m^*. This means that in this limiting case they are the same for electrons and holes. Figures 2c


a
b
c
d
e
f
CdSe
E_0(PbSe) - E_0(CdSe)
m/m^*
κa
m/m^*(PbSe) - m/m^*(CdSe)
t_m(PbSe) - t_m(CdSe)
t_m(CdSe)
Energy, E_0 (eV)
E_0 (eV)
a^{-2} (nm^{-2})
ΔE_0 (meV)
κa and m/m^*
$\Delta(m/m^*)$
Hopping integral, t_m (meV)
Relative difference (%)
NC radius, a (nm)
NC radius, a (nm)
1.2
1.0
0.8
0.6


c
d
CdSe
PbSe
1.2
1.0
0.8
0.6
m/m*
κa
κa and m/m*
NC radius, a (nm)
NC radius, a (nm)
4
8
12
16
1.0
1.5
2.0
2.5
3.0
3.5

WIDTH OF THE BAND

In SC structure with 6 nns

$$\Delta = 12t = 12U_0\gamma$$

CdSe: a=1.5, a=1nm , $\Delta = 120\text{meV}, 600\text{meV}$

Note that $\gamma = \gamma_m 2a / b \exp[\kappa(2a - b)]$

THE MASS AT THE BOTTOM OF THE BAND IS

$$m_{sc} / m = \frac{\mathrm{h}^2}{2tb^2 m} = \frac{6\mathrm{h}^2}{\Delta b^2 m}$$

b=2a a=1.5 nm., 1 nm $m_{sc} / m = 6.7; 0.7$

Dark Band Mobility

The dark conductivity depends on the ratio of the band width Δ to the temperature T

At $k_BT < \Delta$, transport within parabolic spectra, where $E_{\boldsymbol{k}} = E_0 + \Delta E_0 + \hbar^2 k^2 / 2m_{sc}$

The scattering transport time in parabolic spectra $\frac{1}{\tau_k} = \frac{16\pi U_0}{\mathrm{h}} \chi^2 \frac{a^3}{b^3} \frac{m_{sc} a^2 U_0}{\mathrm{h}^2} ka$.

Using standard transport theory we obtain the mobility for *nondegenerate* electron gas $\mu_d = \mu_d^{max} \left(\frac{b}{2a} \right)^{11/2} \exp\left[5\kappa a \left(1 - \frac{b}{2a} \right) \right]$

where the maximum mobility is reached at $b=2a$ $\mu_d^{max} = \frac{2^8}{3\pi^{3/2}} \frac{ea^2}{\mathrm{h}} \frac{\gamma_m^{5/2}}{\chi^2} \sqrt{\frac{U_0}{k_B T}}$

For degenerate electron gas when $E_F >> k_BT$

$$\mu_d = \frac{e\tau_k(E_F)}{m_{sc}} ,$$

where τ_k is calculated with $k = \sqrt{2m_{sc}E_F}/\hbar$.

Temperature Dependence of the Mobility at all Temperatures

High temperature : temperature much larger than band width $k_B T >> \Delta$

Temperature enters into kinetic equations only through energy derivative of Boltzmann function:

$$f = \exp(-\varepsilon / k_b T)$$

For all electrons in the band $\varepsilon << k_B T$ and the derivative is equal to $-(1/(k_B T))f$

Mobility: $\mu_d = \frac{e\bar{\tau}}{m_{sc}} \frac{t}{k_B T}$ where $\bar{\tau} = \frac{1}{4\pi^3} \int_{-\pi}^{\pi} d\eta_x d\eta_y d\eta_z \sin^2(\eta_x) \tau_{b\boldsymbol{\eta}}$

with dimensionless variables $\boldsymbol{\eta} = \boldsymbol{k}/b$.

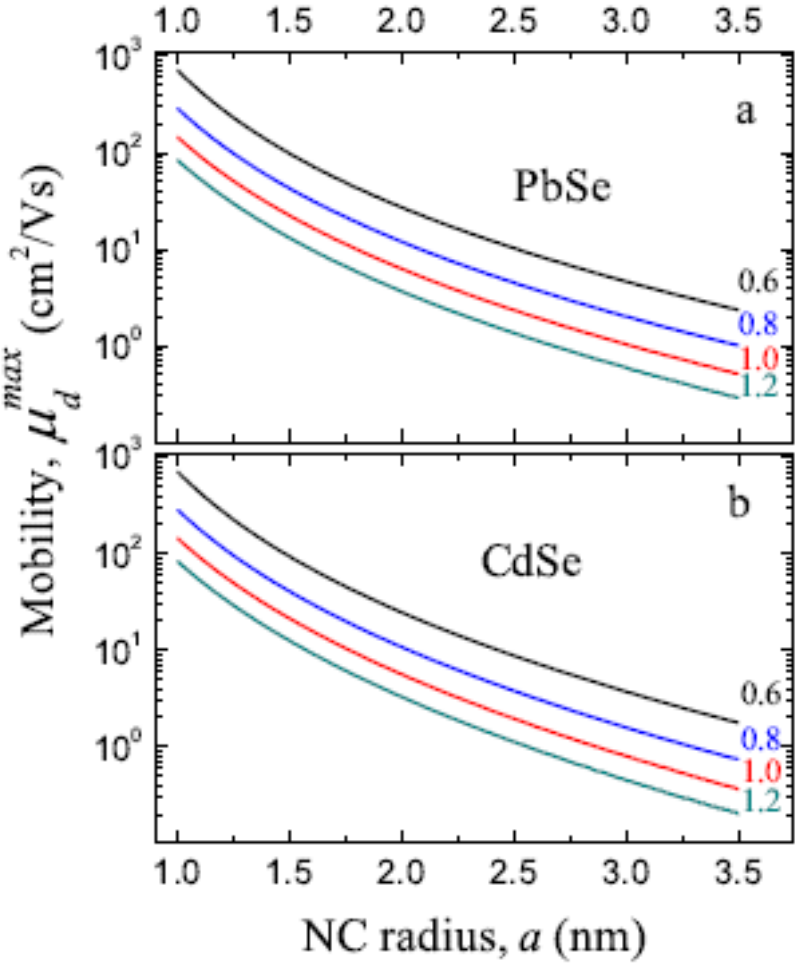
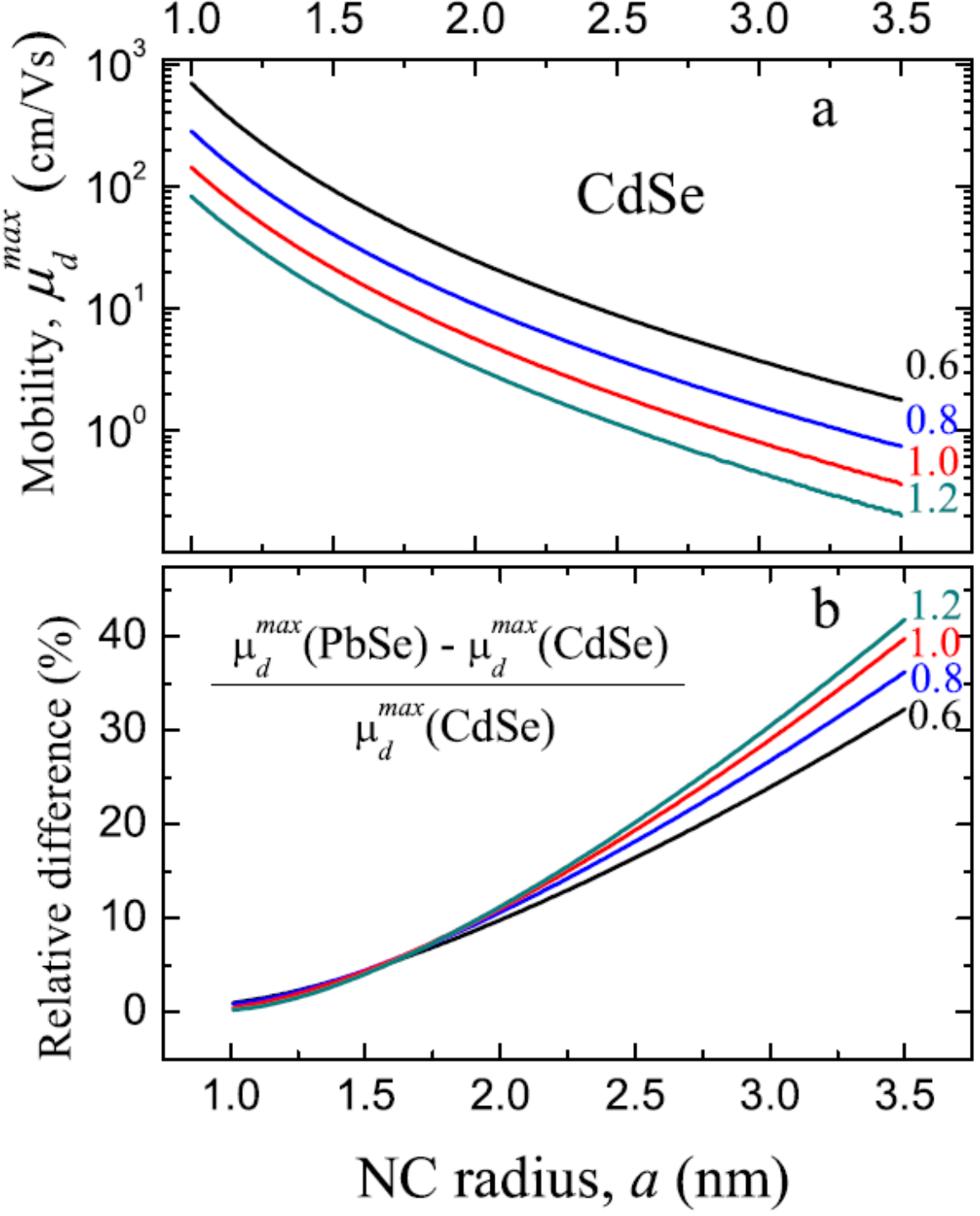
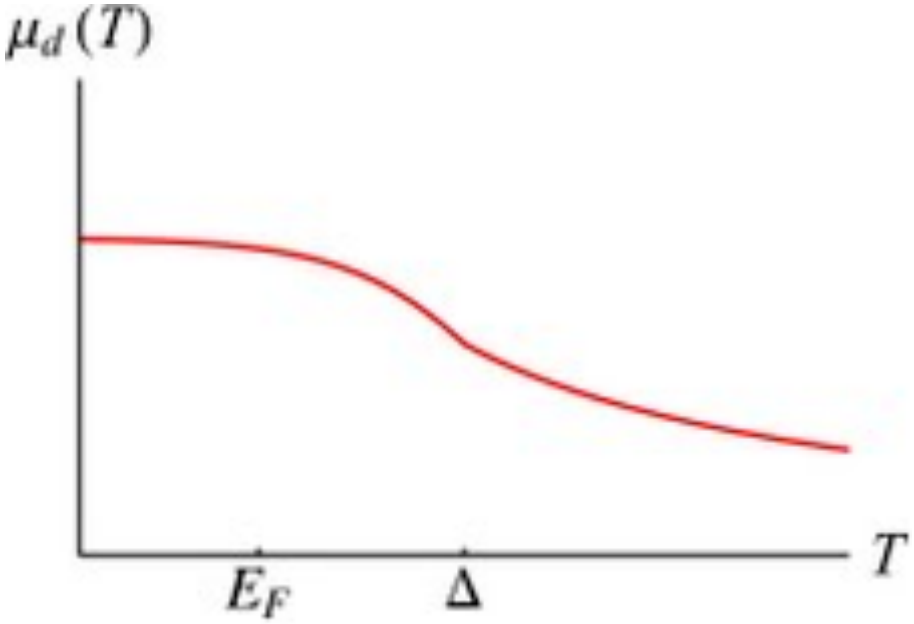


FIG. 3. The dependence of maximum dark mobility μ_d^{max} on a NC radius calculated for CdSe and PbSe NCs using Eq. (21) at room temperature $T = 300$ K and NC size dispersion $\chi = 5$ %. Calculations conducted for for $U_0 = 0.6, 0.8, 1.0$ and 1.2eV takes into account nonparabolicity of the conduction band [31]


a
CdSe
Mobility, μ_d^{max} (cm/Vs)
10^3
10^2
10^1
10^0
0.6
0.8
1.0
1.2
b
$\frac{\mu_d^{max}(PbSe) - \mu_d^{max}(CdSe)}{\mu_d^{max}(CdSe)}$
Relative difference (%)
40
30
20
10
0
1.2
1.0
0.8
0.6
1.0
1.5
2.0
2.5
3.0
3.5
NC radius, a (nm)

SCHEMATIC T-DEPENDENCE OF THE DARK CONDUCTIVITY



Dark Conductivity and Localization

Localization occurs if a typical fluctuation of the energy of the NC ground state, E_0, exceeds the band width, Δ, by a some critical numerical factor X_c, when $E_0 > X_c\Delta$. Most probable source of E_0 fluctuations is the fluctuations of the NCs radii ξ_a:

$$\delta E_0 = a(\partial E_0(a)/\partial a)\xi_a/a = a(\partial E_0(a)/\partial a)\chi\,, \quad \text{in parabolic regime } \delta E_0 = E_0 2\chi\,.$$

For rectangular distribution of E_0 within the interval $[-E_0/2, E_0/2]$ the critical broadening width, $E_0{}_c$ was found to be $E_0{}_c / \Delta = X_c \approx 2.67$.

If random variable has rectangular distribution $-\chi/2 \le \xi_a/a \le \chi/2$

The critical broadening width

$$\langle \delta E_0(a) \rangle = a(\partial E_0(a)/\partial a)\chi = 2.67\Delta$$

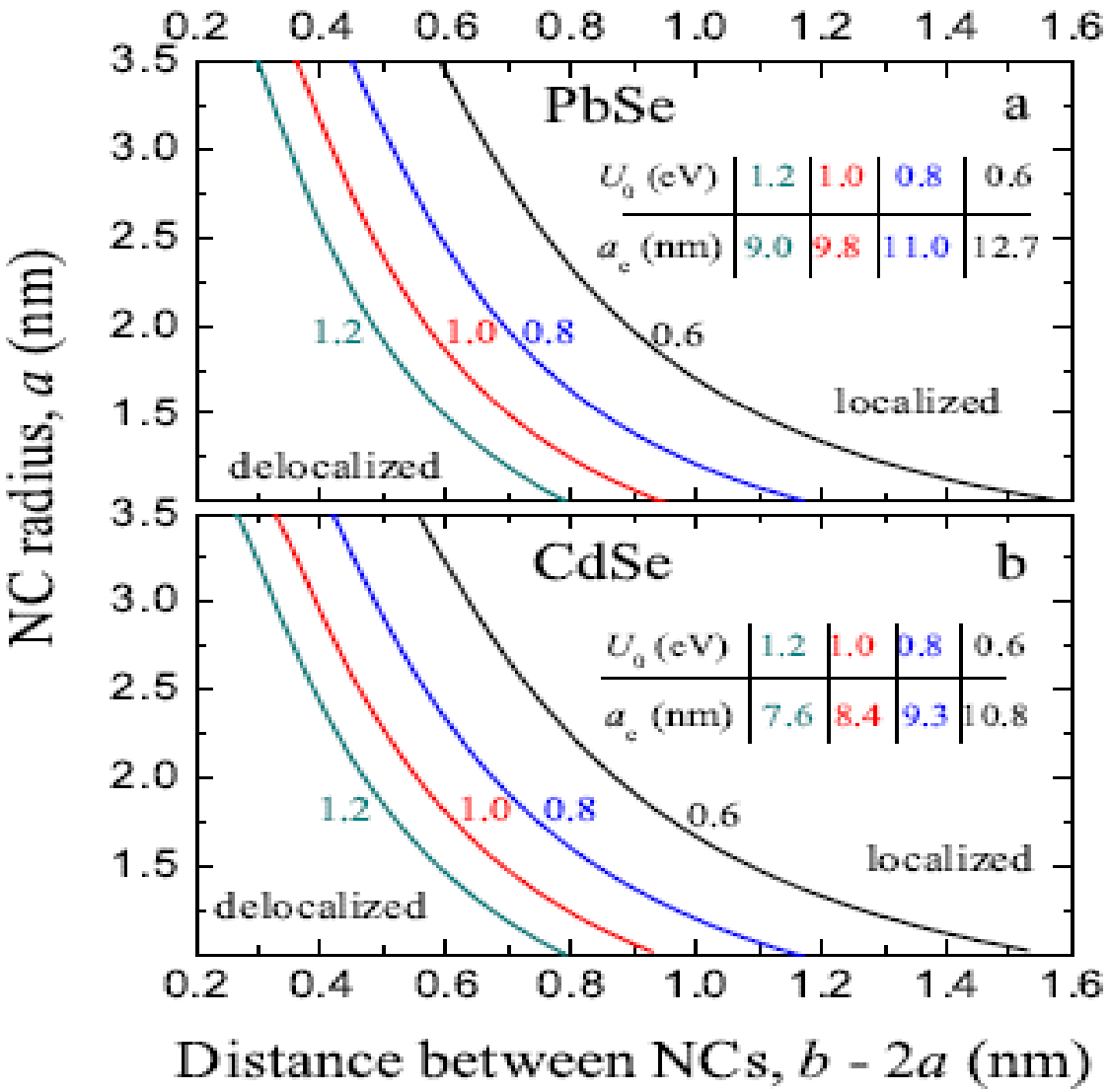


FIG. 4. Phase diagram which separate the delocalized from localized states. Calculations that conducted for PbSe (a) and CdSe (b) NCs with dispersion $\chi = 0.05$ for $U_0 = 0.6, 0.8, 1.0$ and 1.2 eV take into account nonparabolicity of the conduction band [31]. NCs remain in the localized state even at $b - 2a = 0$ if the radius a is larger than a_c (shown in insets).

The Mott transition

The band conductivity can be also suppressed by the Mott transition, that occurs even in the perfectly ordered system due to electron-electron interaction if the band is half filled. The transition is usually described in the framework of Hubbard's model. In the ordered array of NCs, the tight binding approximation should be modified by adding the energy of interactions of two electrons with the different spin orientation occupying the same NC (the Hubbard energy).The metal-insulator transition occurs in 2- and 3-dimensional cases if the Hubbard energy is larger then the band width The Hubbard interaction results in the energy gap between occupied and unoccupied states in the half field band, transforming metal into dielectric. The Hubbard gap can be observed in the optical absorption. If the Hubbard gap is smeared by disorder, the Anderson transition provides localization at all feeling factors inside the lowest band.

Correlation of dark conductivity and photoconductivity

Without any disorder the overlapping ground states of the NCs form a band with a relatively high mobility. In this case the Auger processes are suppressed by the momentum conservation. In reality, even on the metallic side of the Anderson transition the metallic band may include a very small part of all NCs. The others form clusters of one ,two and more overlapping NC's that may provide the Auger ionization but does not participate in the dc conductivity. The number of such clusters gradually decreases with decreasing disorder. In a general case there are NCs that provide metallic type conductivity and there are NCs creating high energy electrons for the photoconductivity. As a result the increase of a dark conductivity should correlate with the decreasing production of photoelectrons.

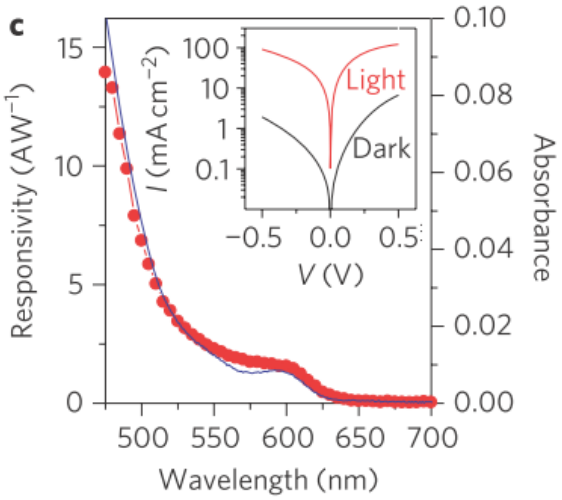
Discussion of Experimental Results on Photoconductivity

Auger-stimulated photocurrent could explain two orders of magnitude increase in current under optical excitation reported initially for array of In_2 Se^{2-}-capped CdSe/CdS core-shell NCs.

1. The increase of the carrier concentration in the ground conducting state is not sufficient for the explanation.

2. The similarity of spectral dependence of photo-current responsivity and absorption coefficient indicates that each photon absorbed by charged NCs transfers the resident electron into highly conductive state.

3. These states are quasi-free electrons whose mobility is at least two orders of magnitude higher than the mobility of electrons in ground states.



*Jong-Soo Lee. et. al. Nature Nanotechnology, 2011, **6**, 348*

Discussion of Experimental Results on Photoconductivity

Existence of highly mobile quasi-free carriers created by photons is convincingly demonstrated by experiments conducted in PbS NC solid.

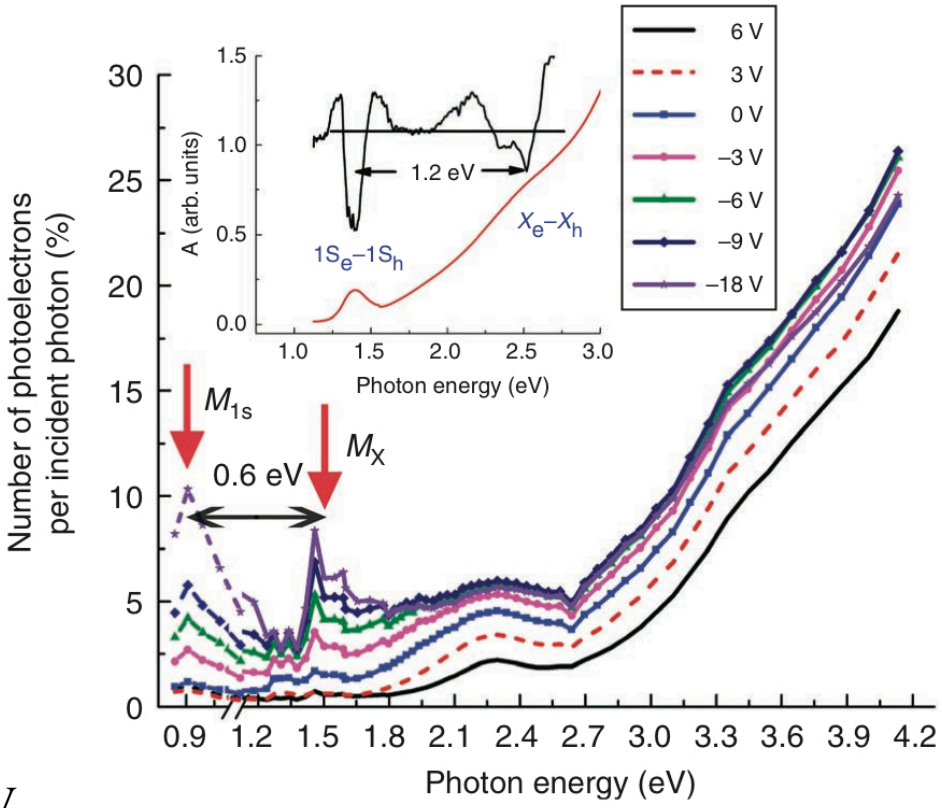
P. Nagpal and V. I. Klimov, Nature Communications **2**, 486 (2011)

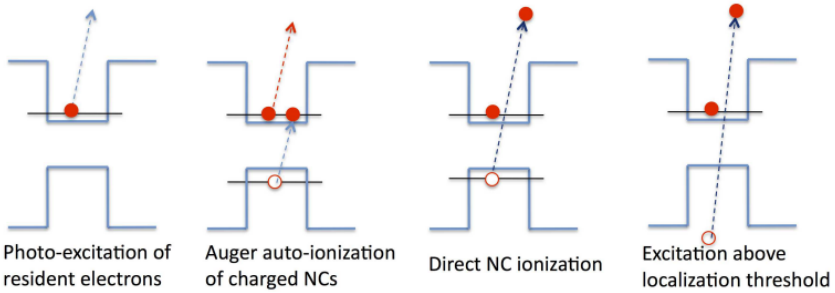
1. Burst of photoconductivity at U_0 ≈ 0.9eV connected with photo-excitation of resident holes above the NC ionization threshold

2. Burst of photoconductivity at 1.5 eV can be explained by Auger auto-ionization of charged NCs .

3. Addition broad bump in the photocurrent near $Eg + U_0$ ≈ 2.2 eV can be explained by direct NC ionization.

4. The additional feature at 3.3 eV can be explained by excitation above the localization threshold of the NC solid at $E_g + 2U_0$ ≈ 3.1 eV.





Discussion of Experimental Results on Dark Conductivity

The largest dark mobility of 27 $cm^2/(Vs)$ was reported in the array of closely packed CdSe NC with $2a$= 3.9nm.

*Ji-Hyuk Choi et. al. Nano Lett. 2012, **12**, 2631−2638*

Such mobility indeed could be reached in ordered array of NCs with NC size dispersion σ =5% and confinement potential U_0< 1eV.

Summary

1. We developed a theory of the photo- and dark conductivity in ordered arrays of NCs. Electron transport properties were calculated for scattering by structural defects of super-crystal, namely small fluctuations of the radii and positions of NCs.
2. For dark conductivity, we found the the diagram in axis a and b separating Anderson localized states with the hopping conductivity and band states with the metallic type conductivity. The possibility of the Mott transition is also considered
3. We propose a new mechanism of photoconductivity triggered by very efficient Auger recombination of electron-hole pairs at the band edge of NCs, which transfers electrons localized in the NCs into high energy quasi-free states of the NC array. This leads to the 2 - 4 orders of magnitude increase of the photo-current because the mobility of these states is 4 - 5 orders of magnitude larger than the mobility of electrons in the ground state.
4. Our theory predicts a correlation between dark and photo conductivitiy.

Four Mechanisms of Nearly Free State Photo-activations

Each mechanism requires a different photon energy.

Photons with energy above the NC band gap create quasi-free electrons via so called Auger auto ionization of charged NC. Possible only if the NC contains at least one resident electron.

Auger photoexcitation mechanism is unique property of NCs because the rate of Auger processes in NCs is much larger than the rate of the radiative recombination. As a result quasi-free carriers are generated with almost 100% probability.