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# Local field-induced optical properties of Ag-coated CdS quantum dots

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**Abstract:** Local field-induced optical properties of Ag-coated CdS quantum dot structures are investigated. We experimentally observe a clear exciton peak due to the quantum confinement effect in uncoated CdS quantum dots, and surface plasmon resonance and red-shifted exciton peak in Ag-coated CdS composite quantum dot structures. We have calculated the Stark shift of the exciton peak as a function of the local field for different silver thicknesses and various sizes of quantum dots based on the effective-mass Hamiltonian using the numerical-matrix-diagonalization method. Our theoretical calculations strongly indicate that the exciton peak is red-shifted in the metal-semiconductor composite quantum dots due to a strong local field, *i.e.*, the quantum confined Stark effect.

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**OCIS codes:** (300.6470) Spectroscopy, semiconductor; (300.1030) Absorption; (260.6580) Stark effect

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## 1. Introduction

Metal-coated nano-particles show a large and fast third-order optical nonlinearity due to the surface plasmon resonance [1, 2, 3], opening possibilities for all-optical switching devices. The collective charge oscillation causes a large resonant enhancement of the local field inside and near the particle. This field enhancement is used in surface-enhanced Raman scattering and is currently being studied for potential applications in nonlinear optical devices. In semiconductor quantum dots (QDs) coated with a noble metal, coupling between the plasmon resonance from the metal and the quantum size effect of the semiconductor QD may give rise to new properties that can lead to new types of nano-composite material systems and also widen applications for noble nano-devices [3, 4]. At present, therefore, there is much ongoing effort to synthesize semiconductor-metal nano-composite materials [3, 4, 5, 6, 7].

Recently, E.H. Jeung et. al. reported that a red-shift of the exciton absorption peak was observed in Ag/CdS metal-semiconductor composite QDs [8]. The CdS QDs were made by gamma ray irradiation of an aqueous solution containing cadmium sulfate and 2-mercaptoethanol and were subsequently covered with silver [5, 8]. The measured absorption spectra showed an exciton peak shifted from the bare CdS QD as well as surface plasmon resonance due to the silver layer. In this paper, we investigate the local field-induced optical properties of CdS/Ag core/shell semiconductor-metal composite QD structures. In particular, the red-shift of the exciton peak as a function of the local field is calculated for different silver thicknesses and various core radii based on the effective-mass Hamiltonian in the presence of external electric field using the numerical-matrix-diagonalization method [9]. We theoretically confirm that the red-shift of the exciton peak in the semiconductor-metal composite QDs can be explained by the confined Wannier-Stark states due to a strong local field. The Wannier-Stark state is the energy spectrum of a crystalline solid in an electric field [10].

## 2. Matrix elements in exciton-Hamiltonian

The exciton states in the presence of an external field are described by the Hamiltonian [9]

$$H = H_e + H_h + V_{eh} + H_F. \quad (1)$$

$H_{e(h)}$  is the kinetic energy of the electron(hole),  $V_{eh}$  is the Coulomb interaction between the electron and hole, and  $H_F$  is the additional interaction of the electron and the hole in the Wannier equation [10].

The exciton wave function  $\Phi(r_e, r_h)$  is determined by the following Schrödinger equation under the external field

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_h} \nabla_h^2 - \frac{e^2}{\epsilon_d |r_e - r_h|} - eF \cdot r_e + eF \cdot r_h \right] \Phi(r_e, r_h) = E \Phi(r_e, r_h) \quad (2)$$

where  $\epsilon_d$  is the dielectric constant of the QD,  $E$  is the energy of the confined exciton, and  $F$  is the electric field inside the QD. This equation cannot be solved analytically without solving the Wannier equations.

The quantum confined exciton wave function may be written on the basis of symmetry requirements as [9]

$$\Psi(r_e, r_h) = \sum_{n_e n_h l_e l_h LM} C(n_e n_h l_e l_h LM) \Phi_{n_e l_e n_h l_h LM}(r_e, r_h) \quad (3)$$

where the basis vectors are

$$\Phi_{n_e l_e n_h l_h LM}(r_e, r_h) = \sum_{m_e m_h} \langle l_e l_h m_e m_h | LM \rangle \phi_{N_e}(r_e) \phi_{N_h}(r_h) \equiv |n_e n_h l_e l_h LM \rangle. \quad (4)$$

Here,  $\langle l_e l_h m_e m_h | LM \rangle$  is the Clebsch-Gordan coefficient in the Condon-Shortley convention where L and M are the quantum number of the total angular momentum and its z component, respectively, and  $N_{i(=e,h)}$  is a quantum number set  $\{n_i, l_i, m_i\}$ .  $\phi_{N_i}(r_i)$  is a single particle wave function in the absence of an electric field and neglects the Coulomb interaction.  $C(n_e n_h l_e l_h LM)$  is determined by diagonalization of the Hamiltonian with the basis vectors.

In general, the matrix elements in the exciton-Hamiltonian are defined by

$$\langle n_e n_h l_e l_h LM | H_e + H_h + V_{eh} + H_F | n'_e n'_h l'_e l'_h LM \rangle \equiv \delta_{NN'} H_0 - \hat{V}_{NN'} + \hat{F}_{NN'}. \quad (5)$$

The exciton energies and wave functions are obtained from the diagonalized matrix elements. The kinetic energy matrix,  $H_0$ , is diagonal and depends only on the related single particle states. The corresponding energy of a confined particle is, therefore,

$$E_{nl} = E_g + \frac{\hbar^2}{2m} \frac{\alpha_{nl}^2}{R^2} \quad (6)$$

where  $\alpha_{nl}$  is the  $n$ th root of the eigenvalue equation  $j_l(x) = 0$ .

The matrix elements of the Coulomb interaction between the electron and hole can be calculated in the coupled states as

$$\hat{V}_{NN'} = \langle n_e l_e n_h l_h LM | \frac{e^2}{\epsilon_d |r_e - r_h|} | n'_e n'_h l'_h LM \rangle. \quad (7)$$

The matrix elements of the Stark effect can be evaluated as

$$\hat{F}_{NN'} = \langle n_e n_h l_e l_h LM | eF(r_h \cos \theta_h - r_e \cos \theta_e) | n'_e n'_h l'_e l'_h L' M' \rangle \quad (8)$$

with the relation of

$$\begin{aligned} \int d\Omega Y_{lm}^*(\theta, \varphi) \cos \theta Y_{l'm'}(\theta, \varphi) &= \left[ \frac{(l+m)(l-m)}{(2l-1)(2l+1)} \right]^{1/2} \delta_{l,l'+1} \delta_{mm'} \\ &+ \left[ \frac{(l'+m)(l'-m)}{(2l'-1)(2l'+1)} \right]^{1/2} \delta_{l,l'-1} \delta_{mm'}. \end{aligned} \quad (9)$$

Using the numerical matrix diagonalization method in the calculated total Hamiltonian, we can compute the exciton wave functions and energy levels.

### 3. Optical properties of QDs in the presence of local field

The optical absorption coefficient in the presence of a local field is determined by the electron-hole pair energy levels and the dipole moment matrix elements, which are obtained from the results of the numerical matrix diagonalization method. In the presence of a plasmon oscillating surface charge, the absorption coefficients of the silver coated QD can be obtained from the

optical dielectric constants,  $\epsilon_q$  and  $\epsilon_{sh}$ , of the CdS core and Ag shell, respectively. For noble metals at optical frequencies, the dielectric function can be expressed as

$$\epsilon(\omega) = \epsilon_q(\omega) + \epsilon_{sh}(\omega). \quad (10)$$

The optical susceptibility,  $\epsilon_q(\omega)$ , of CdS QDs is written as

$$\epsilon_q(\omega) = 1 - 4\pi \sum_e \frac{|d_{0e}|^2}{(\omega_e - \omega) + i\gamma_e} \quad (11)$$

where  $\gamma_e$  is the excitonic broadening constant and  $\omega_e$  is the one-pair ground state energy.  $d_{0e}$  is the dipole moment between the ground state and the one-pair state and is given by

$$d_{0e} = \langle \Psi_{eh} | P^+ | 0 \rangle = p_{cv} \int dr \Phi_{n_e l_e n_h l_h LM}(r, r)^* \sum_s \sigma(s, -s) \quad (12)$$

where the factor  $p_{cv} \equiv e \langle v | r | c \rangle$  comes from the overlap integral of the conduction and valence Bloch wavefunctions, and  $\sigma(s, -s)$  is the spin part.

The dielectric function,  $\epsilon_{sh}(\omega)$ , of the nanoshell, which are contributed by Drude-like electrons and interband transitions  $\epsilon(\omega)_{inter}$ , is given by [3]

$$\epsilon_{sh}(a, \omega, \Gamma) = \left(1 - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma}\right) + \epsilon(\omega)_{inter} \quad (13)$$

where the size-dependent electron scattering is  $\Gamma = \gamma_{bulk} + Av_F/a$ . Here,  $\gamma_{bulk}$  is the silver bulk collision frequency,  $a$  is the shell thickness and  $v_F$  is the Fermi velocity ( $2.05 \times 10^8$  cm/s for silver).  $A$  is a parameter determined by the geometry,  $\omega_p$  is the bulk collision frequency, and  $\epsilon_{sh}(a, \omega)$  is related to the  $\epsilon_d$  of the CdS QD. We have applied the Mie's theory to obtain the optical properties of the metal-coated QD. However, the Maxwell-Garnett method may also give similar results when a metal volume concentration is sufficiently low [11].

#### 4. Results and discussion

The following parameters were used for the numerical calculation: [12]  $m_e(CdS) = 0.18m_0$ ,  $m_h(CdS) = 0.7m_0$  with  $m_0$  being the electron mass in free space and the dielectric constants  $\epsilon_d(CdS) = 8.5$ . The CdS/Ag QD is embedded in an aqueous medium of dielectric constant  $\epsilon_a = 1.78$ . We used the nine lowest single particle states of electrons and holes for the numerical calculation.

Figure 1 shows the measured absorption spectra of pure CdS and CdS/Ag QDs of radius  $R = 1.3$  nm with silver thickness of 0.35 nm. The real Ag-CdS composite core-shell structure is presented in the reference [8]. The dashed line is the measured linear absorption of the pure QD and shows the lowest exciton absorption peak at 4.01 eV. The dotted line is the measured spectrum of the CdS/Ag QD. Absorption peaks are apparent between 3.0 eV and 4.5 eV, and a new peak appears at 3.36 eV from the plasmon resonance, originating from the coated silver on the CdS semiconductor QD. This plasmon resonance corresponds to a silver thickness of 0.35 nm. The pre-existent absorption peak at 4.01 eV has shifted by 0.09 eV to a lower energy 3.92 eV as well as broadened due to the surface plasmon. We propose that the red-shift of the absorption peak is attributed to local-field enhancement by the metal surrounding the semiconductor core. The local field is estimated to be approximately  $1 \times 10^6$  V/cm for the observed red-shift of 0.09 eV. The solid line in Figure 1 shows the calculated absorption spectrum in the presence of the electric field. From the measured and calculated curves, we conclude that the shift of the lowest exciton peaks in the QD occurs due to surface plasmon oscillations in the metal coating.

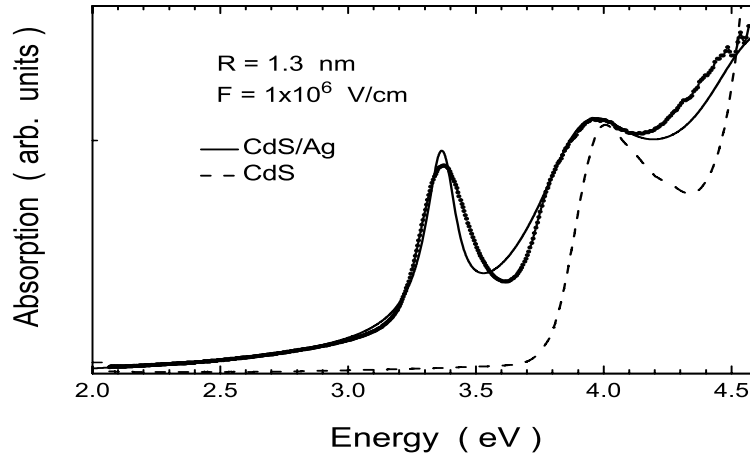


Fig. 1. Absorption spectra of pure CdS quantum dot of radius 1.3 nm and Ag-coated CdS quantum dot. Dashed and dotted lines are the measured absorption spectra of the pure and Ag-capped QDs, respectively. Solid line is the calculated absorption spectrum of the capped QD with silver thickness of 0.35 nm in the presence of an electric field  $1 \times 10^6$  V/cm.

Figure 2 shows the calculated Stark shift of various electron-hole pair states as a function of the induced local electric fields in a Ag-coated CdS QD with radius of  $R=1.3$  nm. The energy reference point of the internal local electric field has been set to zero. Various electron-hole pair states are denoted by their angular momentum quantum numbers: SS(PP) corresponds to  $1s(p)_e$  and  $1s(p)_h$  single states while SD and DS states are composed of  $1s(d)_e$  and  $1d(s)_h$  single states. Thus, SS denotes the lowest exciton state with total angular quantum number  $L=0$ , PP is the lowest exciton state with total angular quantum number  $L=1$  and SD and DS are exciton states with total angular quantum number  $L=2$ . The quantum confined Stark effect(QCSE) is clearly demonstrated as exciton energy levels shift towards the low energies as applied electric field increases. The shift of the exciton peaks is proportional to the strength of the electric field, consistent with the Wannier Stark ladder of quantum wells. However, in the strongly confined 3-dimensional system, the Stark shift is not linear, but rather squarely proportional to the strength of the electric field. The amount of shifting of the SS exciton is more than those of PP, DS, and SD excitons. The Stark shift is larger in the lower total angular quantum number in the symmetry charge distribution system. Comparing the Stark shifts of  $(1d_e1s_h)$  and  $(1s_e1d_h)$ , the Stark effect is dominant in lower angular momentum and lower effective mass.

Figure 3 shows the energy shift of the SS exciton state as a function of the QD radius,  $R$ , for a CdS/Ag QD experiencing electric fields of  $1 \times 10^6$  V/cm and  $5 \times 10^5$  V/cm [14]. The exciton energy shift is calculated by  $\Delta E_{ex}(R) = E_{ex}(F = 0, R) - E_{ex}(F, R)$ , and is a function of both the QD radius and the applied electric field. As shown, the degree of Stark shift is much larger for larger QDs compared to smaller QDs. The QCSE on excitons in QDs depends on the induced electric dipole moment of the exciton,  $eR(\langle z_h \rangle - \langle z_e \rangle)$ , which is related to the averaged distance between the electron and hole in the z-direction [9]. Furthermore, the induced electric dipole moment increases as the applied electric field increases. Therefore, the Coulomb interaction between the electron and hole competes with the Stark effect in determining the induced electric dipole moment of the exciton. Excitons in larger QDs have larger induced effective electric dipole moments. These effects are further

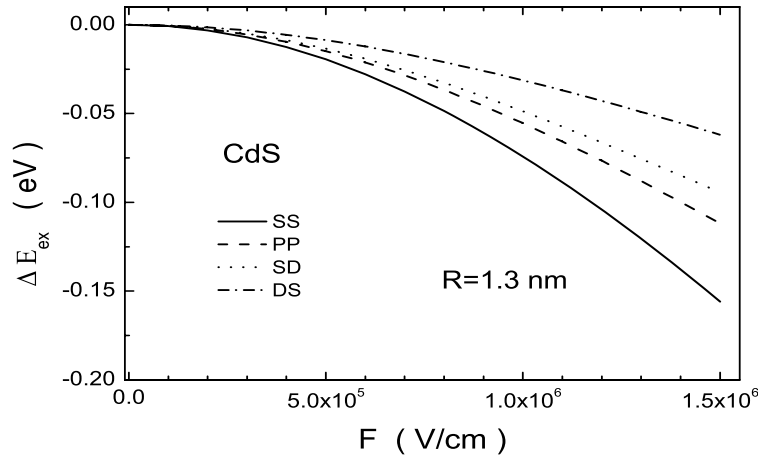


Fig. 2. Calculated Stark shifts of various electron-hole pair resonances as a function of the local field inside CdS QD (radius = 1.3 nm) coated with a 0.35 nm layer of silver. SS and PP:  $1s(p)_e$  and  $1s(p)_h$  exciton states with  $L=0$  and  $L=1$ , respectively, SD and DS:  $1s(d)_e$  and  $1d(s)_h$  exciton states with  $L=2$ .

increased in higher applied electric fields. Since excitons in larger QDs and in higher electric fields have larger induced effective electric dipole moments, the amount of Stark shift is much larger [9]. In the lower field region, the Stark effect is weaker and the electron and hole behave more like a classical exciton pair, which induces a small effective electric dipole moment. For small QDs the ground state of the exciton can be described well with an s-type trial wave function. However, for larger QDs the Coulomb interaction becomes important and the actual eigenstates are a mixture of single particle states with different angular momenta.

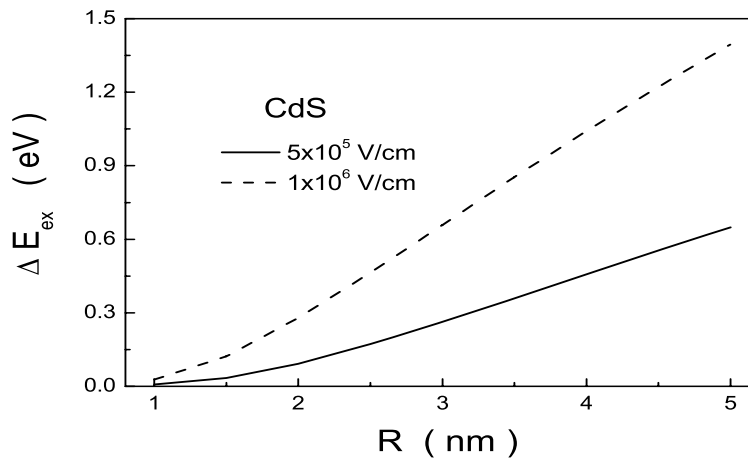


Fig. 3. Stark shifts of the lowest (SS) exciton resonance for the silver coated CdS/Ag quantum dots as a function of QD radius in fixed local fields of  $5 \times 10^5$  V/cm (dashed line) and  $1 \times 10^6$  V/cm (solid line).

Figure 4 shows calculated absorption spectra of CdS/Ag quantum dots with varying thicknesses of silver. The shift of the exciton peaks is caused by changes in the surface plasmon

density resulting from the changing silver thickness. The plasmon resonances are placed at low energies with increasing Ag thickness since the electron energy in the strong confinement regime heavily depends on the thickness of the metal [13]. We assume that the plasmon charge density decreases with increasing Ag thickness because the number of generated surface carriers remains constant despite different Ag thicknesses. As a natural consequence, it follows that as the Ag thickness is increased, the induced local electric field inside the QD is weakened, resulting in less red-shift of the exciton peak in CdS QDs.

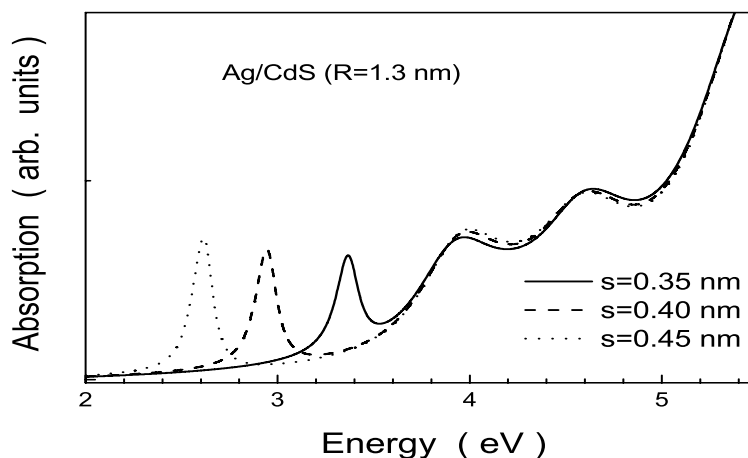


Fig. 4. Calculated absorption spectra of CdS/Ag quantum dots of radius 1.3 nm for various silver thicknesses of 0.35 nm, 0.40 nm and 0.45 nm. The solid line is the same absorption spectrum as in Figure 1 for a Ag thickness of 0.35 nm.

## 5. Conclusion

We have experimentally observed a red-shifted exciton peak in Ag-coated CdS QD composite structures and theoretically calculated the degree of red-shift as a function of the Ag shell thickness, which directly affects the strength of the induced local field inside the QD. Our calculations were based on the effective-mass Hamiltonian using the numerical-matrix-diagonalization method. In particular, we found that the degree of Stark shift is strongly dependent on the induced effective electric dipole moments and the exciton binding energy due to the local electric field is strongly reduced for small QDs. Our results strongly indicate that the red-shift originates from the local-field enhancement by surface plasmons, *i.e.*, the quantum confined Stark effect.

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