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New features of excitonic emission in metal nanoparticle/semiconductor quantum dot nanosystem

Yu.V. Kryuchenko *, D.V. Korbutyak

Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41 prosp. Nauky, Kyiv 03028, Ukraine

HIGHLIGHTS

- The light emission by a QD cannot in principle be regarded as that of a point dipole.
- This provides higher emission efficiencies in metal NP/semiconductor QD nanosystem.
- Satisfactory agreement is observed between the calculated and experimentally measured PL spectra in the CdTe QD/silver NP nanosystem.

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ABSTRACT

We study theoretically the excitonic emission properties of a hybrid nanosystem composed of a spherical metal nanoparticle (NP) and a spherical quantum dot (QD). We show that electromagnetic field (EMF) emitted by a single QD has only dipole, quadrupole, and octupole components, i.e., QD cannot in principle be regarded as an oscillating point dipole, which emits infinite series of multipoles. This leads to a substantial deviation of the characteristics of QD excitonic emission from the emission characteristics of point dipole (molecular fluorophore) located in a vicinity of metal NP at small interparticle distances. The observed fluorescence spectra of the CdTe QD/Ag NP nanostructure are found to be in good agreement with the calculated ones.

1. Introduction

Hybrid metal-semiconductor nanostructures (HMSNs), where excitonic and plasmonic properties of the constituent parts can be combined, have attracted increasing interest in the last years due to the substantial progress in their fabrication techniques and wide prospects of their practical applications. Different aspects of the exciton-plasmon interaction in HMSNs including nonlinear Fano effect, exciton coherent dynamics, optical bistability and nonlinearity, and four-wave parametric amplification arising from the nonlinear optical response have been intensively studied by many research groups (see, e.g., [1–4]). However, in the existing theories concerning the excitonic emission in such nanostructures QD is erroneously considered as an oscillating point dipole like emitting atom or molecular fluorophore (the EMF emitted by an oscillating point dipole and corresponding electromagnetic density of states contain contributions from infinitely large number of multipoles, see, e.g., [5,6]). Most likely this is due to the fact that scalar electric potential, which is produced by the QD exciton up to the moment of its radiative recombination (the potential being a superposition of the weighted dipole potentials of all crystal unit cells of the QD with the weight coefficients in a form of the exciton envelope wave function), really has a typical form of a point dipole potential $\varphi_i(\mathbf{r}) = ed_{\mathrm{exc}}\mathbf{r}\cdot\boldsymbol{\alpha}_i/(\varepsilon_{\mathrm{eff}}\, r^3)$ (see, e.g., [7]), where e is the elementary charge, d_{exc} is the excitonic dipole length, which takes values in the range from a few tenths of Å to a few Å depending on the semiconductor, $\boldsymbol{\alpha}_i$ are the orts along the directions of corresponding dipole moments, indices $i = 1, 2, 3$ correspond to three crystal axes. Such representation of the QD as a point dipole is quite reasonable when considering the direct Förster-type resonant energy transfer (FRET) from the excitons in QD to the plasmons in NP without participation of photons.

Our study was motivated by the simple and obvious fact that excitonic emission is nothing more than generation of the transverse electromagnetic field by QD (instead of the longitudinal electric field $\mathbf{E}_{\mathrm{L}} = -\nabla\varphi_i(\mathbf{r}) \sim r^{-3}$) and suspicion that this field differs from that radiated by an oscillating point dipole with corresponding consequences for the excitonic emission in the hybrid nanostructure.

* Corresponding author.
E-mail address: kryuchenko@isp.kiev.ua (Yu.V. Kryuchenko).

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The explicit expressions for the EMFs generated on the internal surface of QD at the excitonic emission are given in Appendices A and B. These basic expressions were not written in our previous works [8,9] for the lack of place. However, all results concerning the excitonic emission enhancement in the hybrid nanostructure, which have been obtained in [9], are based just on these expressions. As seen from these expressions, the EMFs emitted by a QD really differ substantially from those radiated by an oscillating point dipole [5]. Besides, we present here the results of a comparison between calculated emission efficiencies of the CdTe QD and equivalent point dipole located in a vicinity of metal NP and the results of a comparison between measured and calculated photoluminescence (PL) spectra of the CdTe QDs located in a vicinity of silver NPs.

2. Electromagnetic field generated on QD internal surface under excitonic emission

The method we use to calculate the EMF emitted by a single QD is similar to that used to calculate the scalar electric potential of the QD. Within this method each crystal unit cell inside the QD is considered as a point dipole emitter and contributions of all crystal unit cells into the total emitted EMF are taken with the corresponding weight coefficients in a form of the exciton envelope wave function. Justification for such an approach is presented in our previous work [8]. We consider here a case of nonresonant excitation when only QD is excited directly (in a case of resonant or close to resonant excitation the NP could be excited directly as well contributing to an additional enhancement of the QD absorption and subsequent excitonic emission [6,7]). The calculations of the EMFs emitted by QD are made accounting for the orientation of the QD crystal lattice relatively to the QD+NP coordinate system.

The QD+NP nanosystem with spherical QD and NP has been characterized by three spherical coordinate systems. Two of them are those with the centers in the QD and NP shifted to each other by a distance D (see Fig. 1). The relationships between the coefficients of EMF multipole expansions in these two shifted to each other spherical coordinate systems have already been found in [8]. They allow separate use of the QD and NP spherical symmetry despite the QD+NP nanosystem is nonspherical as a whole (contrary to the case of a point dipole in a vicinity of metal NP). The crystal structure orientation in QD is characterized by a third coordinate system with crystal axes $\{X_{cr}, Y_{cr}, Z_{cr}\}$. Standardly, source exciton wave functions in a QD are expressed in the crystal coordinate system (correct wave functions in a case of semiconductor with a cubic crystal lattice structure and a fourfold degenerate valence band Γ_8 are presented in [9]). However, in order to calculate EMFs in the QD+NP nanosystem these wave functions and point dipole moments of the QD lattice sites should be rewritten in the $\{\tilde{X}, \tilde{Y}, \tilde{Z}\}$ coordinate system with the $\tilde{Z}$-axis directed along the line connecting QD and NP centers. All related transformations are described in [9].They allow us to calculate the EMF emitted by the QD excitons in a form of EMF multipole expansions with multipole coefficients being functions of the Euler angles $\{\Psi_e, \theta_e, \varphi_e\}$, which characterize crystal lattice orientation in the QD.

For calculating the EMF emitted by the fivefold-degenerate states of the dark excitons in QD, which are characterized by quantum number $F=2$ of the exciton total angular momentum [9,10], the following effective exciton wave function should be used:

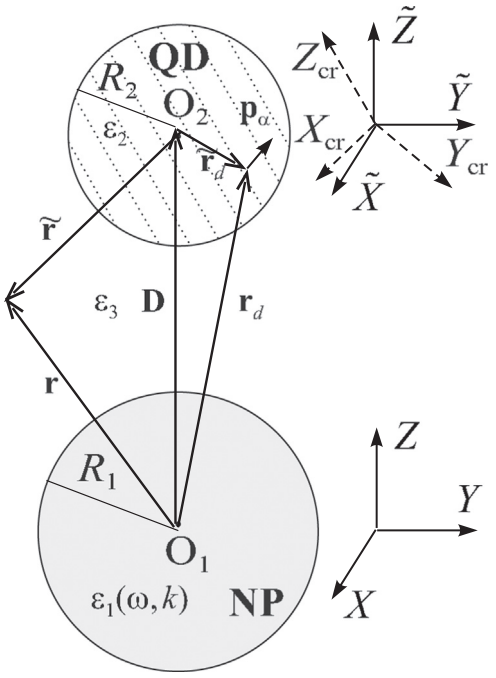

Fig. 1. Schematic of QD+NP nanosystem.

$$\Psi_{ex,2}(\tilde{\mathbf{r}}_e^{cr}, \tilde{\mathbf{r}}_h^{cr}) = \frac{1}{\sqrt{5}}[a_L \Psi_{ex}^{el-el}(2, 0; \tilde{\mathbf{r}}_e^{cr}, \tilde{\mathbf{r}}_h^{cr}) + b_L \Psi_{ex}^{el-el}(2, 1; \tilde{\mathbf{r}}_e^{cr}, \tilde{\mathbf{r}}_h^{cr}) + c_L \Psi_{ex}^{el-el}(2, -1; \tilde{\mathbf{r}}_e^{cr}, \tilde{\mathbf{r}}_h^{cr}) + d_L \Psi_{ex}^{el-el}(2, 2; \tilde{\mathbf{r}}_e^{cr}, \tilde{\mathbf{r}}_h^{cr}) + f_L \Psi_{ex}^{el-el}(2, -2; \tilde{\mathbf{r}}_e^{cr}, \tilde{\mathbf{r}}_h^{cr})], \quad (1)$$

where $\Psi_{ex}^{el-el}(F, F_z; \tilde{\mathbf{r}}_e^{cr}, \tilde{\mathbf{r}}_h^{cr})$ is the exciton wave function in the electron-electron representation (see [9,10]) of the state characterized by quantum number F of the exciton total angular momentum and magnitude F_z of its projection onto the Z_{cr}-axis; a_L, b_L, c_L, d_L, and f_L are the arbitrary phase factors. Such form of the effective wave function is caused by the fact that the five degenerate states of dark excitons have equal probabilities of being populated under external excitation of the QD. The arbitrariness of the phase factors reflects the incoherent nature of the exciton population of these states.

Respectively, for calculating the EMF emitted by the threefold-degenerate states of the bright excitons in QD with $F=1$, the effective wave function should be written as follows:

$$\Psi_{ex,1}\left(\tilde{\mathbf{r}}_e^{cr}, \tilde{\mathbf{r}}_h^{cr}\right) = \frac{1}{\sqrt{3}}\left[a_U \Psi_{ex}^{el-el}\left(1, 0; \tilde{\mathbf{r}}_e^{cr}, \tilde{\mathbf{r}}_h^{cr}\right) + b_U \Psi_{ex}^{el-el}\left(1, 1; \tilde{\mathbf{r}}_e^{cr}, \tilde{\mathbf{r}}_h^{cr}\right) + c_U \Psi_{ex}^{el-el}\left(1, -1; \tilde{\mathbf{r}}_e^{cr}, \tilde{\mathbf{r}}_h^{cr}\right)\right], \quad (2)$$

where a_U , b_U, and c_U are analogously the arbitrary phase factors.

In a case of excitonic emission from the exciton states with the quantum number F of the exciton total angular momentum the EMF that is generated on the internal QD surface can be written according to Eq. (16.47) [11] as follows:

$$\mathbf{E}_{QD,2}^{i}(\tilde{\mathbf{r}}; F) = \sum_{l,m}\left\{\frac{i}{k_0\varepsilon_2}\tilde{a}_{2,E}^{i,F}(l, m) \times [\nabla_{\tilde{\mathbf{r}}} \times h_l(k_2\tilde{r})\mathbf{X}_{l,m}(\tilde{\Omega})] + \tilde{a}_{2,M}^{i,F}(l, m) h_l(k_2\tilde{r})\mathbf{X}_{l,m}(\tilde{\Omega})\right\}, \quad (3)$$