Study of Electric Field Caused by Semiconductor Quantum Dots in Close Proximity to DNA Origami

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INTRODUCTION

DNA origami is a scaffolded DNA nanostructure that has attracted vast research interest in the past decade. DNA origami can be functionalized with a variety of biological molecules such as proteins and enzymes [1], as well as other probe materials such as semiconductor quantum dots and metal nanoparticles [2, 3]. In this paper, semiconductor quantum dots functionalized with single-stranded DNA are bound to DNA origami through complementary DNA strands on the surface of the origami. The quantum-dot--origami structure was modeled using a one-dimensional model of the energy states in a quantum dot, Debye screening for the electrolytic environment, and band bending theory. The photoluminescence (PL) spectra of the quantum dot-origami structure were obtained. A shift in PL spectra was observed and confirmed by the proposed model.

THEORY AND MODEL

In one-dimensional quantum mechanical model, the conduction band of a quantum dot can be described as a square well. However, with a presence of a negative electric field, the conduction band of a quantum dot can be estimated by a triangular potential well because of the band bending effect, and the lowest eigenenergy can be approximated by [4]:

$$E_{QD} = E_{gap} + \left(\frac{\hbar^2}{2m_e^*}\right)^{\frac{1}{3}}\left(\frac{9\pi e\mathcal{E}}{8}\right)^{\frac{2}{3}} + \left(\frac{\hbar^2}{2m_p^*}\right)^{\frac{1}{3}}\left(\frac{9\pi e\mathcal{E}}{8}\right)^{\frac{2}{3}} - Fd - \frac{3.536e^2}{4\pi\epsilon_{QD}\epsilon_0 a}$$

where E_{gap} is the band gap of a quantum dot, $\hbar$ is reduced Planck's constant, m_e^* and m_p^* are the effective mass of the electron and the hole respectively, ϵ_{QD} is the relative dielectric constant of a quantum dot, and a is the width of a quantum dot. The second and third terms represent the confinement effect in the conduction band and the valence band respectively, resulting from the solution of Airy function [5]. The energy band structure is given in Figure 1.

Since origami is a negatively-charged molecule, it produces a negative electric field. Both the origami and the attached quantum dot are in water-based electrolytic buffer, and the electric field produced by the origami decays exponentially:

$$\mathcal{E}_{\text{origami}}(z) = \frac{\sigma}{4\pi\epsilon_{water}\epsilon_0} e^{-z/\lambda_D}$$

where σ is the charge density of origami, z is the distance from origami, and λ_D is the Debye length. The parallel component of the electric field at the boundaries should be continuous, so we can estimate the electric field inside a quantum dot by:

$$\varepsilon_{QD} = \frac{\epsilon_{water}}{\epsilon_{QD}} \varepsilon_{water}\big|_{z\ at\ edge of\ QD}$$

RESULTS AND DISCUSSION

The model outlined in the previous section has been compared with experimental results. PL measurements were obtained using USB4000 Ocean Optics spectrometer with a 380-nm LED as the excitation source. Plain CdSe quantum dots with 565-nm emission yielded a spectrum with the emission peak around 565 nm, as expected (Figure 2a). The same quantum dots exhibited an emission peak at 535 nm when bound to 7249-base-pair DNA origami molecule (Figure 2b).

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This 30-nm shift can be explained using the band bending theory described above, and as shown in Figure 1. Because the origami's large negative charge results in band bending and an increase in the quantum dot's band gap, it follows that the quantum dot's emission wavelength will shift.

CONCLUSION

A quantum-dot--DNA origami structure has been modeled using a one-dimensional model of energy states in quantum dot, Debye screening for the electrolytic environment, and band bending theory. Photoluminescence experiments were conducted and results were compared with the model. A spectral shift in the PL was clearly observed and well explained by the proposed model.

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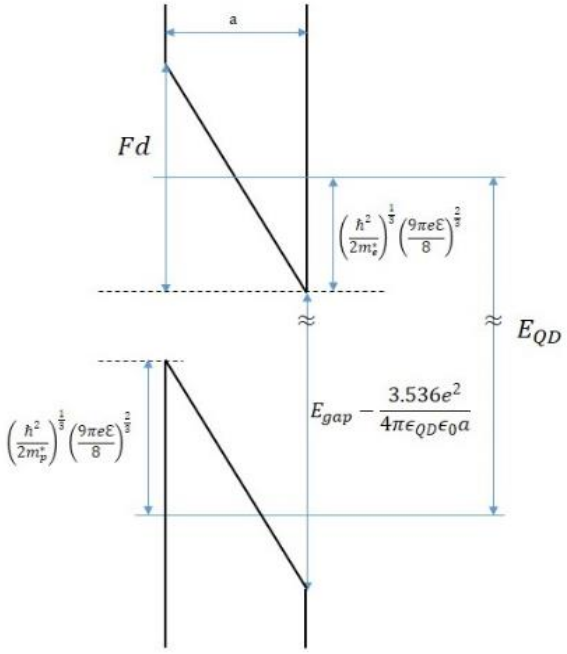

Fig. **1**. The energy band structure of a quantum dot in a negative electric field.

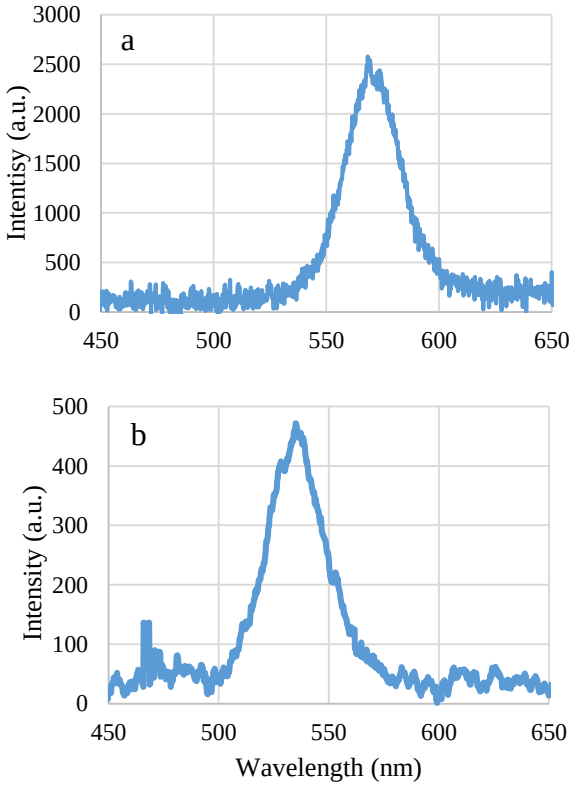

Fig. 2. Photoluminescence spectra of plain 565-nm-emission quantum dots (a) and 565-nm-emission dots bound to DNA origami (b).

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