



Surface charge induced Stark effect on luminescence of quantum dots conjugated on functionalized carbon nanotubes

W. Wang^{a,b}, G.K. Liu^{a,*}, H.S. Cho^b, Y. Guo^b, D. Shi^b, J. Lian^c, R.C. Ewing^d

^a Chemical Science and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, United States

^b Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH 45221, United States

^c Department of Mechanical, Aerospace & Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States

^d Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109, United States

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ABSTRACT

A significant blue shift of the luminescence of CdSe/ZnS quantum dots (QD) conjugated with functionalized multi-wall carbon nanotubes (CNT) is investigated. The observed Stark shift is due to the local electrostatic field induced by the carboxylic anions on the CNT surface. A theoretical model is developed to evaluate the contribution of the surface charges to the observed spectral shift (up to 0.59 eV). Based on the present model, the Stark shift provides an effective method for evaluating the density of carboxyl groups on the surface of functionalized CNTs and can be used as a charge detector for QD–nanostructures.

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1. Introduction

As previously reported by Emedocles and Bawendi [1] under an external electric field, the discrete excitonic states of a quantum dot (QD) [2,3] exhibit both polar and polarizable characteristics of Stark effect. The corresponding Stark shifts of the photoluminescence of QDs can be expressed as a linear and quadratic function of the applied electric field. One can expect that the luminescence of QDs would also exhibit Stark effect under a local electric field induced by surrounding cations or anions of nanostructures in polar solvent. In fact, it is known that, as a result of ionization of the carboxylic acid, the surface of a carboxyl functionalized CNT is highly negatively charged when dispersed in water [4,5]. For charge dispersion on the CNT/electrolyte interface, a net electric field can be induced statically around the CNT, whose strength is proportional to the density of carboxyl groups on the CNT surface. Thus, Stark shift of the photoluminescence of the QDs that electronically isolated but physically conjugated to the surface of CNTs might be an ideal probe of the on-site characteristics of functionalized CNT surface as well as the photodynamics of the conjugated QDs.

It is also reported that covalent attachment of luminescent QDs through carboxyl group (–COOH) on carbon nanotubes (CNT) is essential to construct various CNT based multi-functional novel nanostructures in the applications of biosensors for DNA/proteins detecting [6,7] and cancer diagnosis [8]. Since the density of the –COOH functional group on MWCNT surface after the functionalization treatment has never been quantitatively studied yet, con-

ventionally, the time consumed for precipitation after an ultrasonic re-dispersion of the reaction products in water is applied to phenomenally illustrate the degree of functionalization on MWCNT surface [4,9]. However, the agglomerate time is not the universal physical quantity to characterize the local functionalization feature on the surface of CNTs. The Stark shift induced by surface charge on the CNTs provides a more effective method for measuring the density of the functional groups. With all of those thoughts together, we have prepared a QDs conjugated CNT system and investigated its spectroscopic properties. We have further developed a simple theoretical model for quantitative interpretation of the observed results.

2. Experimental results

The QD–CNT system we studied was prepared using Qdot 800 ITC amino (PEG) quantum dots with emission wavelength at 800 nm supplied by Invitrogen Corporation (Carlsbad, CA) and multi-wall CNTs provided by Applied Sciences Inc. After the surface functionalization by plasma coating [10], various amount of multi-wall CNTs is dispersed into a 5 μ l QD solution (8 μ M), respectively. With the positively charged amino-polyethylene glycol (PEG) outer coating on the surface of CdSe/ZnS nanocrystal [11], individual QDs are bounded to the surface of carboxyl group functionalized CNTs by electrostatic attraction. Luminescence spectra of the QD–CNT system were recorded at room temperature with excitation of an Ar ion laser at 465 nm.

Fig. 1 shows the bright-field TEM image of QDs on the surface of the CNTs. As can be seen in Fig. 1, the QDs are distributed on the nanotubes via surface conjugation. Note that the CNTs were plasma coated with acrylic acid thin film before the conjugation

* Corresponding author. Fax: +1 6302524225.

E-mail address: gkliu@anl.gov (G.K. Liu).

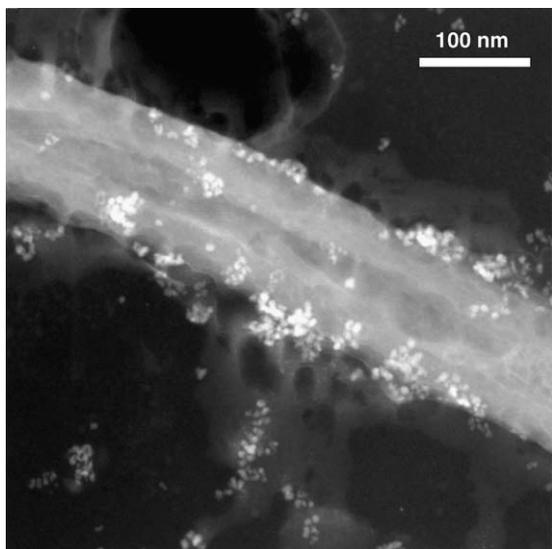


Fig. 1. Bright-field TEM image of carbon nanotubes with surface deposited quantum dots.

process [10]. The image clearly shows that the quantum dots are well attached onto the surfaces of the carbon nanotubes.

Whereas the commercial CdSe/ZnS QDs emit characteristic luminescence with wavelength centered at 800 nm [11], in the present work, a blue shift of this band is observed from the QDs that conjugated to the surface functionalized CNTs. Fig. 2 shows the luminescence spectra of the QD–CNT samples, with 0.01 mg (Sample b), 0.02 mg (Sample c) and 0.05 mg (Sample d) of carboxyl-group functionalized CNTs in comparison with the spectrum of the QDs only sample. Apparently, both the wavelength shift and the intensity of the QD–CNT luminescence depend strongly on the concentration of CNTs diluted in the solution.

As shown in Fig. 2, the peak of luminescence band of QD shifts as a function of the amount of CNTs in the solution. When the number of CNTs is limited, not all QDs in the solution could attach the surface of functionalized CNT. Some QDs are still suspended in the solution with luminescence wavelength near 800 nm, while others may aggregate together on the CNT surface and experience

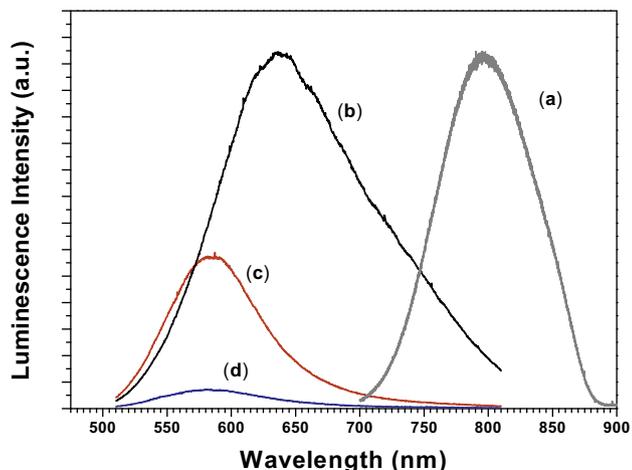


Fig. 2. Comparison of room temperature luminescence spectra of Qdot 800 ITK amino QDs (a) with QDs conjugated to the surface of 0.01 mg (b), 0.02 mg (c) and 0.05 mg (d) functionalized carbon nanotubes.

less effect of the surface charges than those fully adhered. As a result, their emission band undergoes inhomogeneous shifts. In fact, as shown in Fig. 2, the line width is primarily about the same as that of the free QDs, which is generally known as the result of inhomogeneous broadening induced by size distribution. Though the intrinsic emission of those QDs at 800 nm still could be observed in the 0.01 mg sample, the majority of QDs has already been conjugated on the surface of CNTs with luminescence emission wavelength centered at 635 nm (Sample b). When the CNTs in the QDs contained solution increase to 0.02 mg and higher, the number of available conjugate sites are also increased in the system. As a result, almost all of the QDs in the electrolyte precursors are conjugated to the surface of the functionalized CNTs and subjected to a more homogeneous surface electrostatic field. Thus, no emission is observed at 800 nm for Samples c and d as shown in Fig. 2. Given that the amount of QDs in all three samples is same, the average number of $-\text{COO}^-$ that each QD can experience at the surface of the CNT also increases as more CNTs are added. Therefore, we observed a larger Stark effect on the QDs, and the luminescence band of the QDs becomes narrower and exhibits a more symmetric line shape. The decreasing in the detected QD luminescence intensity is presumably due to the re-absorption of the luminescence photons by the CNTs in the visible spectral region [4,12,13]. As a result, the luminescence emission from the samples with the concentration of functionalized CNTs more than 0.05 mg is too weak to be recorded in our experiment.

3. Theoretical analysis

The observed blue shifts for the studied samples with different amount of CNTs are listed in Table 1. In order to quantitatively evaluate the influence of surface charge on the QD luminescence. The interfacial chemical structure between a QD and CNT is schematically shown in Fig. 3a. Some other minor species such as $-\text{CONH}-$ (amide) may form in aged samples. However, the formation of amide in a carboxylic acid with an amine requires dehydration, which is slow at room temperature and may not occur in aqueous solution from the point of view of chemical equilibrium. So we believe that the dominant functional groups on the CNT/QD interface are carboxylate anions and $[-\text{RNH}_3^+]$ in the fresh prepared samples from which our measurements were conducted. With the sodium borate buffer in solution (pH 8.5), the carboxyl group releases a proton from the carboxylic anion ($-\text{COO}^-$), while the surface of the QD is positively charged due to the primary amine functional group in the coating layer [11]. As a result, the QD is adsorbed to the CNT surface via a long-range electrostatic attraction. Due to the spherical shape of the QD, there is no integrated static electric field at the center of the QD. Moreover, the distribution of free anions and cations in the electrolyte near the QD/electrolyte interface is also spherically symmetric with respect to the center of each QD. In time average, the effect of the dynamical electric field induced by position fluctuation of these free ionic charges can also be neglected. Thus, the dominant contribution to the in situ microscopic electric field is from the negative charges on the surface of the CNT. After binding of the QDs on the CNT, the local charge distribution on the surface of the CNT is shown schematically in Fig. 3b.

As shown in Fig. 1, R_0 , the radius of the CNT and r_0 , the radius of QD in our samples are around 53 nm and 4 nm, respectively. Because R_0 is much larger than r_0 , the outer curved surface of the CNT adjacent to the QD can be treated approximately as a flat plane, as shown in the $i-j$ plane in Fig. 3c with respect to the center of the individual QD. The net electrostatic field at the center of QD $(0,0,r_0)$ in the k -direction generated by the surface charge at r is expressed as

Table 1Variation of Stark shift as a function of surface functionalized carbon nanotube in the 5 μL , 8 $\mu\text{mol/L}$ quantum dot solution.

Mass of functionalized CNTs in sample (mg)	0.005	0.01	0.015	0.02	0.04	0.05
Observed blue shift (cm^{-1})	3189	3242	3582	4594	4867	4730

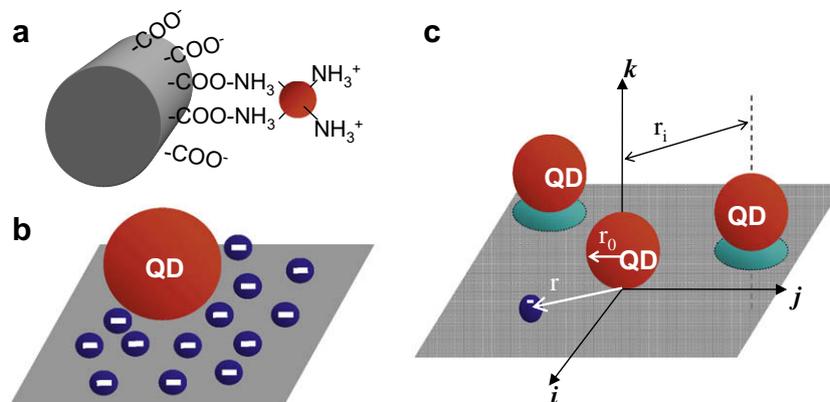


Fig. 3. Schematic view of QD-CNT coupling. (a) Binding QDs to the surface of CNT by a long range electric attraction. (b) On-site environment of QDs on the surface of a carboxyl-group functionalized carbon nanotube in electrolyte solvent (water). The net positive charge on the QD surface is ignored. (c) Coordinate system for the proposed model. The circle with negative sign stands for the anchored carboxylic anion ($-\text{COO}^-$) on CNT surface in (b) and (c).

$$dE_z = -2\pi \frac{1}{4\pi\epsilon_r\epsilon_0} \frac{\sigma r dr}{r^2 + r_0^2} \cdot \frac{r_0}{\sqrt{r^2 + r_0^2}}, \quad (1)$$

where σ is the negative charge density on the CNT surface which is proportional to the number of the anchored ionized carboxyl groups per unit area; E_z is the electric field in the k -direction with a negative value, which means that the polarization field is anti-parallel to the k -axis; and ϵ_0 and ϵ_r are vacuum permittivity and dielectric constant of solution, respectively. After integration of Eq. (1) over the CNT surface, we have

$$E_z = -\frac{1}{2\sqrt{2}} \frac{\sigma}{\epsilon_r\epsilon_0}. \quad (2)$$

Since the anchored negative charges on the CNT surface are neutralized locally when QDs are conjugated, the contribution of surface charges where another QD is located should be excluded from Eq. (2) for the QD in consideration. Assuming the average distance between QDs is greater than their diameter, the influence of negative charges within the projection area (turquoise oval in Fig. 3c) of the i th neighbor QD on the CNT surface can be expressed as

$$E_{z_i} = -\frac{1}{2} \frac{\sigma}{\epsilon_r\epsilon_0} \frac{r_0^3}{2(r_0^2 + r_i^2)^{3/2}}, \quad (3)$$

where r_i is the distance between the considered QD and the i th QD nearby as shown in Fig. 3c. The actual electric field at the center of the considered QD $(0,0,r_0)$ is reduced to

$$E_z = -\frac{1}{2\sqrt{2}} \frac{\sigma}{\epsilon_r\epsilon_0} \left(1 - \sum_i \frac{r_0^3}{\sqrt{2}(r_0^2 + r_i^2)^{3/2}} \right), \quad (4)$$

where the summation is over all the surrounding QDs.

Under the influence of such local electric field, E_z , above the CNT surface, Stark effect is expected on the excitonic states of the QDs. According to the observation of Empedocles and Bawendi, the Stark effect of QD states may exhibit both polar and polarizable characters, namely the excited state energy shifts can be expressed as a linear and quadratic function of the local field [1]

$$\Delta = \mu E_z + \frac{1}{2} \alpha E_z^2, \quad (5)$$

where Δ is the energy shift for the luminescent state, and μ and α are projections of the excited state dipole and polarizability along the electric field. When the average distance between the conjugated QDs on CNT surface increases significantly, the influence of neighboring QDs as shown by Eq. (3) could be ignored. Substituting Eq. (2) into Eq. (5), we find that

$$\sigma \approx 2\sqrt{2}\epsilon_r\epsilon_0 \left(\sqrt{\mu^2 + 2\alpha\Delta_{r \rightarrow \infty}} - \mu \right) / \alpha, \quad (6)$$

where \bar{r} stands for the average distance between QDs attached the CNT surface. We assume that \bar{r} is much smaller than the CNT radius. Eq. (6) indicates that the charge density can be evaluated from the Stark shift Δ of the luminescence band of QDs well-separated on the CNT surface.

Instead of experimentally determining the value of $\Delta_{r \rightarrow \infty}$ in Eq. (6), the density of QDs on CNT surface can be expressed as

$$\frac{N_{QD}}{A_{CNT}} \approx \frac{1}{\pi\bar{r}^2}, \quad (7)$$

where A_{CNT} is the total functionalized surface area of CNTs and N_{QD} is the total number of quantum dots on the surface of CNTs. On the other hand, the total mass M_{CNT} in the QD-CNT system is proportional to the total surface area of CNTs. Therefore, in the samples with a fixed number of QDs

$$\bar{r}^2 \propto M_{CNT}, \quad (8)$$

where M_{CNT} is the mass of CNTs added into the sample. After combination of Eqs. (4), (5), and (8), the Stark shift can be evaluated as a function of the total mass of CNTs in the samples.

$$\Delta = \Delta_{r \rightarrow \infty} - B \frac{1}{M_{CNT}^{3/2}}, \quad (9)$$

where B is a coefficient of positive value, which is related to the average diameter of the CNTs in sample. The first term in Eq. (9) is the upper limit of the blue shift, which represents the case of extremely dilute dispersion of QDs on CNT surface, and in principle, can be evaluated by fitting Eq. (9) to the experiment data. Moreover, from Eq. (9), we can also see that

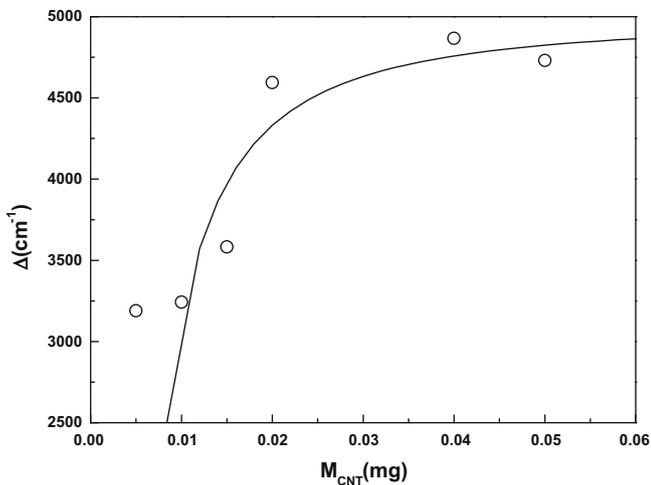


Fig. 4. Variation of blue shift Δ as a function of the total mass of CNTs. Circle dots are experimental data and the solid line is the least square fit of the experimental data to the model described by Eq. (9).

$$\frac{\partial \Delta}{\partial M_{\text{CNT}}} = \frac{3}{2} B M_{\text{CNT}}^{-5/2} > 0, \quad (10)$$

which indicates that the surface charge induced Stark effect leads to a blue shift in QD luminescence. The more CNTs added into the sample, the larger the Stark shift is induced. This prediction is consistent with the spectroscopic results shown in Fig. 2 and Table 1. A plot of the least square fitting of Eq. (9) to the observed blue shifts as a function of the mass of CNT in the sample is shown in Fig. 4.

As shown in Fig. 4, the theory agrees well systematically with the experimental data. The fitting results in the values of the parameters as $\Delta_{r \rightarrow \infty} = 4991 \text{ cm}^{-1}$ and $B = 1.865 \text{ cm}^{-1} \text{ mg}^{3/2}$. With $\alpha = 3.2 \times 10^5 \text{ \AA}^3$, $\mu = 92 \text{ Debye}$ [1] and $\epsilon_r = 80$ for water substituted into Eq. (6), the density of surface charge σ can be evaluated as $1.33 \times 10^{-19} \text{ C/nm}^2$, which means that there are approximately $0.832/\text{nm}^2$ anchored -COO^- anions on the CNT surface in the samples. Moreover, since almost all of the -COOH functional groups are ionized to form -COO^- in the sodium borate buffer with pH 8.5 [11], the average carboxyl functional group density on the surface of the CNTs after the plasma treatment is approximately 83 per 100 nm^2 .

4. Conclusions

In studies of the luminescence properties of QDs on the surface of CNTs, we have demonstrated a surface charge induced Stark effect on the quantum-confined emitting state of QDs conjugated on the surface of CNTs. It is shown that the local electrostatic field on the functionalized CNT surface has a significant influence on the excitonic states of QDs and can induce a Stark shift up to 0.59 eV, which is much larger than the electron-hole binding energy. It is assumed that the Stark shift of QD luminescence exhibits a linear and quadratic function of the local field, which is consistent with the previous observations for single free QDs. Moreover, in modeling the Stark shifts, we have developed a method to evaluate the carboxyl group density on the functionalized CNTs. Because of the extremely large polarizability α ($\sim 10^5 \text{ \AA}^3$), nano scale size r_0 ($\sim 10^{-9} \text{ m}$), and high quantum efficiency of luminescence emission, Stark shift of QD photoluminescence facilitates a very sensitive probe of the local surface functional group on the functionalized CNTs. Such a system may be utilized as a charge detector for other QD-nanostructure systems as well.

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