Characterization of CdSe Nanocrystals and their Interaction with Micellar Aggregates by Means of Capillary Electrophoretic Techniques

S. Oszwaldowski, L. Vasicek, T. Tonev and K.P. Roberts

The University of Tulsa, Tulsa, OK, USA, kproberts@utulsa.edu

Abstract

Stable water soluble surfactant coated CdSe nanocrystals with trioctylphosphine (TOP) were obtained by a process of dynamic surface coating with cationic, anionic, and non-ionic surfactants. The surfactant-coated CdSe/TOP nanocrystals were characterized by complementary techniques of UV-VIS and photo-luminescence spectrophotometry, as well as by means of a capillary zone electrophoretic technique. The results revealed an integral relationship between the degree of change in photoluminescence and shift in migration in capillary electrophoresis for surfactant-coated CdSe/TOP nanocrystals. Therefore, the combination of electrophoresis and spectrophotometry can serve as valuable techniques for the measurement of such surface modifications on quantum dot nanocrystals.

Keywords: CdSe; Nanocrystals; Dynamic coating; Capillary electrophoresis; Quantum dots

1. Introduction

Semiconductor nanocrystals, or quantum dots (QDs), have received great interest from the biological and medical communities due to their unique optical and electronic characteristics. As QDs become broadly applied for use for in vitro biological research (e.g., cell labeling, DNA assays, etc.), there is a great demand for obtaining water-soluble and biocompatible QDs. The emergence of QD surface-modification chemistry has provided several unique strategies that render the QDs useful as biological probes. Molecules that have been utilized to alter polarity of QDs include amphiphilic polymers, phospholipids, dendrimers, oligomeric ligands, bifunctional molecules and genetically modified proteins. However, the transformation of QDs passivated by hydrophobic groups (e.g., TOP, TOPO) into useful biocompatible probes has suffered from poor conversion yield, complexity in surface modification, and high precursor costs. Thus, there have been reports of surface transformation of non-water soluble nanoparticles using dynamic surface coating using long-chain hydrocarbon surfactants [1-3]. However, control of such surface transformations could tremendously benefit from a more clear understanding of the coating process.

Therefore, in the present work, we have investigated various coating procedures for obtaining water soluble CdSe/TOP nanocrystals, and once coated, characterization of the degree of coating, stability, and water-solubility was elucidated by means of spectrophotometric and capillary electrophoresis methods.

At present, capillary electrophoresis (CE) is regarded as the most powerful separation technique. The technique is highly efficient for the separation of charged as well as non-charged compounds, particles, nanoparticles, as well as microbial (viruses, bacteria etc.). Recently, CE was applied for separation of quantum dots according to size with a size differential of 3-5 nm [4,5].

In the case of particles, it was established that particle migration can be described by means of the following equation:

$$\mu = (\zeta \, \varepsilon \, \varepsilon_0 / 1.5 \, \eta) \cdot f(\kappa a), \qquad (1)$$

where ζ is zeta potential, ε, is the dielectric constant ε_0, is the permittivity of vacuum, η, is the viscosity of solution and $f(\kappa a)$ is a dimensionless function, which depends on κa (the ratio of the radius of the core particle to the electrical double-layer thickness) [6]. Under the same separation conditions, the migration depends on zeta potential as well as on a hydrodynamic size of QDs. As both of these parameters are a function of the surface architecture of nanocrystals, the technique is useful for characterization of surface phenomena, which is an important factor for development of various methods based on these parameters.

2. Results and discussion

2. 1. Preparation of surfactant-coated CdSe/TOP nanocrystals and characterization by means of spectrophotometry

In the present work, the surfactant coating procedure with was investigated with the use of non-ionic (TX 101), anionic (SDS) and cationic (CTAB) surfactants. It was concluded that all three of these surfactants allow coating the CdSe/TOP nanocrystals, and that this process transforms non-water soluble nanocrystals into water soluble nanocrystals. The coating process was optimized and it was found that the formation of a chloroform/surfactant emulsion was the key factor for the process. The resultant product from surfactant coating through this process was analyzed by UV-VIS and photoluminescence spectrophotometry, and it was concluded that the core size of CdSe nanocrystals was unaffected by the coating process. Figure 1 shows the UV-VIS and photoluminescence spectra of 2.9 nm CdSe/TOP nanocrystals dissolved in chloroform, as well as for after coating with the surfactant, CTAB.
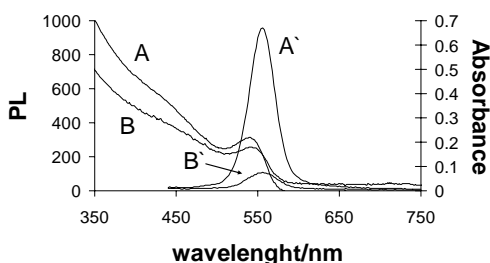

Figure 1. UV-VIS (A, B) and PL (A`, B`) spectra of 2.9 nm CdSe/TOP nanocrystals dissolved in various media: (A, A`), chloroform; (B, B`), CTAB. Concentration of CdSe nanocrystals: 1.2×10^{-6} mol L^{-1} (UV-VIS) and 3×10^{-7} mol L^{-1} (PL).

It was established that the surfactant coating process leads to a decrease of photo-lumninescence of CdSe/TOP nanocrystals. Figure 2 shows an example of the influence of surfactant concentration for a cationic surfactant (CTAB) on the photoluminescence of the coated nanocrystals.
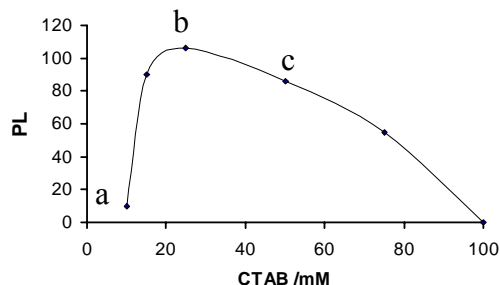

Fig. 2. The influence of the concentration of CTAB on the photoluminescence of 2.9 nm CdSe/TOP nanocrystals. The (a, b, c) denotes samples analyzed electrophoretically (Fig. 3).

It has been previously reported that a decrease in photoluminescence is related to the exchange of ligands at the surface of nanocrystals. In this case, ligands containing (sulfur, nitrogen)-atoms leads to quenching of the photoluminescence of CdSe/(TOP, TOPO) nanocrystals after the ligand exchange process. In the present work, it was established that the lowest decrease in photoluminescence was observed for the non-ionic surfactant, Triton-X (TX-101), whereas a decrease in photoluminescence was observed for ionic surfactants (CTAB and SDS), and was more pronounced with CTAB than with SDS. Therefore, in comparing non-ionic vs. ionic surfactants, it can be concluded that the presence of a charged group in the structure of the surfactant molecule has a more drastic impact on the quantum yield of Cd/Se nanocrystals, as evidenced by the decrease in photoluminescence.

A second observation is that the effect on the quenching process (CTAB>SDS) is related to the hydrophobic interaction between the hydrophobic CdSe/TOP and a molecules of a surfactant. As CTAB is able to quantitatively transform a hydrophobic CdSe/TOP nanocrystal into a surfactant soluble species at lower concentration than SDS, it indicates that the van der Waals interaction between the hydrophobic TOP group and hydrocarbon chain of the surfactant dictates the efficiency of the coating process. In this case, the C16 hydrocarbon chain of CTAB has a greater affinity and coating probability than does the C16 hydrocarbon chain of SDS, and, thus, optimal surfactant coating with CTAB occurs at a lower concentration than with SDS.

2.2 Characterization of surfactant coated CdSe/TOP QDs by means of capillary zone electrophoresis

A capillary electrophoresis method was applied for separation of surfactant coated CdSe/TOP nanocrystals, where it was observed that the migration of surfactant coating CdSe/TOP nanocrystals was a function of the concentration of surfactant used for coating. As shown in Figure 3, migration time as well as sample stability is drastically affected by the concentration of CTAB used in the coating CdSe/TOP nanocrystals.
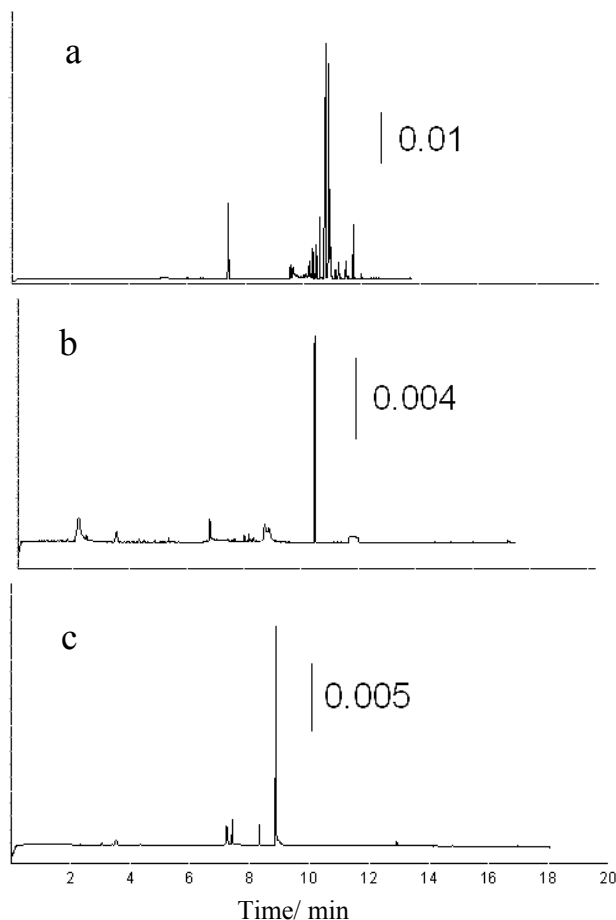
Figure 3. Electropherograms of CdSe/TOP nanocrystals coated with CTAB surfactant. Concentration of CTAB used for coating process: a, 10 mM; b, 25 mM; c, 50 mM.

A similar dependence (shift in migration vs. concentration of surfactant used for coating) was observed when anionic surfactant SDS was used for coating CdSe/TOP nanocrystals (Fig. 4).
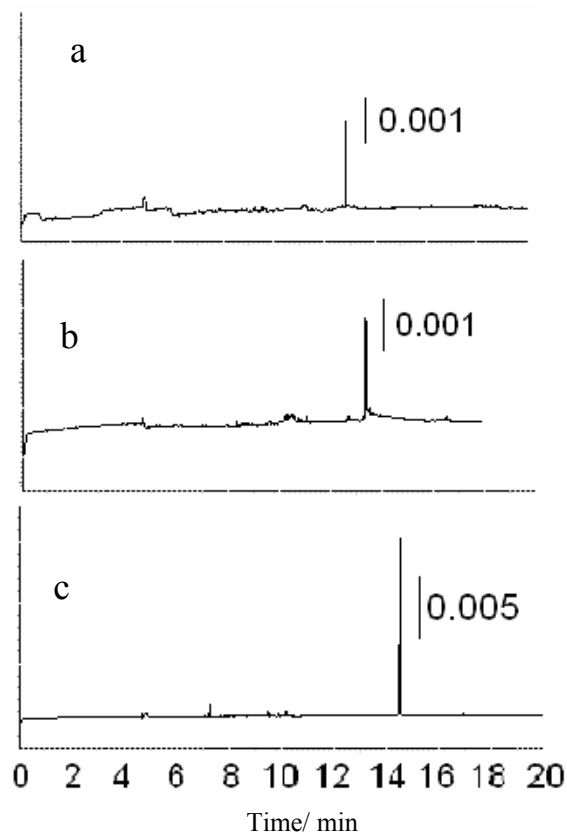
Figure 4. Electropherograms of 4.9 nm CdSe/TOP nanocrystals coated with SDS. Concentration of SDS used for coating process: a, 50mM; b, 100mM; c, 250 mM.

As can be seen in both Fig. 3 and Fig 4., a clear shift in electrophoretic migration due to coating of CdSe/TOP with CTAB to a shorter migration time is observed, whereas, with SDS, the trend was a larger migration time with increased surfactant concentration.

2.3 Rationalizing observed effects for surfactants coating CdSe/TOP – nanocrystals in terms of photoluminescence spectra and electrophoretic mobility

As mentioned above, it was observed that at low surfactant concentration (10 mM CTAB) no photoluminescence was observed (Fig. 2), due to an aggregation of QDs in this milieu. In terms of capillary electrophoresis, the electropherogram obtained at this CTAB concentration shows the presence of multiple narrow peaks (spikes) of high intensity (Fig. 3a), which is reported to be characteristic for the formation of an aggregate of nanoparticles [7]. However, an increase in surfactant concentration

resulted in the formation of a single peak with much smaller intensity, which means that the formation of stable CTAB-coated CdSe/TOP nanocrystals had taken place. Furthermore, it was observed that an increase in CTAB concentration during the coating process resulted in a decrease in migration of the CTAB-coated nanocrystals (Fig. 3b,c), which points out the direct relationship between an increase in CTAB concentration and a shift in migration of surfactant coated nanocrystals. On the other hand, it should be noted that the same coating process leads to a decrease in photoluminescence of CTAB-coated CdSe/TOP nanocrystals (Fig. 2, points: b, c). Thus, it can be summarized that there is a direct correlation between a decrease in photoluminescence (Fig. 2) and a decrease in electrophoretic migration (Fig. 3) due to CdSe/TOP coating with CTAB, which means that both techniques are sensitive towards surfactant additions to the surface architecture of CdSe/TOP nanocrystals.

What is more, it is generally accepted that the charge-to-size ratio governs the separation in capillary electrophoresis of nanoparticles. Therefore, the general equation which describes the electrophoretic mobility due to coating process can be written as:

$$\Delta\mu = \frac{\Delta q}{2\pi\eta\Delta r} \qquad (2)$$

where, $\Delta\mu$ is the shift in electrophoretic mobility due to coating process, because of: Δq (change in charge of nanoparticle), and Δr (change in hydrodynamic radius).

In the present work, the dynamic coating procedure has an appreciable impact on QD parameters which should be taken into account in order to model the migration of such modified nanocrystals. First, the charged surfactant coating increases both the charge of QDs (Δq), as well as the hydrodynamic radius (Δr) and that both factors effect the migration of CTAB-coated QDs. However, for SDS-coated QDs, both factors lead to an increase in their migration. It was concluded that, in the case of the CTAB coating, the charge-to-size (hydrodynamic) ratio increases with an increase in the surfactant concentration (Fig. 3), which indicates that the rate change in charge is greater than it is in hydrodynamic size.

Another parameter to characterize the migration of QDs in CE can be deduced from photoluminescence spectra taken as a function of surfactant concentration (Fig. 2). From these results, it can be concluded that, due to the coating process, a dynamic exchange exists between the hydrophobic TOP and the charged surfactant at the surface of CdSe nanocrystal. This dynamic exchange, therefore, influences both CE migration and the photoluminescence of the QDs (Figures 2 and 3), which provides a mechanism for enhancing differences between these nanocrystals based on the charge-to-size ratio, which inevitably expands the migration window available for particle separation by capillary electrophoresis.

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