Characterization of CdSe nanocrystals coated with amphiphiles. A capillary electrophoresis study

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Abstract We have synthesized CdSe nanocrystals (NCs) possessing a trioctylphosphine surface passivation layer and modified with amphiphilic molecules to form a surface bilayer. The NCs covered with single amphiphiles are not stable in aqueous solution, but a mixed amphiphilic system is shown to provide stability in solution over several months. The solutions of the modified NCs were characterized by UV-Vis absorbance, photoluminescence, and transmission electron microscopy. An electrophoretic study revealed two operational modes. The first relies on the enrichment of NCs using a micellar plug as a tool. The accumulation of NCs at the plug-electrolyte buffer interface results in a sharp peak. By controlling the electrophoretic conditions, nanocrystals were forced to exit a micellar plug into an electrolyte buffer. We conclude that a system consisting of modified nanocrystals and a micellar plug can act as a mixed pseudomicellar system, where modified nanocrystals play the role of pseudomicelles.

Keywords Capillary electrophoresis · Separation · Nanocrystals · CdSe · Surfactants · Focusing · Mixed micelles

Introduction

Nanocrystals (NCs) possess unique electrooptic properties suitable for a variety of applications ranging from biological sensing to photovoltaic. Recent progress in the development of functional, versatile metallic and semiconducting NCs for use in workable devices has led to the need for methods for monitoring NCs properties, such as size distribution, surface charge, and reaction efficiencies of various surface functionalization strategies [1]. Instrumental tools for determining nanocrystals size and size distribution have been well established for UV-Vis spectrophotometry, photoluminescence, electron/probe microscopy, dynamic light (DLS) and X-ray scattering [2, 3]. However, elucidation of surface properties, particularly in solution, is less well developed. For example, modification of a crystal surface to provide water solubility by exchanging hydrophobic surface ligands with hydrophilic ligands or formation of a lipid bilayer with amphiphiles can drastically affect nanocrystals properties such as hydrodynamic radii, zeta potential, NC diffusion rates, cytotoxicity, luminescence quantum efficiency, and longevity. However, techniques such as TEM (transmission electron microscopy) and X-ray scattering can only probe the nanocrystal inorganic core and not the surface coating [4]. As well, even when UV-Vis and DLS have been applied to estimate properties of NCs, such as hydrodynamic radius and solution stability [4], these techniques typically require large sample concentrations and are often at the lower edge of the size range capabilities of most DLS instruments.
Capillary electrophoresis (CE) is uniquely suited, with its open tubular design, for characterization of NCs and their reaction products in solution due to the high separation efficiency, water-based separation media, as well as intrinsic migration behavior of nanostructures in an applied electric field [reviews: 5–9].

It is generally accepted that electrophoretic migration of nanoparticles is much more complex phenomenon than migration of a typical solute. For a charged spherical particle dispersed in a electrolyte the following forces have to be considered: (i) the electrostatic force exerted by the applied electric field, (ii) Stokes friction, (iii) electrophoretic retardation, and (iv) relaxation effects [5, 10]. Depending on particle size (speaking precisely, the value of \( \kappa a \)—the ratio of the hydrodynamic radius of the particle (\( a \)) to the electrical double-layer thickness (\( \kappa^{-1} \)), Helmholtz-Smoluchowski, Hückel-Onsager or Henry’s equation, respectively, should be used for characterization of the particles migration [11].

For particles at the nanoscale, the Henry’s equation seems to be the most appropriate, however with the limitation that \( \zeta \)-potential should be <25–50 mV [11]. Many studies have substantiated that nanoparticles migration velocity is reliant on zeta potential and particle size \((\zeta, a)\) [5, 6, 10].

In order to overcome limitations enforced by those effects some non-conventional modes of capillary electrophoresis were recently tested. Thus, the successful separation of CdTe nanocrystals according to size with the size span 2.6 nm was recently proposed with the use of capillary gel electrophoresis with polymer as sieving medium [12]. The method was recently extended toward CdSe/ZnS NCs [13]. Next, the reversed electrode polarity stacking mode of CE with the use of anionic surfactant was examined for the enrichment of Au nanoparticles and an increase in the detection of particles, up to \( 10^3 \) fold was reported [14–16]. Also, analytical capillary isochromatophoresis was tested for the characterization (effective charge, \( \zeta \) potential) of semiconductor nanoparticles [17].

The present work is an extension of works recently released [18–20], where amphiphile coated CdSe NCs were used to the characterization of electrophoretic phenomena for particles at nano scale. It was proven that coating of nanostructures with amphiphilic molecules can be a convenient way in order to solubilize them in aqueous solutions, thereby introducing a surface charge at NC/water interface with consequent electrostatic double layer sufficient for the particles migration under aqueous electrophoresis conditions. For this anionic, cationic as well as non-ionic amphiphiles can be used, which assure appropriate electrostatic character of a coated NCs. Coated in this way NCs can be regarded as an equivalent of NCs with voluminous ligands, which can be either a model for NCs with bulky biological ligands (charged or uncharged) or as a convenient test particle for evaluating novel analytical procedures for bio-functionalized NCs. This part of the work was supported by molecular modeling at \( ab \) initio DFT level, to support the experimental data in relation to ligands exchange or CdSe NCs coating with amphiphilic molecules. This tool was previously applied in work [20] for estimating interactions surface of crystal CdSe and ligands.

As the consequence of coating phenomena a novel electrophoretic technique was introduced recently, where a micellar plug was applied as a tool for the preconcentration/separation of amphiphile coated nanocrystals [19, 20]. This is a direct consequence of phenomena observed in work [18], where an interaction of amphiphile coated CdSe NCs with regular micelles was found to be higher than NCs affinity to aqueous phase. Based on recently released works [18–20], it can be concluded that the main features of the novel system were as follows. The NCs coated with voluminous ligands (amphiphile, DNA) can be regarded as a micelle-like object (a pseudomicelle), able to form a mixed pseudomicellar system with regular micelles. Because of this, the NCs can migrate within a micellar plug, which allows NCs to accumulate at micellar/micelle-free boundary, in the form of a sharp peak (focusing). This is the enrichment phenomenon with the enrichment efficiency \( \sim20 \) (SEF\textsubscript{height}, sensitivity enhancement factor) [19]. Modifying the electrophoretic conditions, the NCs release from a micellar plug to background electrolyte (BGE), in controllable fashion, was available. Formally, this is demixing of mixed pseudomicellar phase, the phenomenon of highly interest to the colloidal science. Note that the scheme outlined above is a new tool in the separation science that particles able to form a pseudomicellar system can be separated from these unable to create such a system [19, 20].

In this context, it is worth noting, that the previous studies indicate that several hydrophobic nanostructures can be made water soluble using amphiphilic molecules. These include nanocrystals [21–26], single-walled nanotubes [27–29] and fullerenes [30]. In each case, an ionic head group of an amphiphile introduces a surface charge on a nanostructure with consequent electrostatic double-layer sufficient for the separation under aqueous electrophoretic conditions. These solubilization techniques have led to additional encapsulation procedures [3], separation methods using centrifugation [31], and capillary electrophoresis separations [18–20, 30, 32, 33]. In work [21], a shift in color profile of Au nanoparticles coated with molecules (e.g. surfactants) was related to particles electrophoretic mobility, which can a sign of complexity in the nanoparticles/CE system. Issued last works [34, 35], dealing with nanoparticles dispersed in solution of reversed micelles, show that effects: nanoparticles separation, enrichment for charged nanoparticles and coagulation, can be explained by DLVO theory (Deryaguin-Landau-Verwey-Overbeek).
Experimental

Reagents

All chemicals and reagents used herein were of analytical grade. For synthesis of the TOP-coated CdSe nanocrystals, cadmium oxide (~1 micron, 99.5%), selenium powder (100 mesh, 99.999%), trioctylphosphine (TOP, 90%) from Sigma-Aldrich (St. Louis, USA, http://www.sigmaaldrich.com) and 1-octadecene (ODE) from Acros Organics (Morris Plains, USA, http://www.acros.be/) were used. Aqueous amphiphile solutions were prepared from SDS (sodium dodecyl sulfate), DOSS (dioctyl sulfosuccinate sodium salt), CTAB (cetyltrimethylammonium bromide), Triton N-101 (polyoxyethylene nonylcyclohexyl ether), Triton X-100 (polyoxyethylene (10) isooctylphenyl ether), Brij 30 (polyethylene oxide dodecyl ether), Igepal CO-210 (polyoxyethylene (2) nonylphenyl ether, average M, = 294), PVP (polyvinylpyrrolidone) average M, = 1,300,000, sodium cholate, CHAPS (3-

Characterization of coated CdSe nanocrystals 347

Preparation of TOP-coated CdSe nanocrystals

The hydrophobic TOP-coated CdSe nanocrystals were prepared from cadmium oxide and elementary selenium using referenced procedures [36]. Briefly, the selenium precursor was prepared by combining elementary selenium and TOP at room temperature. The cadmium precursor was prepared from cadmium oxide, ODE, and oleic acid at 250 °C. Prepared solutions were mixed at different temperatures for the appropriate time period to obtain the desired size of CdSe nanocrystals. The resulting CdSe/TOP nanocrystals were purified by adding a large volume of acetone followed by adding methanol until a slightly turbid solution was obtained. The mixture was left to stand overnight. Larger NCs precipitated after the mixture stood overnight, but smaller NCs required centrifugation (3,000 rpm, 15 min). The pure nanocrystals were washed with methanol and then dissolved in either toluene or hexane for extended storage or in chloroform for the preparation of amphiphile-coated NCs.

TEM sizing of core CdSe QDs

The size of CdSe core structures (2.8 nm; UV-VIS λ, = 537 nm) was measured using the JEOL JEM-2100 Scanning Transmission Electron Microscope (STEM) (Oklahoma State University). One drop of a dilute sample of CdSe/TOP NCs in chloroform or CdSe/TOP/N-101 solution prepared in 10 wt. % N-101 was placed onto a Formvar coated copper grid, allowed to settle for 20 s, and wicked away using an absorbent tissue. Size analysis was performed on digital images captured with an ImageJ V. 1.34 s program.

Nanocrystal surface modification

The samples of modified CdSe/TOP NCs were prepared by adding 200 µl chloroform solution of CdSe/TOP
Modification of surface of CdSe/TOP NCs

Hydrophobic CdSe/TOP NCs were phase transferred into aqueous media by forming a reverse-lipid bilayer on NC surface, using an amphiphilic molecules, i.e., CdSe/TOP→CdSe/TOP/amphiphile. This was facilitated using non-ionic, ionic, and polymeric amphiphilic molecules shown in Figure S1. It was found that among these amphiphiles the most stable aqueous solution for CdSe NCs coated with amphiphiles, was obtained using R-COONa derivatives (LA, OA) or non-ionic surfactant Triton N-101 (≥1 week). Amphiphiles (R-SO3Na; DOSS, SDS) provide stable dispersion for CdSe/TOP NCs, for more than just a few hours, where larger NCs (>3 nm) were the least stable. Many other single amphiphile coatings did not allow for adequate NCs dispersion in aqueous medium or quickly aggregates. Note that an appropriate concentration range of an amphiphile is necessary for effective dispersion of CdSe/TOP NCs and maintaining the highest as possible PL of NCs. In this situation (Fig.1), the NCs aggregation occurs at lower concentration of an amphiphile, due to lack of effective coating, whereas the limit of the highest amphiphile concentration relies on the its intrinsic solubility in water.

Additional experiments revealed, that the long term stability (>4 months) of amphiphiles coated CdSe/TOP NCs was obtained using a pair of ionic/non-ionic amphiphiles for NCs coating. Examples of this system are shown for the visual inspection (Fig. S3, supporting materials). In this case, the NCs dispersed in solution of a pair of ionic/non-ionic amphiphiles were coated with ionic amphiphiles. This is based on the observation that both native CdSe/TOP NCs dissolved in an organic solvent (hexane, chloroform) and this coated only with the non-ionic TX-100 amphiphile (CdSe/TOP/TX-100) have high level of normalized photoluminescence (PL per 0.1 absorbance unit, Fig. 2b). This was significantly reduced due to NCs coating with a pair of ionic/non-ionic amphiphiles (Fig. 2b), despite the highest NCs solubilization obtained in this situation (Fig. 2a). Both parameters (AU, PL) were summarized in Fig. 2c, d for representative anionic, non-ionic...
and cationic surfactants, examined in the present work, with the same conclusion.

These observations were supported by theoretical data for the CdSe crystal and selected ligands in terms of ligands binding to the crystal surface [20]. For this the theoretical tool – molecular modeling at DFT level was applied (Electronic Support Section, Figs. S13, S14, S15, S16 and S17). Both results (experimental and theoretical) lead to the one general conclusion that there are, at least, two coating mechanisms for CdSe NCs using amphiphilic molecules. This can be explained based on a model of the passivation of InP nanocrystals by TOPO (trioctylphosphine oxide) ligands [40], shortly discussed in Electronic Support Section, that passivation relies on two phenomena: (i) crystal—ligand, and (ii) ligand—ligand interaction, both having similar importance in terms of binding energy. For CdSe/amphiphile system, analysed in the present work, it can be stated that dispersion of CdSe/TOP NCs using only R-SO$_3$- amphiphile (SDS, DOSS) leads to less stable CdSe/amphiphile system. This can be concluded from experimentally demonstrated short-term NCs stability, lack of a peak for CdSe/amphiphile NCs during CZE run, as well as from the theoretical model. In this case, based on the model of the surface passivation, it can be stated that surface ligand—amphiphile (TOP ↔ amphiphile) interaction is the main cause for dispersing CdSe/TOP NCs, whereas interaction: crystal—amphiphile, can be negligible. On the other hand, the CdSe/TOP NCs coating with only R-COO$^-$ amphiphile (LA, OA) ensures more stable CdSe/amphiphile system, as concluded from enhanced stability of NCs over time, the presence of a peak for NCs in CE, as well as theoretical model. In this case, the binding of amphiphiles, according to passivation model, is due to both interactions (crystal—amphiphile and surface ligand—amphiphile, respectively), which definitely enhance the CdSe/TOP/R-COO$^-$ overall stability.

In the present work, it was stated that CdSe/TOP NCs were better dispersed using a pair of amphiphilic molecules (non-ionic/ionic) than using an individual amphiphile. In this case, another effect should be considered, that nanocrystals can be incorporated into a micelle structure. According to the ref. [22] surfactants with single alkyl chain did not form a structure of pseudoaggregate (NC trapped inside micelle) and limited stability for the structure was found using surfactant with two alkyl chains (eq. DOSS). The best results in terms of

Fig. 2 Upper (a, b). Spectra for CdSe NCs due to solubilization of CdSe/TOP NCs (2.4 nm, first exciton band, $\lambda$=508 nm) using a non-ionic or a pair of ionic/non-ionic surfactants. a, UV-Vis spectra, b, photoluminescence spectra (PL). Samples of CdSe NCs: A, in chloroform, B, dissolved in TX-100 and C, in mixture of TX-100/CTAB. As an insert in (b) is comparison of the normalized emission efficacy (PL per 0.1 AU) reflecting the PL effect, due to NCs solubilization in these surfactants. Below (c, d). Coating and emission efficacy due to solubilization of CdSe/TOP NC in selected pairs of amphiphilic surfactants. Data summarized for CdSe NCs sizes=2.7–3.3 nm. Figures: c, coating efficacy in the form of absorbance of the NCs solution (first exciton band of NC in UV-Vis); d, the normalized emission efficacy (PL per 0.1 AU) for NCs solutions according to coating. Abbreviations: CdSe, chloroform solution of CdSe (50 $\mu$L of 2–5 $10^{-6}$ M CdSe NCs per 500–300 $\mu$L of chloroform). Coating with: only non-ionic surfactants (TX-100, N-100; 10% w:w) (examples of coating with single amphiphile) and pairs of surfactants: 10% TX-100 (w:w) containing 100 mM of ionic surfactants: (anionic) SDS sodium dodecyl sulphate; DOSS, dioctyl sulfosuccinate; (cationic) CTAB, cetyltrimethylammonium bromide; CP, 1-dodecylpyridinium chloride. Sample preparation: (50 $\mu$L of 2–5 $10^{-6}$ mol l$^{-1}$ CdSe/TOP NCs per 300 $\mu$L of surfactant solution). An example of CdSe/TOP being solubilized in a pair of non-ionic surfactant/polymer (TX-100/PVP; 0.5 g 10% TX-100 and 0.022 g PVP) is shown for comparison.
stability of a pseudoaggregate have been reported using a mixture of surfactants (a mixture of \(n\)-poly(ethylene glycol) phosphatidylethanolamine (PEG-PE) and phosphatidylcholine (PC)), where a pseudoaggregate was found to be more stable over time, compared with this, applying the individual PEG-PE or PC micelle. In the present work, a micelle of non-ionic amphiphile (TX-100, N-101) was applied. Specifically for TX-100, the micelle radius 4.3 nm and even wider was reported, depending on actual micelle shape \([41]\). This allows build a temporary pseudoaggregate containing nanocrystal (core and surface hydrophobic ligands) trapped inside a micelle structure or covered by a layer or bilayer of amphiphiles. In this situation, a direct contact between CdSe/TOP NCs and aqueous phase can be restricted and possible follow—up reactions, under the well—known term—microreactor, are available. This is supported by literature, where surfactant micelles or microemulsion droplets \([24, 25, 42]\) were applied to transfer NCs between phases, in order to build a protective layer around a CdSe/ZnS nanocrystal (case of silica coating). This effect can facilitate attachment of selected amphiphiles to a surface of CdSe crystal, which acting alone (single amphiphile) can slowly/incomplete substitute or coat native surface ligands (TOP, TOPO), promoting nanocrystals aggregation in aqueous conditions, as mentioned above.

To summarize, coating with a pair of ionic/non-ionic amphiphiles, can be an effective tool to disperse the nanocrystals in aqueous media, even using amphiphilic molecules with low binding energy between a crystal and an amphiphile or even in this situation, where amphiphiles can passivate only selected faces of a nanocrystal, as concluded from the theoretical model (Electronic Support Section).

Migration behavior of amphiphile coated CdSe NCs

Based on CZE, the preliminary experiments using CdSe NCs coated with a particular ionic amphiphile (SDS, DOSS, LA or OA) confirm conclusions given in the previous section. Therefore a peak for these NCs coated with \(R\)-COO\(^{-}\) amphiphiles (OA, LA) was obtained. Contrary to this, no peak for these NCs was seen, applying \(R\)-SO\(_3\)^\(-\) amphiphiles (DOSS, SDS) for coating. In the latter case, the peak absence is due to amphiphiles come off from the CdSe crystal as these amphiphiles have been defined as a weakly bound to facets of the CdSe crystal.

An interesting capillary electrophoretic phenomena have been reported recently \([19, 20]\), when a non-ionic amphiphile was applied to the sample containing nanocrystals coated with ionic amphiphiles. In this situation, using CZE or MEKC, the peak of NCs was visualized, irrespective of applied an ionic amphiphile used for NCs coating (weakly or strongly bound to CdSe NCs). An example of this, namely NCs dispersed in TX-100/DOSS was included to electronic support section (Fig. S4, supporting materials). This example also explains the detection scheme applied in the present work, that wavelength \(\lambda=245\) nm is suitable for detecting both micellar plug and NCs simultaneously, whereas \(\lambda>300\) nm is selective for NCs only.

The aim of the present section is a deeper insight into the migration mechanism for NC/plug system. For this water soluble, electrically neutral CdSe/TOP/N-101 NCs (CdSe NCs dispersed in the non-ionic N-101 amphiphile) was applied due to results presented in the previous section (Fig. 2), that N-101 affords for better NCs dispersion in aqueous solution. Moreover, aqueous solution of such modified NCs was found to be stable over time and no aggregation or precipitation was seen for at least 1 week.

Further discussion will be conducted on the basis of three experiments (Fig. 3 and Figs. S5, S6, Electronic Support Section). In the first experiment (Fig. 3), to the sample containing CdSe/TOP/N-101 NCs and aqueous phase can be restricted and possible follow—up reactions, under the well—known term—microreactor, are available. This is supported by literature, where surfactant micelles or microemulsion droplets \([24, 25, 42]\) were applied to transfer NCs between phases, in order to build a protective layer around a CdSe/ZnS nanocrystal (case of silica coating). This effect can facilitate attachment of selected amphiphiles to a surface of CdSe crystal, which acting alone (single amphiphile) can slowly/incomplete substitute or coat native surface ligands (TOP, TOPO), promoting nanocrystals aggregation in aqueous conditions, as mentioned above.

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Characterization of coated CdSe nanocrystals

EOF position for neutral NCs. Therefore, an appearance of a peak of NCs at the plug/BGE border denotes the presence of charged NCs in this situation; this despite injection of uncharged NCs. In this case, the transformation of an electrically neutral NC into a negatively charged NC, irrespective of a way of NCs coating (by a single amphiphile, or using a pair of amphiphiles), was confirmed. Moreover, coating of NCs with anionic amphiphiles, the presence of negatively charged NCs, is discussed. Moreover, only CZE mode was applied in order to avoid additional equilibria related to MEKC mechanism. Note, that NCs coating with ionic amphiphiles, which leads to formation of electrically charged NCs, was confirmed twice in the present work. In this situation, migration of NCs within NC/plug system is controlled solely by migration phenomena available for mixed micelles, e.g. length of the plug, as confirmed later (Figs. 5, 6, S10). Note, that the effect is universal and applying a pair of amphiphiles as a plug, the accumulation of various nanostructures at plug/BGE boundary was reported recently (NC/DNA, NC/silica shell/DNA or NC/derivative of 1,10-phenanthroline) [19, 20]. In this case, the transformation of a nanostructure (e.g. NC/DNA) into a micelle-like object (NC/DNA//amphiphile) enables build a pseudomicellar system with regular micelles. Based on this, nanoparticles able to build a stable pseudomicellar system can be distinguished from those unable to do this by electrophoresis [19].

Next experiments, based on MEKC methods (Figs. S5, S6, supporting materials), are continuation of discussion presented in the previous works [18–20]. The aim of the Fig. S5 was to demonstrate the presence of a strong interaction between a CdSe/amphiphile and a regular micelle, which enforces the CdSe/amphiphile to migrate along with a micellar phase. In this situation, in all cases, a shift in peak position to \( k' = \infty \) position for charged or uncharged NCs (e.g. from \( k' = 0 \) to \( k' = \infty \) → neutral NCs) does support the idea about pseudomicellar phase discussed upper. Figure S6 depicts an impact of the concentration of a non-ionic surfactant in the sample plug and confirms the role of a non-ionic surfactant in the transformation of peak of CdSe/amphiphile NCs. In this case, the observed transformation: peak (MEKC)→ peak (focused NCs) is in agreement with similar transformation using CZE method applied to CdSe NCs coated with LA, as reported in ref. [19].

**Fig. 3** Effect of a kind of an anionic amphiphile in the sample plug on the formation of a focussed peak for CdSe/TOP/N-101 NCs. Sample: CdSe/TOP NCs, size 3.6 nm, dispersed in non-ionic amphiphile N-101 (10%). Injection: a, only sample of CdSe/TOP/N-101 NCs/10% N-101 (w/w); b, sample of CdSe/TOP/N-101 NCs containing N-101 5% (w/w)/0.28 M C\(_{5}\)H\(_{11}\)SO\(_{3}\)Na; c, sample of CdSe/TOP/N-101 NCs containing N-101 5% (w/w)/0.22 M C\(_{12}\)H\(_{25}\)SO\(_{3}\)Na. Conditions: electrolyte buffer, 10 mM sodium tetraborate; voltage, 25 kV; applied in order to avoid additional equilibria related to MEKC mechanism. Note, that NCs coating with ionic amphiphiles, which leads to formation of electrically charged NCs, was confirmed twice in the present work. In the first section it was established that a decrease in PL for CdSe NCs dispersed in a pair of amphiphiles is related to NCs coating with an ionic amphiphile. Another proof comes from the gel electrophoresis experiment (Fig. S7, supporting materials). By comparing migration of commercially available carboxyl derivative (NC-COO\(^-\), Evident T2-MP EviTags, carboxy functionalized) with migration of CdSe NCs coated with anionic amphiphiles, the presence of negatively charged NCs, irrespective of a way of NCs coating (by a single amphiphile, or using a pair of amphiphiles), was confirmed. Moreover, coating of NCs
is a rapid process as the sample of NC/TOPO mixed with the aqueous solution of an ionic amphiphile, just before GE run, shows the peak of CdSe/amphiphile.

The present section is continuation of recently released results [19, 20], dealing with focusing of NCs using NC/plug system. Several experiments, included to the present section, enable characterize the system. Based on NCs dispersed in a pair of amphiphiles, applied as the sample plug, the linear relation between peak (area, height) for focused NCs and concentration of NCs ($c_{CdSe}$) (Fig. S8, supporting materials) confirms: (i) quantitative accumulation of NCs, due to transfer NCs from the entire sample plug to the plug/BGE boundary, and that (ii) the transport and accumulation concerns nanocrystals being dispersed in a plug, but not being in the form of aggregates (otherwise both migration time and peak height should be random [5]).

The transport of NCs under NC/plug system was further analysed applying various voltages. It was observed (Fig. 4, frames a-d) that a decrease in applied voltage (20, 14, 10 and 4 kV, respectively) leads to an increase in electrophoretic mobility ($= \mu_{app} - \mu_{EOF}$) of negatively charged NCs. However, contrary to typical band broadening of solutes with increasing migration time, the peak of focused NCs, located in a wider micellar plug, remains sharp. Moreover, there is an apparent distinction in peak area applying low vs. high voltage (frame e). Thus, at lower voltage, a peak area of NCs reached its the highest value, which means optimal state in mutual velocities (plug vs. NCs). A decrease in a peak area at higher voltage denotes the

![Fig. 4](image-url)  
Focusing of CdSe/TOP//SDS NCs due to migration of NCs within a micellar plug and characteristic of the peaks for CdSe coated with a pair of TX-100/SDS or TX-100/DOSS amphiphiles. Figs. a-d, visualization of focused peaks for CdSe/TOP//SDS NCs, core size 2.9 nm. Voltage applied: a, 20 kV; b, 14 kV; c, 10 kV and d, 4 kV. Injection: 35 mbar/5 s. Sample preparation: CdSe/TOP NCs dispersed in 0.5 g 10% TX-100 with 0.032 g SDS. Electrolyte buffer: 5 mM sodium tetraborate. Positions of EOF were denoted by vertical arrows. As an inset, frame d is DAD spectrum for CdSe/TOP//SDS NCs obtained during a CE run. Frame e, peak area dependence on applied voltage. Electrolyte buffer: 5 mM (A, C) and 3 mM (B) sodium tetraborate.
presence of side effects. This can be partial aggregation (dimers, trimers, and so on) imposed by high energy field or distribution of NCs between plug and BGE, as well as NCs exit (plug $\rightarrow$ BGE).

In order to recognize the focusing effects more deeply a set of experiments were undertaken using sequence of two plugs, where a sample plug containing NCs was the first plug followed by a micellar plug free from NCs (Figs. 5, 6 and S10). In this instance, throughout all experiments (Figs. 5, 6 and S10), the sample of CdSe NCs dispersed in a pair of amphiphiles (TX-100/DOSS) (CdSe NCs, size 3.6 nm, concentration $5.2 \times 10^{-6}$ mol l$^{-1}$) was the first plug, about 3.3 cm length. The second plug was a pair of TX-100/DOSS amphiphiles. The concentration of TX-100 (10% w:w) in both plugs was kept constant. The experimental variables were DOSS concentration in a plug or the length of second plug, respectively.

First experiment (Fig. 5) shows an effect of a dilution of a sample plug by means of solution of TX-101 (10% w:w). In this instance, the concentration of both (NC, DOSS) were diminished ($[\text{TX-100}] = \text{constant}$). A linearity between NCs peak features (area, height) and NCs concentration was seen, which confirms the similar relation discussed upper (Fig. S8, supporting materials). The meaning of the experiment is that transport phenomena for NC/plug system are universal for this system, despite implementation of various configurations (one plug vs. two plugs). Also, the migration of NCs from the first plug, through the second plug, to plug/BGE boundary additionally confirms the state of NCs being dispersed in plug (no aggregation). Under this state, transport of NCs through two micellar plugs was available, under electrophoretic conditions applied.

In next experiment (Fig. S10, included to supporting materials due to many details) an impact of DOSS concentration in the second plug on the transport of NCs was analysed. For this detection, using two wavelengths allows monitor both NCs and plug simultaneously ($\lambda = 245$ nm) or NCs only ($\lambda = 330$ nm), respectively. Similarly to the previous figure, the first plug was a sample plug (NCs dispersed in TX-100/DOSS; plug length 3.3 cm) and the second plug was mixture of amphiphiles only (TX-100/DOSS; plug length 6.4 cm). Similarly to the previous figure, the transport of NCs throughout two plugs was the effect observed. The difference is, that a decrease in content of DOSS in the second plug, leads to: (i) shift in migration time

Fig. 5 Two plugs system. Impact of the concentration of an ionic amphiphile (DOSS) in the first plug on peak shape of CdSe/DOSS NCs. Frames (left side): a, two plugs system with the first plug containing 10% TX-100 (w:w), 0.148 mol l$^{-1}$ DOSS and $5.2 \times 10^{-6}$ mol l$^{-1}$ CdSe NCs; b, the same system, first plug: 10% TX-100, 0.074 mol l$^{-1}$ DOSS and $2.6 \times 10^{-6}$ mol l$^{-1}$ CdSe NCs; c, ibidem, 10% TX-100, 0.037 mol l$^{-1}$ DOSS and $1.3 \times 10^{-6}$ mol l$^{-1}$ CdSe NCs; d, two plugs system with first plug: 10% TX-100 and 0.148 mol l$^{-1}$ DOSS (blank). As the second plug, a pair of amphiphiles 10% (w:w) TX-100, 0.148 mol l$^{-1}$ DOSS, were applied for (a-d). Conditions: BGE 10 mM sodium tetraborate, applied voltage 20 kV, detection UV-vis $\lambda = 330$ nm, selective for CdSe NCs (NC size, 3.6 nm). Length of a plug: first 3.3 cm, second 6.4 cm. Right side. Frame (e), the relation between peak area (red line) or height (blue line) and $c_{\text{CdSe}}$.
of plug and related with this migration of NCs, (ii) compression of the length of the plug, depicted by sloping, dashed lines (Fig. S10). Compression of the plug, due to decrease in the content of an ionic amphiphile in a micellar segment in between BGE, is in agreement with ref. [43], and (iii) gradual broadening of NCs peak throughout the second plug (Fig. S10, frames c, d). Note, that this example shows the complexity in NC/plug system. Thus, taking into account conductivity of sample plug (0.21 mS) vs. micellar plug (0.011 mS) (plug 1 and 2, respectively; frame e, Fig. S10), as well as difference in mobility, that sample plug > micellar plug (frames d, e) as concluded from relation: mobility of mixed micelle = f(ratio non-ionic/ionic surfactant) from ref. [43], it can be stated that isotachophoretic version of electrophoresis can occur in this situation (remark of anonymous reviewer). On the other hand, only a plug with sufficient content of an ionic amphiphile can effectively support pseudomicellar state of NCs within plug. Evidently, insufficient DOSS content in a plug enforces a pseudomicelle to release surface bound amphiphiles to the environment.

Fig. 6 Comparison of one and two plug systems, as well as impact of the length of the second plug on migration and peak shape of CdSe/DOSS NCs. Frames: a, one plug system (CdSe NCs, size 3.6 nm, dispersed in TX-100/DOSS); b, two plugs system with 3.3 cm second plug; c, two plugs system with 6.4 cm second plug and d, two plug system with 11.7 cm second plug. As the first plug the CdSe NCs dispersed in a pair of surfactants (0.6 g 10% (w:w) TX-100/0.148 mol l\(^{-1}\) DOSS) was applied through frames a-d, plug length 3.3 cm. As the second plug a pair of surfactants (0.6 g 10% (w:w) TX-100/0.148 mol l\(^{-1}\) DOSS) with various lengths (3.3, 6.4 and 11.7 cm, respectively) was applied. Conditions: \(c_{CdSe}=5.2 \times 10^{-6}\) mol l\(^{-1}\) (first plug), BGE 10 mM sodium tetraborate, applied voltage 20 kV, detection UV-vis 245 nm (inset frame a, \(\lambda=330\) nm to monitor NCs only). Inset frame e, the two plugs system, without NCs (blank). Right side are graphic interpretations of each run, where upper is the starting situation and below is the situation observed at detector (orange, first plug; yellow, second plug and red, NCs). Note, that due to the NCs transport from the first plug to the plug/BGE boundary, both plugs (1+2) are TX-100/DOSS layers free from NCs, denoted as yellow.
thereby precluding efficient accumulation of NCs at plug/BGE boundary. Thus, the broadening of a peak of NCs observed here, can be due to one dominant effect or as a result of superposition of both effects mentioned.

Moreover, the effect of the peak broadening does prove again the presence of NCs being in the form of dispersed solutes rather than aggregates, since a shift in a peak shape, from focused peak (at high DOSS content) to broaden peak (at low DOSS content), concerns the state of a solute and should not impact the state of an aggregate.

The third and final experiment (Fig. 6) shows the effect of the length of second plug (range: 3.3–12 cm) at constant length of a sample plug (3.3 cm). It was observed that despite ratio in lengths, up to four, the transport of NCs (first plug → second plug/BGE boundary) was found to be efficient since peak height of NCs was seen roughly independent from the length of the second plug. Obviously, this is confirmation of a pseudomicellar state of NCs as only this state (vs. aggregates) allows NCs to migrate efficiently in a micellar environment. On the other hand, the experiment (Fig. 6) shows a new, interesting situation that NCs from a sample plug (matrix) can be selectively transported into a pure micellar environment, far away from a matrix. This is a new method for solutes extraction from a sample, in combination with efficient preconcentration in the form of focused nanostructures and will be analysed in details in future works.

Effect of modification of electrolyte buffer on migration of CdSe/TOP/amphiphile NCs

It was found that NCs could be forced to migrate outside the micellar plug by modifying electrolyte buffer—due to an increase in ionic strength or by adding organic modifiers, such as methanol or acetonitrile, to a background electrolyte buffer. This issue was shortly scrutinized in Fig. S9 (supporting materials) based on mentioned previous works. One of consequences of BGE modification is the separation of plain nanoparticles from these bioconjugated with DNA, which enables estimate yield of bioconjugation [19]. In the present work, conditions for NCs release from the plug was analyzed taking into account the conductivity factor for BGE and plug, respectively. For this BGE based on potassium chloride was used as this salt is used typically in conductometric experiments (e.g. calibration of conductivity electrode). Figure, which depicts this experiment, was posted on Electronic Support Materials, due to many details included (Fig. S11, supporting materials). In agreement with the previous report [19] and Fig. S9 (supporting materials), the NCs release from the plug to BGE was seen at higher ionic strength of BGE, that conductivity $\beta_{\text{BGE}} > \beta_{\text{plug}}$ (frame f, Fig. S11). The related phenomenon in this context is an impact of BGE conductivity on the length of plug (denoted as $p = t_{\text{END}} - t_{\text{EOF}}$) (frame e, Fig. S11). It was seen that BGE ionic strength influences the $t_{\text{END}}$ (border: plug end/BGE) more than $t_{\text{EOF}}$ (beginning of the plug: side: BGE/plug), which is a sign of different composition of the plug front vs. the plug end. Note that, at $r=0$ a plug was was homogeneous and at $(t_{\text{EOF}} > 0)$ the difference between plug front vs. end, in terms of composition, is due to electrophoresis. Note, that length of the plug ($p$) can be regulated by the plug composition, that decrease in the content of an ionic amphiphile in a plug leads to decrease in a plug length (Fig. S10, supporting materials). The next factor—the peak area of the focused peak, monitored at $\lambda = 330$ nm (frames a–c, Fig. S11), shows that the parameter is insensitive to changes in plug length ($p$). This leads to the conclusion that the border plug end/BGE can accommodate only a limited amount of NCs and additional increase beyond this limit leads to NCs peak broadening at the plug/BGE border or dispersion of NCs throughout the plug.

It was observed in the previous work that organic solvents added to the plug can effectively release NCs from the plug [19]. Based on conductivity experiment, some salts (Li, Na, K, all Cl) were checked and additives, typically MeOH or ACN, lead to decrease or increase the conductivity of an appropriate salt solution, respectively. However applying as BGE the sodium tetraborate containing ACN, the conductivity was found to be fairly constant despite an increase in ACN content in BGE (Fig. 7, frame d). In this situation, NCs exit the plug (Fig. 7, frames b, c) is the effect of the presence of ACN in BGE (conductivity $\beta_{\text{BGE}} = \text{constant}$). On the other hand, under the reverse situation, that ACN was added before a run to the sample plug instead of BGE, even higher content of ACN in a sample plug did not lead to NCs release from a plug (Fig. 7, frame d), which definitely confirms, controllable by a BGE, a release of NCs from a plug/BGE boundary.

There are two final remarks related with issues discussed here. First one concerns a peak shape of NCs being released from a plug, that in some cases the peak is sharp and in some broaden. This issue is shortly discussed in text that accompanies frame g, Fig S11 (supporting materials), as well as in the last section of the present work. Finally, separation of two NCs of different dimensions, using BGE modified by ACN is discussed (Fig. S12, supporting materials) with the conclusion that although an efficient separation of two CdSe NC was obtained, the reason for this is difference in the state of surface of crystal CdSe.

Simplified mechanism for focusing and release of CdSe/amphiphile NCs using a micellar plug

It can be stated, based on capillary electrophoresis experiments, that at least three effects leads to focusing of CdSe/
amphiphile NCs using a plug of mixed micelles. These are: the presence of a plug—thus a segment of phase of mixed micelles in between BGE, high affinity of these NCs to a phase of micelles and additional coating of these NCs with amphiphiles during a run. On the other hand, the migration phenomena observed in the present work may be a special case of mixed micellar system, already analyzed by capillary electrophoresis [45, 46]. This is because CdSe/amphiphile NCs can be regarded as micelle-like objects able to form stable phase with regular micelles as concluded from the first part of the present work and refs. [18–20]. It was reported, that peaks of various fractions of mixed micelles with mobility between 0 and $-3.5 \times 10^{-4} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ were observed, depending on polydispersity in terms of size and composition of mixed micelles [45, 46]. The same can be concluded from ref. [43], that specifically for mixed micelles, mobility depends on ratio: non-ionic/ionic surfactant in a phase of mixed micelles. The mobility is reduced in parallel with a decrease in concentration of an ionic surfactant in a phase of mixed micelles and for the fraction of an ionic surfactant in the phase: 1, 0.4, 0.3 and 0.2, the mobility: $-3.16, -2.55, -2.15$ and $-1.67 \times 10^{-4} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ was estimated, respectively [43].

Focusing of CdSe/amphiphile NCs can be explained based in this remark and the fact reported in the first part of the present work, that coating of CdSe NCs with a pair of amphiphiles is selective, that CdSe nanocrystal coated with an ionic amphiphile is the main product obtained (Fig. 2 and S7, Electronic Support Section). Thus, the whole system can be described in terms of electrically charged NCs dispersed in a phase of mixed micelles. In this situation, there is substantial difference in mobility: CdSe/(ionic amphiphile) vs. mixed micelle, that mobility of CdSe/(ionic amphiphile) $>>$ mobility of mixed micelle, in agreement with the relation above. The diversity in mobility CdSe/(ionic amphiphile) vs. mixed micelle in a micellar plug is enhanced due to the substantial reduction of the drag force for a particle migrated in a micellar phase, because of very low viscosity of the micellar medium.

In order to discuss a release of CdSe/amphiphile NCs from a micellar plug it should be noted that a lack of broadening of a peak of focused NCs in a plug, even

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig7.png}
\caption{Effect of modification of BGE or plug by acetonitrile (ACN). A sample used as a plug was CdSe NCs dispersed in TX-100/sodium laurate (LA) (10% w:w/0.13 M). Frames: a, BGE 10 mM sodium tetraborate; b, BGE 10 mM sodium tetraborate containing 15% ACN; c, BGE 10 mM sodium tetraborate containing 30% ACN. Frame d, modification of a plug by ACN (1:1); BGE, 10 mM sodium tetraborate. Peaks: NCplug, CdSe NCs being in a plug; NC_{BGE}, CdSe NCs released from a plug to BGE. Conditions: voltage 20 kV, detection UV-vis 330 nm in order to visualize NCs only, injection 50 mbar/0.1 min. Each frame was set at the same absorbance scale in order to visualize the effect.}
\end{figure}
Characterization of coated CdSe nanocrystals

Acknowledgements

Conclusions

In the present work, the hydrophobic CdSe/TOP NCs were functionalized using amphiphilic molecules. Two types of NCs coating with amphiphiles have been distinguished, due to the difference in coating mechanisms, regulated by the specific affinity of ligands to a surface of the CdSe crystal. This issue was discussed in the light of data obtained from molecular modeling at DFT level, applied to estimate important interactions in CdSe/amphiphile systems. Analysis of electrophoretic migrations for CdSe/TOP/amphiphile NCs leads to the conclusion that these solutes can be regarded as pseudomicelles, able to form a mixed pseudomicellar system with regular micelles. Because of this, using a micellar plug, the CdSe/TOP/amphiphile NCs can be focused at the boundary between micellar and micelle—free zone. Finally, conditions for demixing of the mixed pseudomicellar system, which allows NCs to be released from the micellar plug, were analyzed with the conclusion that the effect can be controlled by the current electrophoretic conditions.

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