Capillary zone electrophoresis of quantum dots dispersed in mixed micelles: New evidence of the concentration effect

Sławomir Oszwałdowski [a,*], Kenneth P. Roberts [b], Andrei R. Timerbaev [c]

[a] Warsaw University of Technology, Faculty of Chemistry, Chair of Analytical Chemistry, Noakowskiego 3, 00664 Warsaw, Poland
[b] Department of Chemistry and Biochemistry, The University of Tulsa, 600 S. College Ave. Tulsa, Tulsa, OK 74104, USA
[c] Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Kosygin Str. 19, 119991 Moscow, Russia

ABSTRACT

CZE was applied to characterizing a nanoparticle/micellar system, in which CdSe nanoparticles dispersed in a mixture of non-ionic and ionic surfactants are introduced into a capillary to form the sample zone that migrates being sandwiched by the background electrolyte (BGE). Parameters that affect the migration of the surface-modified CdSe nanoparticles and conditions under which they are focused within the micellar zone (or released from it into bulk BGE) were explored, including the sample composition, sample plug length, and applied voltage. The observed migration behavior was analyzed within the framework of a concept of formation of a mixed pseudomicellar system, according to which a nanoparticle coated with an ionic surfactant is treated as a micelle-like entity. It was found out that the nanoparticles are subject to transformation that results in building-up a mixed pseudomicellar system (with regular micelles), with a consequence of exhibiting distinctive migration phenomena. Particularly observed and brought into focus is the event of focusing of the nanoparticles.

1. Introduction

Semiconductor nanocrystals (or quantum dots; QDs) belong to the class of nano-scale inorganic particles and show unique optical properties due to their quantum confinement. These are basically sharp and symmetric emission spectra, high quantum yield, good chemical as well as photo-stability. Moreover, the distinctive feature of QDs manifests in a variety of available surface modifications. These allow for creating a range of systems to recognize biomolecules, such as proteins, peptides, or nucleic acids, which were successfully applied for biomedical imaging. This application issue, as well as the subjects of characterization, surface phenomena, and modification of QDs, was extensively reviewed (see Refs. [1–6] for the most recent coverage).

The review literature in-depth discusses the most important methods in use for the characterization of nanomaterials, pointing out a particular importance of electrophoretic techniques [1,5,7–13]. Such techniques, both in the capillary and the planar configuration, were widely utilized to portray metallic or semiconductor nanostructures in terms of differences in electromigration behavior according to the size and shape of the parent particle, the number and configuration of ligands attached to its surface, and the type of the bioconjugated molecules. Specifically, a direct relation

between the surface architecture of nanoparticles, mostly defined by surface ligands (differing in density, configuration, and type of functionalization), and the data of electrophoretic measurements was highlighted [1,5]. This relation facilitates characterization and control a particle-surface ligand system with the outlook of significant implications.

It should be emphasized, however, that despite significant effort to establish a convenient electrophoretic method for routine practice, there is only a modest progress in such method development. This is mainly due to intrinsic manifold driving forces governing the mobility of (charged) nanoparticles, viz. (i) the electrostatic force exerted by external electric field; (ii) the Stokes friction; (iii) the electrophoretic retardation; and (iv) the relaxation effects [9,13]. Depending on the particle size (strictly speaking, the value of κa, i.e., the ratio of the hydrodynamic radius of a particle (a) to the electrical double-layer thickness, κ^{-1}), Helmholtz-Smoluchowski, Hückel-Onsager, or Henry's equation is to be used for adequate description of the migration behavior [14]. Many studies proved that the migration of nanoparticles is dependent on the zeta potential (ζ) and the particle size [9,13].

Primarily to overcome limitations posed by a complexity of (i–iv) effects, supplementary modes of CE were tested recently. For instance, a successful separation of CdTe nanoparticles with a size increment of 2.6 nm was attained using a polymer as sieving medium [15]. This method was later extended to the CdSe/ZnS QDs [16]. Capillary isotachophoresis was also applied to assess the effective charge and the ζ potential of semiconductor nanoparticles

* Corresponding author. Tel.: +48 22 2347573; fax: +48 22 6282741.
E-mail address: slaosw@ch.pw.edu.pl (S. Oszwałdowski).

[17]. Apparently, the best ever separation in terms of size differentiation was recently reported [18] as based on surface coating of particles with surfactants. Perhaps the most relevant to the subject of this article is the effort of Liu [19] to rectify the challenge of limited concentration sensitivity of CE regarding nanoparticle analysis. With the objective to enrich the Au nanoparticles, the author has introduced large-volume sample stacking mode (with reversed electrode polarity) and achieved up to a 500-fold increase in detectability.

The present work is an extension of our systematic research on developing advanced approaches toward separation and preconcentration of the functionalized QDs using CE [20–23]. Our main strategy is based on exploiting the formation of a mixed pseudomicellar system, with the coated QDs acting as a pseudomicelle. On the basis of this occurrence, a range of endorsing results were previously obtained, including discrimination of an intact QD against its DNA conjugate [21], electric field-mediated transfer of nanoparticles from an aqueous sample to micellar environment [23], and electrophoretic visualization of the QDs functionalized with uncharged surface ligands [22]. Note that common CE methods are unable to resolve these experimental challenges. To alleviate the above-mentioned shortcomings of CE separation of nanoparticles and to gain a deeper insight into the mechanism of focusing of the nanoparticles in micellar systems, the underlying dynamic phenomena have been thoroughly evaluated hereafter.

2. Experimental

2.1. Instrumentation

The CE system equipped with an UV–Vis detector was from Prince Technologies (Emmen, The Netherlands). Fused-silica capillaries with 75 μm I.D. were purchased from Polymicro Technologies (Phoenix, AZ, USA). The capillary length (effective/total) was 60/80 cm. Prior to first use, the capillary was pretreated by flushing sequentially with 0.1 M NaOH, water, and the BGE (5 min each). Between runs, the capillary was conditioned with 0.1 M NaOH (3 min) and BGE (5 min).

2.2. Chemicals and reagents

All chemicals and reagents were of analytical grade quality (unless stated otherwise). For the synthesis of trioctylphosphine (TOP)-coated CdSe QDs [24] (see the Electronic supporting material (ESM) for synthesis and coating), the cadmium oxide (~1 μm; 99.5%), selenium powder (100 mesh, 99.999%), TOP (97%), oleic acid (tech. 90%) (from Sigma–Aldrich, St. Louis, MO, USA), and octadecene (pure, Mallinckrodt, St. Louis, MO, USA) were used. These QDs were characterized in terms of size and concentration using a recently re-examined procedure [25]. Used for modification of the QDs were sodium dodecyl sulfate (SDS), dioctylsulfosuccinate (DOSS), the sodium salt of oleic acid (OA), sodium laurate (pure, from Morton Thiokol, Danvers, MA, USA), and Triton X-100 (TX-100 or polyethylene glycol *tert*-octylphenyl ether). Main structures are presented in the ESM (Scheme 1). CdSe QDs modified by 11-mercaptoundecanoic acid (Sigma–Aldrich) were synthesized according to Ref. [26]. The mixtures of non-ionic surfactant (TX-100; up to 10% (w/w) and anionic surfactants (up to 120 mM SDS or 150 mM sodium laurate, as well as 100 mM DOSS) were prepared. Five to 40 mM solutions of sodium tetraborate obtained from Sigma–Aldrich were used as BGE.

2.3. Procedures

A sample of the CdSe QDs (the typical size in the range of 2.9 – 3.9 nm), dispersed in a mixture of non-ionic and ionic surfactants, was introduced hydrodynamically (typically for 6 s at 50 mbar) from the positive end of the capillary. For particular experiments individual injection conditions were applied to obtain the required sample plug length (L_{plug}). Detection was performed at 245 nm (to monitor both the micellar zone and QDs) or at >300 nm, typically 330 nm (to monitor only QDs). The electroosmotic flow (EOF) was measured for the selected runs using a neutral marker (methanol or acetone). Details of each separation, illustrating a particular electrophoretic effect, are shown in figure captions. In cases where the length of the sample plug introduced under different injection conditions is to be measured, a mixture of TX-100 and DOSS surfactants colored by a dye was used to visualize the plug.

3. Results and discussion

3.1. Functionalization of QDs using surfactants and related migration phenomena

Coating of QDs with surfactants enables charged or uncharged particles to be obtained depending on the nature of the surfactant used. This makes it possible to transfer the functionalized QDs to an aqueous environment and to create a particle/water interface with double electric layer sufficient to make particles migrating. Particle functionalization with surfactants was already analyzed in the literature [27,28]. It was established that: (i) the surface potential of the coated particle is a function of the surfactant concentration in solution [27]; (ii) the binding energy of the surfactant to the particle is similar in magnitude to that for a typical ligand due to particle passivation [29]; and (iii) surfactant coating impacts the hydrodynamic parameters, e.g., actual particle radius. It should be noted that coating, especially with bulkier ligands, can be accompanied by second-order phenomena. These encompass, for instance, enfolding of a particle observed in the case of DNA [30], or a dynamic coating with surfactants when the nanoparticles migrate through a surfactant environment [31]. In a previous study [23], we have evidenced the phenomenon of dynamic coating that resulted in the transformation of an electrically neutral particle into a charged one upon its migration in the presence of the micellar phase. This allowed us to introduce a concept according to which the surfactant-coated particles can play a role of a pseudomicelle capable of forming a pseudomicellar system with regular micelles. Available literature [28] confirms that the binding of a particle coated with surfactants to the micelle is energetically favorable.

Description of the migration of coated nanoparticles appears to be no trivial task due to the dynamic nature of coating by surfactant. Theory states that the mobility of the charged particles is governed by four main forces [9,13] controlled by the hydrodynamic parameters of the particle. An attempt was made to obtain these parameters for CdSe QDs coated with the OA surfactant [32]. A relation between particle surface potential and the surfactant concentration in solution was established [27]. However, it can be seen in Fig. S1 (ESM) that the coating with OA occurs only in a narrow surfactant concentration range. The limiting factors are particle aggregation and surfactant intrinsic solubility. Moreover, the constancy of photoluminescence in this range means that the modification of QD surface by OA reached a maximum. To emphasize, the described experiment (see Fig. S1) proved that the hydrodynamic parameters vary only in a narrow range of bulk surfactant concentration. Apart from optical techniques, the CdSe/OA system was examined by the particle size analyzer, gel electrophoresis (GE), and CE techniques [22]. It was found that size and CE measurements are unsuitable for obtaining the hydrodynamic parameters because of interferences caused by an excess of the surfactant. On the other hand, the GE technique showed that CdSe/OA has a negative charge with a ζ-potential of ca. −20 mV [23].