Analytica Chimica Acta xxx (2018) 1–9

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Characterization of polymer-coated CdSe/ZnS quantum dots and investigation of their behaviour in soil solution at relevant concentration by asymmetric flow field-flow fractionation – multi angle light scattering – inductively coupled plasma - mass spectrometry

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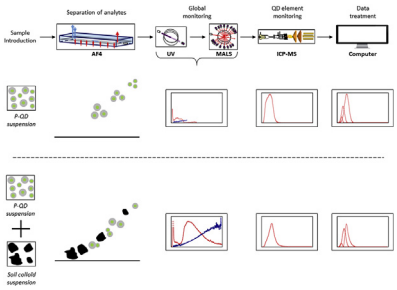
HIGHLIGHTS

- Size and concentration information obtained by AF4-MALS-ICPMS and DLS enables the signal deconvolution to be done reliably.
- The deconvolution of elemental ICPMS enables different QD populations to be identified and also improves AF4 resolution.
- A joint consideration of concentration balance and STEM/X-EDS core-shell data provide dimensional and structural information.
- The deconvolution of the mixture QDs/soil solution signal enables the dissolution/aggregation states of QDs to be evaluated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 September 2017
Received in revised form
2 March 2018
Accepted 19 March 2018
Available online xxx

Keywords:
Nanoparticles
Aggregation

ABSTRACT

A careful separation, identification and characterization of polymer-coated quantum dots (P-QDs) in complex media such as soil solution is the key point to understand their behaviour and to accurately predict their fate in the environment. In the present study, a synthesized CdSe/ZnS core/shell P-QDs suspension, proved to be stable for at least six months, was investigated with respect to P-QDs dimension, structure and elemental composition. Separation of P-QDs and size distribution determination were carried out by Asymmetric Flow Field-Flow Fractionation (AF4) - Multi Angle Light Scattering (MALS). AF4 and MALS were coupled to Inductively Coupled Plasma-Mass Spectrometry (ICPMS) as a selective and sensitive technique for the detection and the characterization of metallic and metalloid analytes. The exploration of element-specific data obtained by ICPMS after AF4 separation enabled the

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https://doi.org/10.1016/j.aca.2018.03.051
0003-2670/

Dissolution
Dimensional information
Elemental analysis
STEM/X-EDS

signal to be deconvoluted reliably. Thus, 3 classes of size populations were identified from the whole population of P-QDs. Additionally, a soil solution and a mix of P-QDs suspension with soil solution were characterized by the same method. This strategy enabled the P-QD population, which interacted with the soil solution, to be determined, this interaction leading either to an aggregation or dissolution of the P-QDs. Reproducibility and recovery of the size distributions and element concentrations were examined for each sample. Complementarily, Dynamic Light Scattering (DLS) and Scanning Transmission Electron Microscopy (STEM) were used jointly with AF4-MALS-ICPMS in order to demonstrate all potentialities of this coupling technique.

1. Introduction

Quantum dots (QDs) generically refer to a broad set of core-shell nanocrystals produced with different compositions, sizes, and coatings depending on the intended applications. According to the protocol followed for their synthesis and their suspension preparation, as well as the protocol implementation (P-)QD batch suspension (i.e. suspension of QDs with or without polymer coating), is generally obtained with unique physicochemical characteristics [1–4]. The increasing use of (P-)QD notably by their incorporation in daily products also brings questions about their release in the environment [5] and consequently about their fate, behaviour in complex media such as soils. The latter is often considered to act as both sinks and reactors for contaminants [6]. Besides, and in general, the very low concentration of engineered nanoparticles (NPs) renders their quantification difficult among natural NPs and, in particular, when their concentration is close to the geochemical background. Typically, engineered NPs released into the environment are found at concentrations of few tens of ng L^{-1} in surface waters and hundreds of ng kg^{-1} $year^{-1}$ in sediments and soils [7]. Hence, reliable analytical tools are required which enable engineered NPs to be detected and quantified in the environment at relevant concentration. The description of nanoparticles needs at least the determination of their size and/or size distribution, their shape and/or structure, and their chemical composition [8]. In suspension, it is essential to know the state of aggregation, as well as the mechanisms of aggregation and/or solubilisation to understand the fate of nanoparticles, or even to evaluate their potential impact on the environment in which they can be found [1,8]. All this still remains critical to obtain.

In order to contribute to the development of analytical methods capable of responding to this challenge, polymer-coated quantum dots (also named P-QDs) are good candidates for model nanoparticles because of their dual inorganic crystalline/organic nature, core-shell structure and solubility properties [9,10]. The high chemical diversity of the coatings used also contributes to the difficulty of apprehending the behaviour of QDs, whether in the analytical system or in the study medium. In addition, the potential toxicity of the constituents released by the QD alteration is also a driving force for new analytical developments [2,9].

Several works dedicated to the development of (P-)QD characterization methods have been described in literature [11,12]. Among the diversity of possible strategies, those based on a physical separation of the analytes followed by a characterization via one or more on-line coupled detectors have proved to be attractive. In particular, asymmetric flow field-flow fractionation (AF4) was used several times [1,8,13–17]. UltraViolet-Visible (UV-Vis) spectrometers remain the most widely used detectors. AF4 was also coupled to molecular fluorescence spectrometry (MFS) [8,15,16]. In this case, the fluorescence properties of the QDs and the dependence of the spectral emission on the core size were used to carry out dimensional analyses. The emission also depends on the nature of the QD coating. This is an additional difficulty for (P-)QD characterization in environmental samples, where natural organic matter (NOM) can also interact with (P-)QDs [15]. Moreover, AF4 was coupled to atomic mass spectrometry (ICPMS). However, only three works implied a coupling between AF4 and ICPMS, for (P)-QD characterisation in synthesis suspensions: First, Bouby et al. monitored cadmium and zinc by single-quadrupole ICPMS (simply noted ICPMS below) and determined hydrodynamic size distributions and geometric diameter from elemental concentration ratios of CdSe/ZnS QDs with various dilutions [13]. More recently, triple quadrupole ICPMS (ICPMS-QQQ) was coupled to AF4 for elemental analysis of CdSe/ZnS QDs stabilized by amphiphilic polymers, or bioconjugated to proteins [8,16]. The resolution and sensitivity of ICPMS-QQQ regarding simple quadrupole ICPMS enabled the four elemental constituents to be determined simultaneously. Other authors used ICPMS (without coupling) to monitor the degradation processes of QDs [18,19]. All these previous works confirm that atomic mass spectrometry is intrinsically a relevant tool for understanding the physicochemical behaviour of QDs with different polymeric coatings in various media including complex polyphasic media such as soils. Complementary to dimensional fractionation, size information is of key interest, and can be obtained by the use of multi-angle light scattering (MALS). Zattoni et al. highlighted the relevance of using AF4-MALS to characterize structured particles such as (P-)QDs and to monitor their stability in suspension [17].

Thus, AF4-MALS-ICPMS has high potential for (P-)QD investigation although the application of this coupling remains relatively scarce so far. In particular, it makes possible to generate a very complementary data set that intrinsically contains dimensional and structural information. This information can be obtained by the combined processing of the ICPMS and MALS signals. However no study using AF4-MALS-ICPMS with such processing for the behavioural study of QDs at low concentration levels in environmental medium had been reported yet.

The objective of the present work is to illustrate the potential of the data processing of elemental information obtained as a function of size by ICPMS coupled with A4F and MALS to characterize polymer-coated CdSe/ZnS core/shell P-QDs and to investigate their fate (aggregation and/or dissolution) in a soil solution. The experimental approach of this work is: (i) to use in a combined way MALS and ICPMS after AF4 fractionation, (ii) to exploit in an optimal way the information intrinsically contained in the recorded signals, as well as those generated by their numerical treatment and joint exploitation (multisignal exploitation), and (iii) to test the relevance of such processing at sub µg (element) L^{-1} scale, which correspond to concentrations likely to be encountered in anthropized environmental media [13]. In order to obtain in a single analysis the elemental information necessary to describe the P-QDs and their state in suspension, Se, Cd and Zn were monitored. In order to evaluate the relevance of the dimensional, elemental

Please cite this article in press as: S. Faucher, et al., Characterization of polymer-coated CdSe/ZnS quantum dots and investigation of their behaviour in soil solution at relevant concentration by asymmetric flow field-flow fractionation – multi angle light scattering – inductively coupled plasma - mass spectrometry, Analytica Chimica Acta (2018), https://doi.org/10.1016/j.aca.2018.03.051