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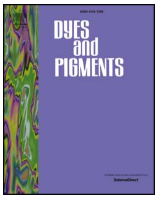

Thin film of CdTeSe/ZnS quantum dots on water subphase: Thermodynamics and morphology studies

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ABSTRACT

Colloidally synthesized semiconductor nanoparticles have been receiving much attention due to their potential application in the area of photovoltaics, optic devices, biology, and medicine. This work explains how semiconductor CdTeSe/ZnS quantum dots (QDs) with the surface modified by trioctylphosphine oxide (TOPO) were dispersed on the surface of water. The studies of the organization and behavior of formation layers of CdTeSe/ZnS were followed by surface pressure-area isotherm measurements, *in-situ* absorption spectroscopy, Brewster Angle Microscopy (BAM) and surface potential measurements. The conducted research shows that CdTeSe/ZnS QDs form a tightly-packed, thin layer at the water-air interface, which can be easily deposited on different surfaces with the Langmuir-Blodgett and Langmuir-Schafer techniques.

1. Introduction

The unusual optoelectronic and physicochemical properties of nanoscale materials have stimulated much interest in this area. Quantum dots (QDs), a class of inorganic fluorophore, typically II-IV semiconductors, are gaining widespread recognition in optoelectronic and biomedical application due to their exceptional photophysical properties, broad absorption spectra together with narrow symmetric, size-tunable emission allowing large achievable Stokes shifts and exceptional resistance to photo- and chemical degradation. Moreover, due to these qualities the nanoscale semiconductor materials find potential applications in quantum dot photovoltaic solar cells, QLED, nonlinear-optics, biology and medicine and, being optically stable markers, they replace traditional dyes [1–4]. Greenham et al. fabricated an inorganic solar cell using CdSe QDs [5], Murray and co-workers use PbSe thin films for field-effect transistor applications [6].

The organization, packaging, and data regarding the behavior of QDs in thin layers are an important problem. So far, these nanoparticles found applications in electronics and were used commercially [4,5]. The mono and multilayers of semiconductor QDs have been studied previously [1–3,7,8], including the use of various techniques such as spin coating [9,10], or layer by layer deposition assembly [11,12], but still few studies have focused on their thermodynamic and organizational behavior in Langmuir layers. We have decided to use a Langmuir technique supported by various additional methods such as the in-situ absorption method, the Brewster angle microscopy (BAM), the surface potential (SPOT), the dynamic light scattering (DLS) and the fluorescence confocal scanning microscopy (FCSM). The Langmuir technique is a highly attractive processing method, especially for colloidal quantum dots, because applications such as the quantum dots solar cell [13–15], quantum dots – dye hybrid solar cell, light-emitting diodes (LEDs) [16] and sensor devices [17] require high-quality mono- or multilayers. Despite the extensive research concerning QD films, very little data on the actual Langmuir layer on the water surface exists. This is an issue of fundamental interest, and it could yield information providing, for example, optimal surface pressures or molecular areas for solid-state transfer of ordered layers.

In this study we demonstrate the formation of compressed Langmuir layers of highly fluorescent CdTeSe/ZnS QDs at the air/water interface which is an excellent medium for the organization study of amphiphilic QDs. These studies provide insight into the fundamental behavior of semiconductor nanoparticles confined in an air/water interface, as well as a nonorganic part of the active layer of a photovoltaic device.

2. Materials and methods

The 5 nm CdSeTe(ZnS) core-shell quantum dots capped with trioctylphosphine oxide (TOPO) surface group in toluene (TL) were purchased from Nanoshel LLC company. The CdSeTe(ZnS) in chloroform were prepared in a two-step process: first, 50 μL of starting material dissolved in toluene was evaporated by a slow nitrogen purge; next, the quantum dots were redissolved in chloroform (HPLC grade).

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The Langmuir monolayers of CdTeSe/ZnS quantum dots were produced with a KSV Instruments Ltd. 2000 Langmuir-Blodgett system with a Teflon trough of 250 cm^2 area, under a laminar flow at a stabilized temperature 19.5 ± 0.1 °C. In our experiments, the subphase used deionized water (electrical resistivity 18.2 MΩ cm), obtained with an ultrapure water purification system (Millipore Corp). To obtain a floating film, the QD suspension was carefully spread onto the subphase and chloroform was allowed to evaporate. The floating film was compressed symmetrically from both sides at the rate of 7.5 cm^2 min^{-1} of surface compression change. Surface pressure versus area (π-A) isotherms was recorded during the film compression to provide repeatability of the transferred density of the layers. Before transferring, the floating films relaxed at a specified surface pressure (π) for 30 min to stabilize the layer. The layers were transferred onto a solid substrate at various surface pressure (45 mN/m, 30 mN/m, 10 mN/m,1 mN/m) with a horizontal transfer involving emerging the substrate from the subphase, in a similar way as it was proposed in our previous work [18,19]. The substrate was emerging at a constant speed of 1 mm min^{-1}. The CdTeSe/ZnS quantum dot layers were deposited on partially covered with 25 nm thick gold layer mica. The substrate was washed in a chloroform bath. The substrates were repeatedly rinsed with ultrapure water before the layer transfer. After the deposition, the samples were dried at ambient temperature for a few hours. The monolayer morphology was visualized in-situ with the Brewster angle microscopy method (BAM) (KSV Nima) at the air/water interface. The light source was a laser diode emitting p-polarized light of 659 nm wavelength with the field of view of 3.6 × 4.0 mm^2 and the resolution approx. 12 μm per pixel. BAM studies were carried out simultaneously under the monolayer compression, using a CCD camera. The reflected light intensity depends on the monolayer properties, such as molecular density and thickness. Surface potential measurements were taken with the non-contact and non-destructive vibrating capacitor method. Surface potential sensor (SPOT) (KSV Nima) recorded ΔV simultaneously with monolayer compression using two electrodes; the vibrating plate located above the water surface and the counter electrode immersed in the subphase. The dynamic range of the measurement was −5 to +5 V, with ± 1 mV sensitivity. SPOT allows to gather data on the packing and orientation of the Langmuir monolayer. Ground state absorption spectra and fluorescence emission spectra were monitored using an Edinburgh Instruments F5 spectrophotometer with a single-photon counting detector. The in-situ electronic absorption spectra of the Langmuir layers were recorded in the range 200–900 nm with an Ocean Optics spectrometer QE65000, which was placed near the quartz window of the KSV instrument. The size of the QDs was determined using Vasco particle size analyzer from Cordouan Technologies which can determine size within 0,5 nm to 10 μm range, the detection angle was 135°.

3. Results and discussion

3.1. Electronic absorption of Langmuir layers and solution

The CdTeSe/ZnS quantum dots were redispersed in chloroform to prepare a base solution with a concentration of ca. 0.1 mg/mL. The dispersion quality was confirmed by the dynamic light scattering (Fig. 1), hydrodynamic diameter of QDs was 15.9 nm. The discrepancy between the size (5 nm) quoted by the manufacturer and the DLS results can be explained by the fact that dynamic light scattering determines the size of scattering centers rather than the size of quantum dots themselves. CdTeSe/ZnS quantum dots are located in micelles which include stabilizer molecules and polarized solvent molecules [20].

Fig. 2 presents the absorption spectra and normalized fluorescence spectra of QD in a chloroform solution. The absorption spectra display the pronounced maximum at 620 nm, characterized by exciton peak showing the quality of QDs. When excited with the wavelength 380 and 405 nm, the shapes of the fluorescence spectra of the QDs are found to be independent of the excitation (Fig. 2) a feature which confirms the homogeneity of the QD sample. After allowing the solvent to evaporate for 30 min, the monolayer at the air/water interface was compressed at the rate of 750 mm min^{-1}. The in-situ absorbance spectra (Fig. 3A) for different surface pressures were obtained by continuous compression of the monolayers by two moving barriers. The observed shape of the absorption spectrum for the Langmuir layer as a function of pressure was the same as for the QD solution. Fig. 3B shows the relationship between absorption and pi-A isotherm for a selected wavelength (250 nm), for which we can distinguish three areas. In the first region (π = 0–18 mN/m), a non-linear increase of absorbance was observed, which is caused by the transition of the layer from gas to liquid phase, and the reduction of pinholes in the layer. The linear nature of the absorbance changes, which can be observed in the second region (π = 18–58 mN/m), was caused by the transition from liquid to condensed liquid phase, which in turn causes an increase of the number of nanoparticles per unit area, and gradual formation of multilayers. The rapid increase of the absorbance in the third range (π > 58 mN/m) was caused by the collapse of multilayers and sudden multiplication of the number of layers.

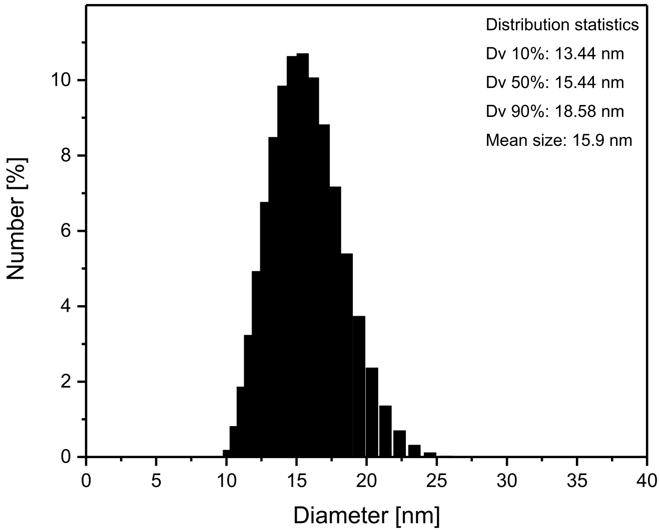

Fig. 1. Dynamic light scattering histogram for the hydrodynamic diameter detection of quantum dots (QDs) in chloroform. The hydrodynamic mean sizes of QDs were 15.9 nm.

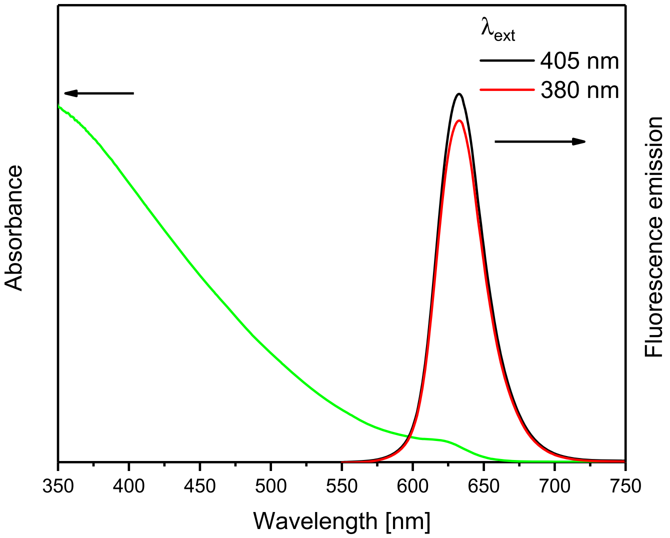

Fig. 2. Absorption (green line) and fluorescence (red and black line) spectra of QDs in chloroform. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)