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Colloids and Surfaces A: Physicochem. Eng. Aspects 284–285 (2006) 35–42
COLLOIDS AND SURFACES A
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Langmuir and Langmuir–Blodgett films of quantum dots

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Received 24 June 2005; received in revised form 8 November 2005; accepted 14 November 2005
Available online 24 January 2006

Abstract

Trioctylphosphine oxide (TOPO) capped CdSe and (CdSe)ZnS quantum dots (QDs) were prepared. The surface chemistry behavior of both QDs at the air–water interface was carefully examined by various physical measurements. Stable Langmuir films were formed for both QDs. The average limiting nanoparticle area derived from the π–A isotherms of the QDs could be used to estimate the average size of the QDs if the thickness of TOPO shell was counted. The epifluorescence image of the QDs Langmuir films revealed an aggregation in 2D during the early stage of the compression process. On the other hand, a diacetylene-peptide (PDA-Cys-Cys-Gly-OH) derivative, namely PDA-CCG, was used to modify the surface of QDs. This modification resulted in a robust and homogeneous Langmuir film, which is photopolymerizable and contains active binding sites for the binding of biomolecules.

Keywords: Langmuir film; Langmuir–Blodgett film; Quantum dots; Polydiacetylene

1. Introduction

Quantum dots (QDs) of II–VI semiconductors (CdS, CdSe, and CdTe) in the size range of 1–12 nm have attracted great interest in both fundamental research and technical applications in recent years [1]. Due to their tunable size-dependent emission with high photoluminescence (PL) quantum yields, their broad excitation spectra and narrow emission bandwidths, the semiconductor QDs have been intensively investigated in versatile applications, including thin-film light emitting devices (LEDs) [2], low-threshold lasers [3], optical amplifier media for telecommunication networks and biological labels [4,5].

Currently, self-assembly of nanoparticles at the liquid–liquid [6] or air–water interface [7] has been investigated. Compressing QDs at the air–water interface could result in the formation of 2D Langmuir films. Advantages of this assembly technique include establishing limiting nanoparticle area, easy manipulation of the films, and interparticle distance control. The latter is of great significance because much of the attention in QDs has been focused on their unique optical properties, which are sensitive to interparticle distance [8] and other factors such as particle size, material composition, nature of surface stabilizing molecules, and surrounding environment.

In the present study, the surface chemistry behavior of two different types of semiconductor QDs, e.g. CdSe and (CdSe)ZnS core-shell QDs was investigated by means of multiple methodologies such as Langmuir and Langmuir–Blodgett (LB) films deposition technique, UV–vis and photoluminescence spectroscopies, as well as transmission electron microscopy (TEM) and epifluorescence microscopies. The surface chemistry properties of four different sizes of CdSe QDs were studied at the air–water interface. The optical properties of the Langmuir and LB films of the (CdSe)ZnS core-shell QDs were also studied by photoluminescence spectroscopy and epifluorescence microscopy.

In order to fabricate highly organized and homogeneous films, a photopolymerizable 2D matrix that combined both the QDs and bioconjugates for biological applications was realized. The diacetylene-peptide PDA-Cys-Cys-Gly-OH (PDA-CCG) derivative was used to modify the surface of QDs. The hydrophobic long alkyl chain of PDA cannot only facilitate the self-assembly of the lipid but also provide the possibility to build a robust 2D matrix through photopolymerization. The PDA-CCG was linked to the QDs through two thiol groups on the cystein residues. Moreover, the biomolecules with free amine

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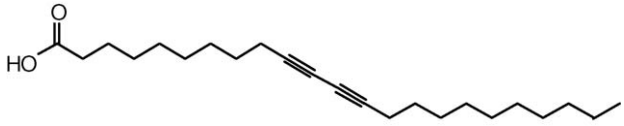
doi:10.1016/j.colsurfa.2005.11.046

groups can be further linked to the carboxyl group of glycine linker. The homogeneity of the Langmuir film of modified QDs was examined by epifluorescence measurements. Following the photopolymerization in 2D, we still observed the homogeneity of the Langmuir film.



10,12-pentacosadiynoic acid (PDA)

2. Experimental

2.1. Materials

Cadmium oxide (CdO), selenium (Se), trioctylphosphine oxide (TOPO), trioctylphosphine (TOP), hexamethyldisilathiane [$(TMS)_2S$], 2-mercaptoacetic acid, diisopropylcarbodiimide (DIC), 1-hydroxylbenzotriazole (HOBt), 1,2-ethanedithiol (EDT), and triisopropylsilane (TIS) were purchased from Sigma-Aldrich (St. Louis, MO). The tetradecylphosphonic acid (TDPA) was obtained from Alfa Aesar (Ward Hill, MA). The diethylzinc ($ZnEt_2$, 15 wt% solution in hexane) was obtained from Acros Organics (Morris Plains, NJ). The 9-fluorenylmethoxycarbonyl protected amino acids (Fmoc-Gly-OH and Fmoc-Cys(Trt)-OH) and 10,12-pentacosadiynoic acid (PDA) were ordered from VWR International, Inc. (West Chester, PA). The starting materials for all the synthesis and surface modification of CdSe and (CdSe)ZnS core-shell QDs were used without purification.

2.2. Synthesis

2.2.1. Synthesis of CdSe and (CdSe)ZnS QDs

The (CdSe)ZnS core-shell QDs capped with TOPO ligand were prepared through a stepwise procedure as described elsewhere. The precursor of (CdSe)ZnS core-shell QDs, nearly mono-dispersed TOPO-capped CdSe QDs, was synthesized by the method reported by Peng and Peng [9]. The CdO and TDPA were used as the Cd precursor and the trioctylphosphine selenide as the Se precursor. The CdSe QDs were prepared by pyrolysis of the Cd and Se precursors in a coordinating solvent, TOPO, at high temperature (250–270 °C). The QDs were collected as powder using size-selective precipitation [10] with methanol followed by drying under vacuum. The average size of the CdSe/TOPO QDs in chloroform solution was determined by UV–vis absorption spectroscopy [11]. In order to perform surface chemistry measurements, an approximate particle concentration of CdSe/TOPO QDs was also determined by UV–vis spectroscopy [11]. Moreover, by applying the total volume of the stock solution, the total number of CdSe/TOPO nanoparticles in a sample could be estimated.

$ZnEt_2$ and [$(TMS)_2S$] were used as Zn and S precursors for the ZnS cap. The amount of Zn and S precursors needed to grow a ZnS shell of desired thickness for each CdSe sample was determined as follows: first, the average size of the CdSe core was estimated from UV–vis data [11]. Next, the number of ZnS molecules necessary to form a shell on per particle of CdSe QDs was calculated based on the volume of individual CdSe QD and the desired thickness of the shell by assuming that the QD core and shell were spherical. The bulk density of ZnS was used in the calculation. Then, the amount of ZnS for one synthesis was calculated by knowing the total number of CdSe/TOPO QDs estimated previously from UV–vis measurements. Finally, the amount of $ZnEt_2$ and $(TMS)_2S$ was calculated from the quantity of the ZnS needed in the synthesis.

The common coating procedure was carried out by adding a $ZnEt_2$ and $(TMS)_2S$ mixture solution drop-wise into a coordination solution (TOPO/TOP as solvent) of CdSe QDs at high temperature under argon atmosphere [12]. Usually, the temperature during coating was lower than that used for growing the CdSe nanocrystals to avoid compromising the integrity of the native cores. The (CdSe)ZnS core-shell QDs were collected as a powder by precipitation and washing with methanol and drying under vacuum.

2.2.2. Synthesis of peptidolipids

The PDA-CCG was synthesized via standard solid phase 9-fluorenylmethoxycarbonyl (Fmoc) chemistry [13]. Wang resin was used as the solid phase; therefore the C-terminal end of the products was carboxylic acid. Two amino acids (Fmoc-Gly-OH and Fmoc-Cys(Trt)-OH) were used to construct the peptide backbone. The coupling reactions were carried out with DIC or DIC/HOBT as activating reagent in dimethylformamide (DMF). The hydrophobic long chain (PDA) was introduced by reacting 10, 12-pentacosadiynoic acid with the peptide using DIC as a coupling reagent. Cleavage of peptides from the resin was completed with cleavage cocktail composed of CF_3COOH (94%, v/v), 1,2-ethanedithiol (EDT, 2.5%, v/v), triisopropylsilane (TIS, 1.0%, v/v), and H_2O (2.5%, v/v) for 3 h. After the cleavage, TFA in the residue was removed with a N_2 stream. Deionized water was used for the precipitation of crude product from the residue. The precipitate was washed several times with deionized water and lyophilized under vacuum. Semi-preparative RP-HPLC was performed on a Waters 2690 separation module. A reversed-phase diphenyl column was used (219TP1010, Vydac Inc.). Two solutions were prepared: (A) 0.1% TFA in water and (B) 0.1% TFA in 2-propanol/acetonitrile (1:1, v/v). Typically a linear gradient (30–70% B within 40 min, flow rate at 2 mL/min) was used. The purity of the PDA-CCG was higher than 95% based on the HPLC data.

2.2.3. Modification of the QDs surface using PDA-CCG

The modification of QDs was achieved through surface ligand exchange reaction. It has been intensively reported that the TOPO ligand could be replaced by free thiol group under mild conditions [14]. In this study, QDs powder was added to the $CHCl_3/CH_3OH$ (5:1, v/v) solution of PDA-CCG and sonicated for 0.5 h. Exchange of the TOPO capping groups with PDA-CCG made the QDs dissolving in the $CHCl_3/CH_3OH$ mixture solution. The removal of the replaced TOPO cap was conducted by reprecipitation of the PDA-CCG-QDs solution