Journal of Inclusion Phenomena and Macrocyclic Chemistry **35:** 157–164, 1999.

Incorporation of Thiol-Stabilized CdTe Nanoclusters into Langmuir-Blodgett Films

G. K. ZHAVNERKO[1], V. S. GURIN[2], A. L. ROGACH[2,3], M. O. GALLYAMOV[4] and I. V. YAMINSKY[4]
[1]*Institute of Physical Organic Chemistry, Belarus Academy of Sciences, Surganova Street, 13, 220072 Minsk, Belarus;* [2] *Physico-Chemical Research Institute, Belarusian State University, Leningradskaja str., 14, Minsk, 220080, Belarus;* [3]*Institute of Physical Chemistry, Hamburg University, Bundesstr., 45, D-20146, Hamburg, Germany;* [4]*Physical Department of Moscow State University, Vorobievy Gory, Moscow 119899, Russia*

Abstract. The methods of incorporating thiol-stabilized CdTe nanoclusters into mono- and multilayer films produced by the Langmuir-Blodgett (LB) technique on the basis of anionic (behenic acid) and cationic (octadecyltrinonylammonium (ODTNA) iodide) surfactants were investigated. ‘Pressure-area’ isotherms, quartz crystal microbalance (QCM), FTIR, atomic force microscopy (AFM) and UV/Vis spectroscopy give evidence on the incorporation of the nanoclusters in LB films. The limiting surface area of the behenic acid monolayer increases with a simultaneous decrease of the film strength. The optical absorption of the films obtained through the incorporation of the clusters acquires the features of CdTe nanocrystals. The noticeable difference in the deposition process was observed for the two types of stabilizing ligands (thioglycerol and mercaptoethanol) used for the CdTe clusters. The bonding of the CdTe clusters with the carboxylic group of behenic acid monolayer is established for the thioglycerol-stabilized clusters.

Key words: CdTe clusters, Langmuir–Blodgett technique.

1. Introduction

Assembled thin films containing ultrafine semiconductor nanoparticles have attracted much interest as an example of a supramolecular system with intermediate molecular-solid properties, and their potential application as nanodevices due to the optical and electrooptical features of the clusters [1–5]. Semiconductor nanoclusters can be considered as giant molecules with a certain number of atoms in both the inorganic core and in the outer shell which is comprised of organic groups, that protect the clusters against spontaneous aggregation [6–8].

One of the main factors responsible for the change of properties in semiconductor nanoparticles is the quantum confinement effect. Nanoclusters with a size of less than a few nanometers, e.g., thiol- or phenylphosphine-stabilized CdS and CdSe [9,10] reveal the pronounced quantum-size effect, and clusters in the wide range of sizes can be identified. The technique of the synthesis of CdTe-clusters yielding stable solutions or solid products (powders) was developed [11].

It is of interest to fabricate thin film materials containing similar nanoclusters deposited on different supports. The properties of such films are provided, not only by the presence of the clusters, but also by their packing and interaction between each other, and with a matrix. The methods of nanocluster incorporation has been reported [12–20]. Hence, the LB method allows to deposit complex metal-organic particles in the form of a solid film from both anionic species such as $[PtCl_6]^{2-}$ [21] or titanyl oxalate $[TiO(C_2O_4)_2]^{2-}$ [22], and cationic species such as different ruthenium complexes [23].

The aim of this work was to incorporate the thiol-stabilized CdTe clusters into LB films with the subsequent deposition onto a solid surface resulting in mono- and multilayer films. The surface-active and film-forming properties of cationic and anionic surfactants in liquid subphases contained CdTe clusters were studied and the films deposited were characterized by optical and IR spectroscopy.

2. Experimental

Behenic acid and octadecyltrinonylammonium (ODTNA) iodide were the materials used for LB films preparation. The colloidal solutions of the CdTe clusters were prepared according to the technique described in [11], using 1-thioglycerol or 2-mercaptoethanol as the stabilizing ligands.

A two-bath automatic computer-controlled Langmuir trough was used for the ‘surface pressure-area per molecule’ (π-A) isotherms (285 K) measurements, and LB films deposition under a compression speed of 0.2–0.3 $Å^2/(\text{mol} \times \text{min})$.

The commercially available 5-MHz, AT-cut quartz crystal microbalance (QCM) was used with a homemade oscillator circuit designed to drive the QCM at its resonant frequency. The mass change Δm for the deposition onto the two sides of a plate was calculated from the Sauerbrey relationship [24] $\Delta f = -2Cf_o^2\Delta m/S$, $C = 4.417$ $(\text{cm}^2/\text{g} \times \text{Hz})$, where S is the area covered by the film, f_o the initial resonant frequency and Δf is the frequency change introduced by loading the mass of the adsorbed film.

Infrared spectra were acquired with a Nicolet ‘Protege 460’ FT-IR interferometer with normal incidence of a beam to the sample surface. The UV/Vis spectra were recorded with a Specord M40 in the range 200–800 nm for multilayered samples.

AFM images were obtained using a Nanoscope IIIa (Digital Instruments, USA) operated in the constant force mode (1.5–5 nN) in air at room temperature. Nanoprobe 100 and 200 mm cantilevers (spring constant of 0.06 and 0.12 N/m) with oxide-sharpened Si_3N_4 integral tips were used. Data were collected at a scan-speed of 5-15 Hz (512 × 512 points). The LB monolayers were prepared by spreading chloroform solutions of surfactants with a concentration of 0.5 mM onto a aqueous subphase of doubly distilled water. To incorporate the CdTe nanoclusters into the

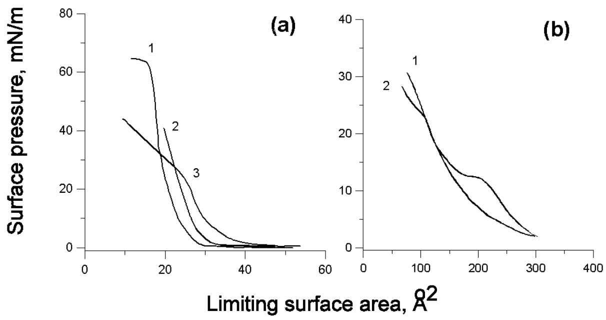

Figure 1. Compression isotherms (283 K) of monolayers of (a) behenic acid and (b) ODTNA iodide obtained at a water surface (1) or subphases with mercaptoethanol-stabilized CdTe (2a) and thioglycerol-stabilized clusters (2b, 3a).

films formed, the aqueous (10^{-5} M) solution of CdTe nanoclusters was introduced into the aqueous subphase. The multilayer films were prepared by the conventional LB method [25]. The deposition was of the Y-type (transfer rate – 4 mm/min). All films were deposited at a constant surface pressure of 30 mN/m.

3. Results and Discussion

The surface-active properties of surfactants studied were compared on a subphase containing the CdTe clusters and a water surface (Figure 1). The isotherms for behenic acid alone had the classical form and the solid condensed film was obtained, in which the limiting surface area per molecule was 20 Å^2 (Figure 1a). The isotherms for behenic acid recorded over CdTe-cluster solutions (Figure 1) showed a larger value of molecular area. The region of ‘solid film’ was not observed for the behenic acid monolayer with a subphase containing the CdTe clusters, and the collapse of this film occurred at about 30 mN/m when the film reached a ‘liquid-solid’ state. Similar observations were seen for the ODTNA iodide surfactant. The obtained film did not reveal any pronounced transitions between the gas-like, liquid, and solid regions when it was obtained on the cluster-containing subphase. This was in contrast to the isotherm recorded on the pure water surface (Figure 1b). The film of cationic surfactant on the solution of the clusters collapsed at a lower value of surface pressure than that on water. The compression modulus E_π (Table I) for both behenic acid and ammonium salt did not vary significantly after the change of subphase composition. The difference only occurred in the value of the limiting surface area (Table I). This suggests a weak effect of clusters incorporated on the mechanical properties of the film.

Table I. Comparison of properties of the monolayer films prepared from the surfactants with and without incorporated CdTe clusters, $E_\pi = A_\pi(\delta\pi/\delta A)$

#	Chemical composition	A_{min} Å^2/mol	$\pi_{collapse}$ mN/m	A_{20} Å^2/mol	$\delta\pi/\delta$ A in middle π region (15–25 mN/m)	E_{20} mN/m
1.	Behenic acid	20.25 ± 0.5	60	21	4.21	87
2.	Behenic acid + CdTe	32.3 ±1	24	26	3.29	86
3.	ODTNA iodide	200±2	30	119	0.26	31
4.	ODTNA iodide CdTe	196±3	22	119	0.26	31

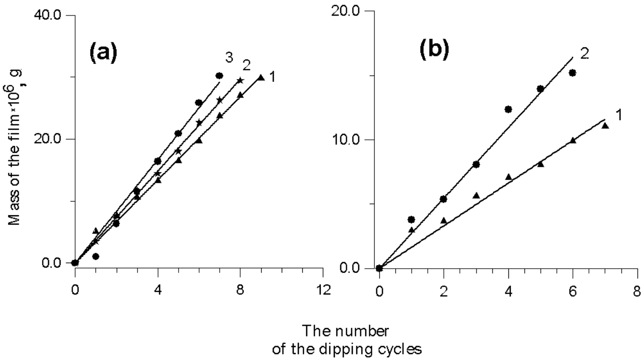

Figure 2. The increase of film mass (Y-type of the film) deposited onto the quartz resonator for behenic acid (a), and ODTNA iodide (b) from a water surface (1) or subphases with thioglycerol-stabilized CdTe (3a, 2b) and mercaptoethanol-stabilized clusters (2a).

Thus, the condensed films with the CdTe clusters can be successfully formed at the water-air interface which opens the possibility of depositing them on some solid substrate.

QCM monitoring clearly revealed the increase of weight of both behenic acid and long-chain ammonium iodide film (Figure 2) during their deposition only from the subphase containing the thioglycerol-stabilized CdTe clusters on a surface of a quartz resonator in comparison with the film of the same compound transferred from the water surface. The linear dependence of the film-mass change on the number of layers observed suggests a good reproducibility of the deposition process. The difference in the mass of the behenic acid monolayer (1.2×10^{-6} g/cm^2) after changing pure water on the subphase containing the thioglycerol-stabilized CdTe clusters can be explained by incorporating the clusters with an estimated amount of the order of 10^{18} mol into the film. In the case of the behenic acid monolayer with the incorporated thioglycerol-stabilized CdTe clusters, the insoluble film was obtained, which remained on the quartz resonator surface after it was treated with benzene or chloroform.

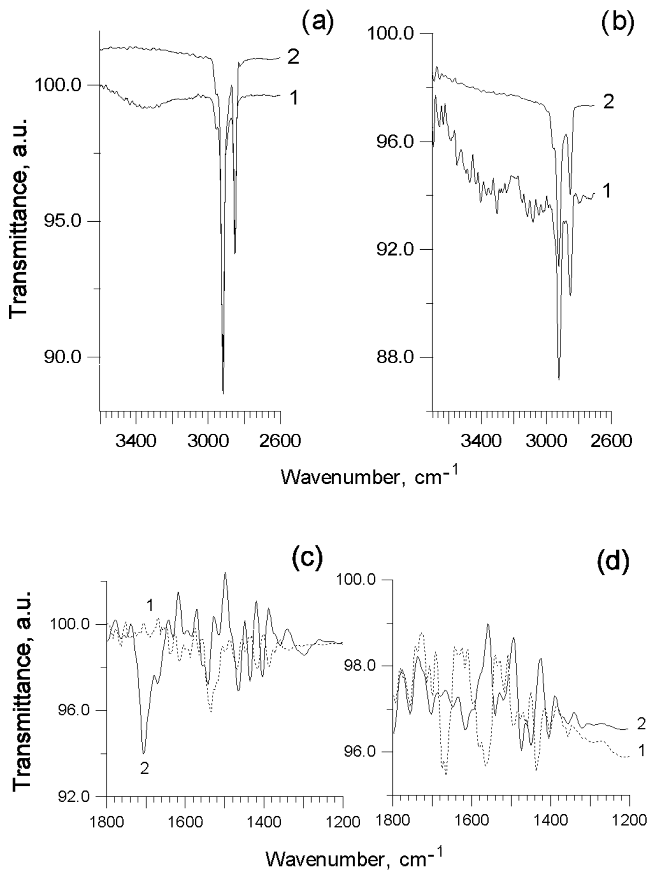

Figure 3. FTIR spectra of multilayer (10Y-type layers) films of behenic acid (a, c) and ODTNA iodide (b, d) films transferred at 30 mN/m surface pressure onto silicon wafers from subphases with thioglycerol-stabilized CdTe clusters (1) or water surface (2).

The FTIR spectra of the films deposited onto IR-transparent silicon wafers were changed significantly for the films obtained with both anionic and cationic surfactants (Figure 3). The bands observed were assigned to the corresponding fundamental vibrations according to the previous spectroscopic studies [26, 27]. The new bands appeared in the regions of 3500–3200 cm^{-1} (with ca. 3350 cm^{-1} maximum) and ca. 1620 cm^{-1} which indicated the presence of water in the CdTe cluster-containing films.

There are bands at 1708 and 1435 cm^{-1} in the spectrum of the behenic acid LB film deposited from the water assigned to the carbonyl-stretching mode and the hydrogen-bonded acid C=O stretching mode, coupled with the OH in-plane deformation mode that were absent in the spectrum of the cluster-containing LB film (Figure 3). Instead, new bands at ca. 1540 and 1420 cm^{-1} were observed, assigned to the asymmetric and symmetric stretching vibrations of COO^{-}, respectively. This fact can be interpreted as a formation of the film due to ionic bonding in the case of

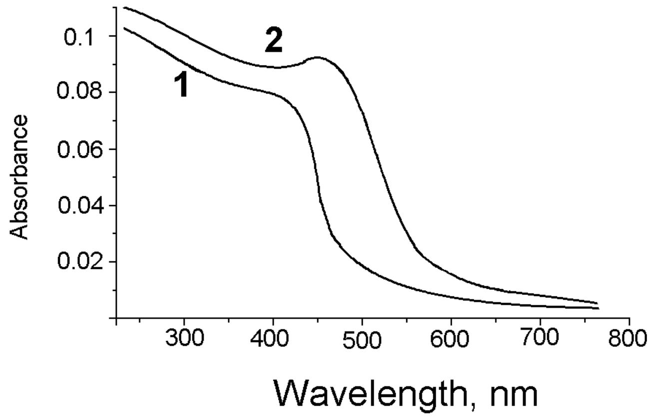

Figure 4. Optical absorption spectra for the multilayer (two-side 15Y-type layers) LB film of behenic acid with incorporated thioglycerol-stabilized CdTe clusters (1), and the spectrum of 10^{-3}M solution of these clusters (2).

behenic acid. The cations can be formed by the CdTe clusters if they have partially negative charges.

The UV/vis absorption spectra were recorded for thioglycerol-stabilized CdTe clusters which gave the best multilayer film. Figure 4 shows the spectrum for the sample with the two-sided 15 Y-type bilayer film. The spectra were shifted to the short-wavelength region (about 40 nm) compared with that of the aqueous solution with these clusters (Figure 4) from which the multilayer was prepared. The spectrum of the film prepared from behenic acid without the CdTe clusters had no features in the visible range. This indicates the incorporation of the clusters in the film with an estimated concentration of the order of 10^{16} cm^{-2} per monolayer.

The morphology of monolayer behenic acid with the incorporated thioglycerol-stabilized CdTe nanoparticles has been studied with AFM. The large-scale AFM inspection of LB film samples indicated the well-defined positional and orientational ordering into the lamella crystals located in the monolayer structure. The molecular resolution on the surface of these crystals has been obtained by scanning a 25×25-nm^2 area. A typical image after the Fourier transformation and cross-section of the image is shown in Figure 5. The spots in the Fourier transform correspond to a rectangular reciprocal space lattice. The clear image and spots in the Fourier transform inset show that this monolayer has a well-ordered lattice. The lattice spacing of the monolayer and the symmetry are noticeably distinguished from those of the mica substrate ($a = b = 0.52$ nm). The secondary structure seen under the molecular net of behenic molecules shown in Figure 5 can be associated with CdTe clusters (dimension 5–7 nm).

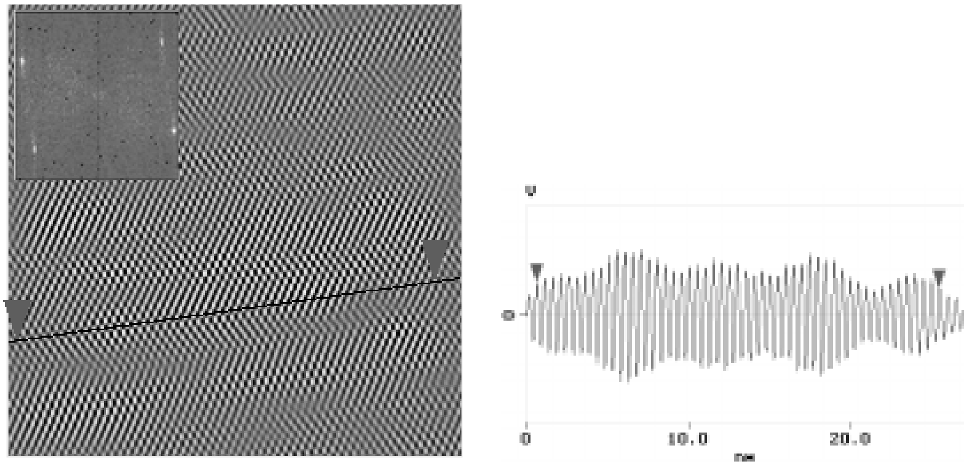

Figure 5. Molecular resolution AFM image with a cross-section analysis of the behenic acid monolayer with thioglycerol-stabilized CdTe clusters transferred on a mica-surface at a surface pressure of 30 mN/m.

4. Conclusions

1. The data obtained with the surface “pressure-area” isotherms, QCM, FTIR and UV/vis spectroscopy showed the possibility of successful incorporation of the CdTe clusters into the Langmuir-Blodgett films prepared from behenic acid and ODTNA iodide.

2. The extraction of the CdTe clusters from the subphase and the FTIR data indicated the ionic interaction between the carboxylic groups of behenic acid molecules and CdTe clusters that can provide the selectivity in the incorporation of the clusters stabilized only by thioglycerol.

3. The CdTe-cluster incorporation changed the behenic acid monolayer properties that provided the molecular resolution AFM images. The clusters were seen as a secondary structure under the behenic acid monolayer.

4. The quantum confinement effect in the optical absorption inherent to the CdTe clusters in solution remained for the clusters incorporated into LB films. The location of the absorption maximum was blue-shifted with respect to that in the solution.

Acknowledgements

We thank Dr N. A. Kotov for fruitful discussions. This work was partly supported by the Volkswagen Foundation, Hannover.

References

1. J. H. Fendler: *Chem. Mater*. **8**, 1616 (1996).
2. M. P. Pileni: *Ber. Bunsenges. Phys. Chem*. **101**, 1578 (1997).
3. A. P.Alivisatos: *J.Phys.Chem*. **100**, 13226 (1996).
4. Z. L. Wang: *Adv. Mater.***10**, 13 (1998).
5. M. Antonietti and Ch. Gültner: *Angew. Chem. Int. Ed.* **36**, 910 (1997).
6. H. Weller: *Angew. Chem. Int. Ed*. **32**, 41 (1993).
7. I. Dance and K. Fisher: *Progr. Inorg. Chem*. **41**, 637 (1994).
8. S. Dehen and D. Fenske: *Chem. Eur. J.* **2**, 1407 (1996).
9. T. Vossmeyer, L. Katsikas, M. Giersig, I.G. Popovic, K. Diesner, A. Chemseddine, A. Eychmüller and H. Weller: *J. Phys. Chem.***98**, 7665 (1994).
10. Y. Nosaka, H. Shigeno and T. Ikeuchi: *J. Phys. Chem.* **99**, 8317 (1995).
11. A. L. Rogach, L. Katsikas, A. Kornowski, D. Su. A. Eychmüller and H. Weller: *Ber. Bunsenges. Phys. Chem.* **100**, 1772 (1996).
12. B. O. Dabbousi, C. B. Murray, M. F. Rubner and M. G. Bawendi: *Chem. Mater*.**6**, 216 (1994).
13. N. A. Kotov, F. C. Meldrum and J. H. Fendler: *J. Phys. Chem.* **98**, 2735, 4506, 8827 (1994).
14. N. A. Kotov, I. Dekany and J. H. Fendler: *J. Phys. Chem.* **99**, 13065 (1995).
15. Z. Y. Pan, G. J. Shen, L.G. Zhang, Z. H. Lu and J. Z. Liu: *J. Mater. Chem*. **7**, 531 (1997).
16. P. J. Werkman, R. H. Wieringa and A. J. Schouten: *Thin Solid Films* **323**, 251 (1998).
17. F. N. Dultsev and L. L. Sveshnikova: *Thin Solid Films* **322**, 303 (1998).
18. J. Leloup, A.Ruaudel-Teixie, A. Barraud, H. Roulet and G. Dufour: *Appl.Surf. Sci*. **68**, 231 (1993).
19. I. Ichinose, N. Kimizuka and T. Kunitake: *J. Phys. Chem.* **99**, 3736 (1995).
20. P. Facci, V. Erokhin, A. Tronin and C. Nicolini: *J. Phys. Chem*. **98**, 13323 (1994).
21. P. Ganguly, D. V. Paranjape and M. Sastry: *J. Am. Chem. Soc.* **115**, 79 (1993).
22. P. Ganguly, D. V. Paranjape and M. Sastry: *Langmuir* **9**, 577 (1993).
23. H. Samha and M. K. DeArmond: *Langmuir* **10**, 4157 (1994).
24. G. Sauerbrey: *Z. Phys.* **155**, 206 (1959).
25. K. B. Blodgett and I. Langmuir: *Phys. Rev.* **51**, 964 (1937).
26. L.J. Bellamy: *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1975.
27. D. Lin-Vien, N. B. Colthup, W. G. Fateley and J. G. Grasselli: *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, Boston (1991).