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Monolayer Topography of Quantum Dots at the Interfaces

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Abstract The stable monolayer and multilayer films of colloidal nanocrystals – quantum dots (QDs) were obtained and studied. It is possible to visualize and characterize morphology (structural integrity, etc.) of the QD monolayers by Brewster angle and fluorescence microscopy techniques. The obtained films can be promising elements of the nanohybrid structures (such as QDs with natural biomembrane fragments and components) in photovoltaic cells and "nanoscale" materials for bio- and nanotechnology.

Keywords: *brewster angle microscopy, fluorescence microscopy, monolayers, biomembranes, quantum dots*

1. Introduction

Much attention has been focused today on the attempts to development and study of nano-biohybrid materials engineered from membrane proteins (the key functional elements of various biomembranes) and nanoheterostructures (inorganic colloidal nanoparticles, transparent electrodes and films) [1,2,3]. This is a rapidly growing field at the interface of materials and life sciences. The mainspring of the development of bioinspired materials and devices is the fact that biological evolution has solved many problems similar to those that humans are attempting to solve in the field of light-harvesting and energy-transferring inorganic compounds [3,4,5]. Along this way, bioelectronics and biophotonics based on proteins and/or quantum dots (QDs) have shown considerable promise. A number of inorganic particles have been explored in terms of bioelectronic device applications, but mixtures or conjugates of membrane protein and QDs have received the most attention [3,4,5].

The Brewster angle microscopy (BAM) technique has become one of the most powerful and attractive tools for the in situ studies of the surfactant molecules forming monolayers and Langmuir-Blodgett films at the interfaces [6]. This technique is based on the change of the refractive index of the water/air interface by spreading surfactant molecules as monolayer. The difference between refraction from monolayer as compared to pure water/air interface is the measured value in order to get the monolayer thickness. The last parameter is proportional to the square root of the reflection intensity. The recording of the reflected light by video-camera in BAM set-up allows the direct observation of the monolayer morphology in the real time and micrometer range [6].

The application of monolayer and BAM technique to study some surfactants and lipids have been reported recently (see [1,6] and references therein). The main advantages of LB technique application to QD film formation is the following: easy manipulation of the films and particular interparticle distance control [7-12]. These parameters are of great importance because much of the attention has been focused on QDs unique optical properties, which are sensitive to interparticle distance, particle size, material composition, nature of surface stabilizing layers etc. [9,10,11].

Fabrication and structural characterization of the monolayer films from colloidal nanocrystals – quantum dots by Brewster angle and fluorescent microscopy techniques are the key tasks of this work.

2. Materials and Methods

The synthesis and properties of the quantum dots covered with trioctylphosphine oxide (TOPO) have been described earlier [12,13,14]. Organic solvents, inorganic salts and quantum dots were bought from Sigma-Aldrich.

Surface pressure (π) - molecular area (A) and surface potential (ΔV) - molecular area (A) isotherms of QD monolayers have been prepared from 20 μl QD solution in hexane (2.16mg/ml) (Figure 1). These isotherms have been recorded on a rectangular trough (dimensions 11cm × 38cm × 0.8cm) made from polytetrafluoroethylene provided with a 2cm wide filter paper Wilhelmy balance and vibrating plate condenser (with Pt plate, 1.5cm diameter, operating at 400Hz). The 1mM QDs solution has been spread onto water (20 ℃) and the monolayers have been compressed by moving the barrier with a constant speed of about 25cm^2/min. The water has been cleaned with a Milli-Q filtration unit of "Millipore Corp." and distilled (resistance is 18MOm, surface tension 72.7mN/m at 20 ℃).

The equipment ("Nanofilm_ultrabam") for Brewster angle microscopy technique and software were generously

given by "Accurion" (Goettingen, Germany) and described in some previous papers [15].

The fluorescent images of the QD monolayers were obtained by confocal microscopy (Leica TCS SP5, Germany) [16,17]. The excitation wavelength was 488 nm and the emission wavelength was 530nm.

3. Results

The studied quantum dots formed stable monolayers with collapse pressure of around 33-35mN/m (Figure 1). The obtained data qualitatively are in agreement with the data described earlier for the same core-shell QDs covered with TOPO [7,8,9,10,11]. There are some quantitative differences with data of R.M. Leblanc group [9,11], where the collapse pressures for CdSe particles (without shell) in monolayers were artificially from 25mN/m depending on the surfactants covered these particles or about 45mN/m for CdSe/ZnS particles (core-shell) covered with the same surfactants.

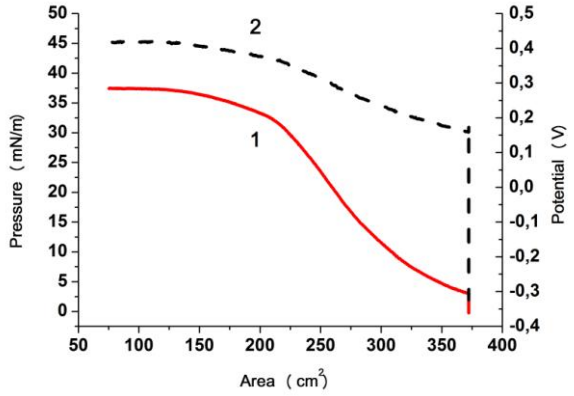

Figure 1. Surface pressure (1) and surface potential (2) vs. molecular area isotherms of QD monolayers

The surface-pressure isotherm (Figure 1, curve 1) indicated the beginning of the liquid-expanded state of QD monolayers (Figure 2, Scheme I) at low pressures (about 2mN/m) and high areas (starting from 370cm^2). The so-called "gaseous-like" phase (Figure 2, Scheme II) at very low pressures (below 0.5mN/m) did not shown because of extremely large areas (above 1000cm^2) could not be reached in the standard experiment. In this state two types of structures can be proposed: the aggregates of QDs covered with TOPO (Figure 2, Scheme I) and monolayers of individual TOPO molecules (Figure 2, Scheme II). The gradual increase in the surface pressure until 15-20mN/m (Figure 1, curve a) can be attributed to various structural changes in the QD aggregates in the liquid-expanded state (Figure 2, Scheme I) of QD monolayers, where the TOPO molecules squeezed from individual monolayer back to the surface of QD particles. The relatively sharp increase in the surface pressure above 15-20mN/m can be attributed to the liquid-condensed state of QD monolayers (Figure 2, Scheme III), where TOPO molecules from different layers of the neighboring QD particles are strongly interpenetrating. On the other hand the surface potential values are increasing gradually by monolayer compression (Figure 1, curve b). So, we did not expect high orientation of individual particles in the interfaces. Although the isotherms of these QDs look like typical π-A isotherms of standard amphiphilic molecules (for example TOPO surfactant) the topography of these films displayed a unique behavior (the transitions between liquid-expanded and liquid-condensed states) that was observed by BAM. In spite of the absence of such distinct transitions (Figure 3 a and b) the BAM measurements revealed aggregation of QDs in large domains with higher brightness as compared to initial one. The relatively sharp decrease in the area by increasing surface pressure from 10 to 30mN/m (Figure 1) can be attributed to the liquid-condensed state of QD monolayers. The further monolayer compression above 30mN/m leads to collapse state at around 35-37mN/m (Figure 1). In this state (Figure 2, Scheme IV) densely packed QDs domains can grow only in Z-direction and become 3-D (3-dimentional or net-like structures), but still highly stable as compared to standard amphiphilic molecules.

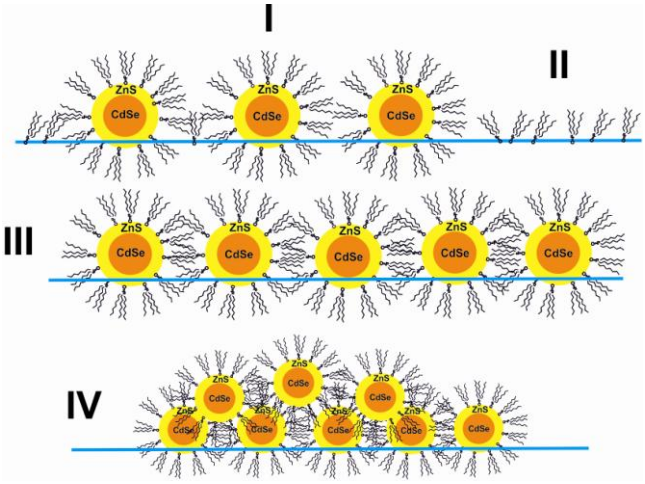

Figure 2. Schematic representation of the QD-TOPO monolayer at the interfaces: I) QDs liquid-expanded state, II) TOPO liquid-expanded state, III) QDs liquid-condensed state, IV) QDs monolayer collapse state

In order to proof our suggestion on QD monolayer topography inspired of obtained isotherms (discussed above) the BAM method was used. The dynamic BAM method is the specially attractive to observe the growing process of QD aggregates at the interfaces (Figure 3a, b) that can be indicated by domain brightness intensity etc.

It is a specially pronounced in the case of visualization of phase separation between liquid-expanded and liquid-condensed phases (Figure 3c). For example, from 10 to 30 mN/m the transition observed not in particular point and consist of two phases (Figure 3c), where these two phases liquid-expanded (left) and liquid-condensed (right) are clearly seen on the same image but divided by sharp and bright border curve. By monolayer collapse one can observe the very bright zones (Figure 3d) that can be attributed to the 3-D growth of the QDs domains (Figure 2, Scheme IV). It is important to underline that dark zones are not the pure water or TOPO surface, but it is another layer of QD domains (Figure 3). Because the brightness is increasing in a few times as compared to Figures 3a and b.

The particular areas per QD in 2-D film can be calculated 3-D as follows: I) $A=\pi*(R_1+R_2)^2$ for liquid-expanded monolayer state, II) $A=\pi*(R_1+R_3)^2$ for liquid-condensed monolayer state, III) $A=\pi*(R_1)^2$ for monolayer collapse state, where R_1 is QD radius in nm; R_2 is the thickness of the TOPO monolayer on QD surface (about

0.7nm [9,11]), R_3 is about half of the thickness of the TOPO monolayer on QD surface, because of the strong interpenetration of TOPO layer from different particles. Thus, the respective theoretical values of the area per QD in 2-D film are follows: I) 25.8nm^2; II) 140.5nm^2; III) 198.4nm^2 in the case of QD.

BAM images of these QDs monolayers have been reported for the first time (Figure 3). Already at the experiments beginning (just after spreading at the air-water interface) these QDs formed monolayers that can be composed of two components (Figure 3a): TOPO molecules (homogeneous black areas) and QD 2-D aggregates (micrometer range light domains). The QD aggregates are growing strongly during monolayer compression and developing so called "net-like structures" of the numerous light domains. It is important to underline that QDs monolayer on 0.1M KCl have almost the same structures as those on the distilled water at low pressures. Further QDs monolayer compression leads to the formation of the rigid 3-D structures in collapse range (pressures about 30-35mN/m) of higher and lower brightness that are in any case have more intensity as initial 2-D monolayers.

The UV-VIS spectra of multilayer film composed 10 QDs monolayer transfer were recordered with the strong band as observed for QD in solution and monolayers reflection spectroscopy. These data prove the structural integrity of QD monolayer films.

As can be seen from the micrographs (Figure 4), obtained by confocal fluorescent microscopy, the QDs formed large bright aggregates. They are mainly combined in the large plain structures with dark holes about 2.0-2.5μm (small bar on the Figure 4a). The large bar of about 10 μm is the general scale for the whole picture, placed in a dark area (showing homogenous TOPO layer). Thus, the confocal fluorescent microscopy data are in agreement with BAM.

The observed QD structures have been enlarged in the Figure 4b in order to observe homogeneous 2-D aggregates as large bright domains (on the right and left side of the picture 4b) in contrast to small dark areas of TOPO layer (at the top, in the middle and at the bottom of this picture). These aggregates have minimal diameter about 159nm (Figure 4b). There are some small extremely bright regions (almost white regions) where the increased fluorescence is due to the increased amount of QDs forming 3-D structures.

This approach is a promising way to fabricate and visualize the monolayer films of colloidal nanocrystals (QDs) that can be useful for design of nanobiohybride structures. Such structures (QDs with natural biomembrane fragments and components [1,2,3,4]) will be the main objects of the future publication.

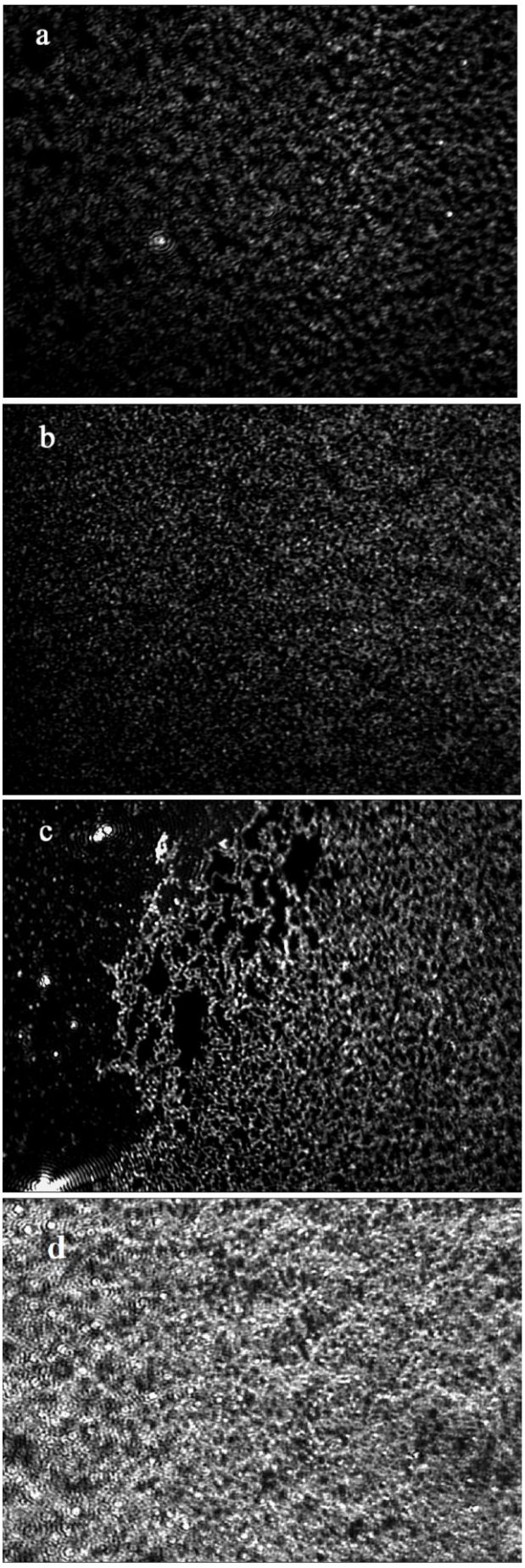

Figure 3. BAM images of the QD monolayers at water-air interface by increasing surface pressures from 0.1mN/m (a) to 35mN/m (d).

4. Conclusion

Fabrication and visualization of the monolayer films of colloidal nanocrystals (QDs) by Langmuir and Brewster angle microscopy techniques are performed. These films can be promising elements of the nanohybrid structures (QDs with natural biomembrane fragments and components) for photovoltaic cells and other"nanoscale" objects for the special tasks in bio- and nanotechnology.

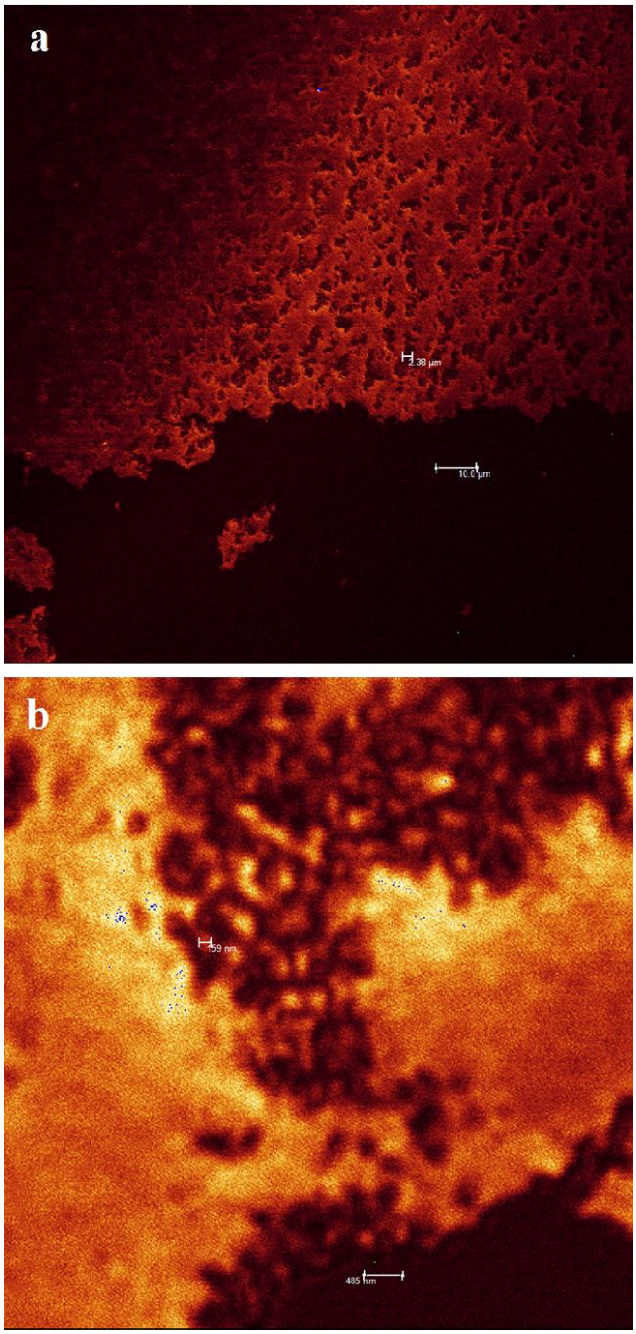

Figure 4. Images of the QD monolayers, obtained by confocal fluorescent microscopy: a) standard picture, b) enlarged picture

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References

[1] Zaitsev, S.Yu., Solovyeva, D.O., Nabiev, I., "Thin films and assemblies of photosensitive membrane proteins and colloidal nanocrystals for engineering of hybrid materials with advanced properties", *Advances in Colloid and Interface Science*, 183-184 14-29. 2012.

[2] Nabiev, I., Sukhanova, A., Artemyev, M., Oleinikov, V., In Elaissari A (editors) "*Colloidal Nanoparticles in Biotechnology*", Wiley&SonsInc, 2008. 133-169.

[3] Rakovich, A., Sukhanova, A., Bouchonville, N., et al. "Resonance energy transfer improves the biological function of bacteriorhodopsin within a hybrid material built from purple membranes and semiconductor quantum dots", *Nano. Lett*, 10, 2640-2648. 2010.

[4] Nabiev, I., Rakovich, A., Sukhanova, A., Lukashev, E., et al. "Fluorescent Quantum Dots as Artificial Antennas for Enhanced Light Harvesting and Energy Transfer to Photosynthetic Reaction Centers", *Angewandte Chemie Intl Ed*, 49, 7217-7221. 2010.

[5] Archer, M.D., Barber, J. In Archer MD, Barber J (editors), "*Molecular to Global Photosynthesis*", Imperial College Press; 2004.

[6] Roldan-Carmona, C., Giner-Casares J.J., Perez-Morales M., Martin-Romero M.T., Camacho L., "Revisiting the Brewster angle microscopy: the relevance of the polar headgroup", *Advances in Colloid and Interface Science*, 173, 12-22. 2012.

[7] Xu, J., Ji, X., Gatt ás-Asfura, K.M., Wang, C., Leblanc, R.M., "Langmuir and Langmuir–Blodgett films of quantum dots", *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 284-285, 35-42. 2006.

[8] Gole, A., Jana, N.R., Selvan, S.T., Ying, J.Y., "Langmuir-Blodgett Thin Films of Quantum Dots: Synthesis, SurfaceModification, and Fluorescence Resonance Energy Transfer (FRET) Studies", *Langmuir*, 24. 8181-8186. 2008.

[9] Orbulescu, J., Leblanc, R.M., In Nagarajan R. (editors) "Nanoparticles: Synthesis, Stabilization, Passivation, and Functionalization", ACS Symposium Series; American Chemical Society, Washington, DC, 2008. 172-189.

[10] Ferreira, P.M.S., Timmons, A.B., Neves, M.C., Dynarowicz, P., Trindade, T., "*Langmuir_Blodgett manipulation of capped cadmium sulfidequantum dots*", Thin Solid Films, 389. 272-277. 2001.

[11] Gattas-Asfura, K.M., Constantine, C.A., Lynn, M.J., Thimann, D.A., Ji, X., Leblanc, R.M., "Characterization and 2D Self-Assembly of CdSe Quantum Dots at the Air−Water Interface", *JACS*, 127. 14640. 2005.

[12] Murray, C.B., Kagan, C.R., Bawendi, M.G. "Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies". *Annu Rev Mater*; 30. 545-610. 2000

[13] Medintz, I.L., Uyeda, H.T., Goldman, E.R., Mattoussi, H. "Quantum dot bioconjugates for imaging, labelling and sensing". *Nature materials*, 4. 435-446. 2005.

[14] Sukhanova, A., Devy, J., Venteo, L., Kaplan, H., Artemyev, M., Oleinikov, V., Klinov, D., Pluot, M., Cohen, J.H.M., Nabiev, I. "Biocompatible fluorescent nanocrystals for immunolabeling of membrane proteins and cells". *Anal. Biochem*., 324. 60-67. 2004.

[15] Benı´tez, I.O., Talham, D.R. "Brewster Angle Microscopy of Calcium Oxalate Monohydrate Precipitation at Phospholipid Monolayer Phase Boundaries". *Langmuir*, 20. 8287-8293. 2004.

[16] Huse, N., Schoenle, A., Hell, S.W. "Z-polarized confocal microscopy". *Journal of Biomedical Optics*, 6(4). 480-484. 2001.

[17] Claxton, N.S., Fellers, T.J., Davidson, M.W. National High Magnetic Field Laboratory, Florida State University, 37 p., Unpublished. *Laser scanning confocal microscopy*, 2005. [E-book]. Available: http://www.olympusfluoview.com/theory/LSCMIntro.pdf.