

Composite Langmuir–Blodgett films of behenic acid and CdTe nanoparticles: the structure and reorganization on solid surfaces

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Abstract

Composite monolayer films of behenic acid and CdTe nanoparticles capped with either 1-thioglycerol or thioglycolic acid were prepared by the vertical and horizontal deposition methods on mica and graphite substrates. The films were studied with pressure–area isotherms, Fourier transform infrared spectroscopy, atomic force microscopy, UV–vis absorption and photoluminescence spectroscopy. New anisotropic material was assembled at interface of solution in result of interaction between of thioglycolic acid stabilized nanoparticles and monolayer film of behenic acid. The structure of the CdTe/behenic acid assemblies was found to be sensitive to the method of preparation and texture of the substrate. On the graphite surface, CdTe-containing films reorganize into lamellae. Assemblies formed on the mica surface can be reversibly translocated between the substrate and the atomic force microscopy (AFM) tip. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Semiconductor nanoparticles attract considerable interest as promising materials for nanoelectronics, optics, and catalysis [1–3]. Formation of ordered thin films of uniform nanoparticles pro-

vides a route to new nanostructured materials. The Langmuir–Blodgett (LB) technique allows the transfer of nanoparticles from solutions into thin films. Compression of nanoparticles at water interface using monolayer film as the surrounding matrix is one of the commonly used method for preparation of composite films [4]. Aggregation of LB films comprising surfactant-stabilized nanoparticles is another possible way to form nano-scale assemblies [5–10]. Nanoparticles can

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also be crystallized under monolayer of a surfactant floating on the surface of aqueous subphase [11,12]. Anisotropic materials can appear in the last case.

Behenic acid monolayer films and their compositions with CdTe nanoparticles were the object of present work. CdTe nanoparticles of nanometer sizes covered with different thiols have also been synthesized in aqueous solutions [13,14] and show size-dependent optical properties allowing their potential use in thin film optoelectronic devices. We have shown earlier [15] that LB monolayers prepared from behenic acid molecules can be cross-linked with 1-thioglycerol stabilized CdTe nanoparticles via carboxylic heads of behenic acid molecules. Two thiol compounds, namely, 1-thioglycerol (TG) and thioglycolic acid (TGA) were chosen in this work to stabilize the CdTe particle surface. Interactions of the terminal groups of these compounds with a plain of behenic acid molecules should provide different behavior of composite films on solid surface. Indeed, the properties of such assemblies were determined not only by presence of the nanoparticles but also by particle–particle and particle–matrix interactions.

In this report, we also describe a method of preparation of composite supramolecular assemblies on solid surfaces. Unusual properties of such assemblies were demonstrated by atomic force microscopy (AFM).

2. Experimental

2.1. Materials and sample preparation

Aqueous dispersions of CdTe nanoparticles stabilized with either 1-thioglycerol (TG) or thioglycolic acid (TGA) were obtained and characterized as described in Refs. [13,15].

Monolayers were prepared by spreading 0.5–0.8 mM chloroform solutions of behenic acid (Sigma Chemical Company) on the surface of doubly distilled water (pH 5.3–5.5) and aqueous solutions of CdCl₂ or CdTe nanoparticles (ca. 0.01–0.05 mM) [15].

Compression was started after the solvent had completely evaporated and the film attained suffi-

cient stability (ca. 15 min). Y-type bilayers were transferred to the substrate by the traditional vertical deposition (VD) method [16]. Z-type monolayers were obtained by the ‘horizontal precipitation’ (HP) method [17,18] on freshly cleaved atomically flat surfaces of mica and highly oriented pyrolytic graphite (HOPG). The surface pressure during the deposition was kept at 20 or 30 mN m^{−1}. <100> silicon wafers were used in Fourier transform infrared (FTIR) spectroscopic measurements.

2.2. Instrumentation

An automated computerized Langmuir trough was used for the film deposition and measurements of surface pressure–area per molecule (π – A) isotherms. The isotherms were recorded at a compression speed of 0.2–0.3 Å²/(molecule × min). The temperature of the subphase was maintained at 290 K.

UV–vis absorption spectra of the multilayer samples (optical absorption $D = 0.1$ – 0.4) were recorded with a Perkin–Elmer Lambda 40 UV–vis spectrophotometer in the spectral range from 250 to 800 nm. Photoluminescence of the samples was measured with a ‘FluoroMax-2’ spectrofluorimeter. Infrared spectra were recorded in air with a Nicolet ‘Protege 460’ FTIR interferometer with the resolution of 4 cm^{−1} (the radiation was incident perpendicular to the sample surface).

AFM images were obtained with a Nanoscope IIIa (Digital Instruments, USA) operated in the constant force mode (1.5–5 nN). 100 mm and 200 mm nanoprobe cantilevers (spring constants of 0.12 and 0.32 N m^{−1}) with oxide-sharpened Si₃N₄ integral tips were used. The device was equipped with a <D> scanner calibrated using the manufacturer’s grating. The applied force was varied over a wide range from several nN up to hundreds of nN. The scanning frequency ranged from 5 to 60 Hz. Temperature drift was minimized by averaging the molecular lattice parameters determined from AFM images (10–20) for various scanning directions. The thermal drift error, estimated by measuring the angle between the principal crystallographic directions of mica (60°), did not exceed 3–5° under the specified conditions. The best

Table 1
Lattice parameters of LB films of long-chain fatty acid derivatives

No.	Material	Substrate	Sample description	<i>a</i> (nm)	<i>b</i> (nm)	Molecular area (nm ²)	
						AFM	π - <i>A</i> isotherm
1	Behenic acid	Mica	Monolayer from water	0.53 ± 0.03	0.77 ± 0.04	0.203 ± 0.007	0.20 ± 0.005
2	Kitaigorodsky ^a , <i>R</i> [0, ± 1] cell		Theory	0.496	0.785	0.195	–
3	Behenic acid	HOPG	Top of the lamella structure	0.50 ± 0.02	0.78 ± 0.06	0.194 ± 0.016	0.330 ± 0.01
4	Behenic acid	Mica	Top of the lamella structure	0.48 ± 0.03	0.77 ± 0.06	0.185 ± 0.017	0.330 ± 0.01
5	Cd arachidate ^b	Mica	Three-bilayer	0.482	0.748	0.180	–

^a Ref. [22].

^b Ref. [21].

subnanometer resolution was achieved by using a high scanning frequency in the friction force mode. Values of the AFM parameters averaged over several dozen images are summarized in Table 1.

3. Results and discussion

3.1. Properties of composite films

Pressure–area isotherms (Fig. 1) show that the behavior of behenic acid monolayers during the compression is strongly influenced by the presence of CdTe nanoparticles in the solution. Indeed, for behenic acid on the surface of pure water the isotherm has a classic shape. The limiting surface area per molecule in the compressed solid film is ca. 20 Å². At the same time, the isotherms recorded on the surface of aqueous solutions of CdTe nanoparticles yield molecular areas that are greater by a few Å² than in the pure behenic acid monolayer. The ‘solid film’ region was never observed for the composite monolayers which collapse at a much lower surface pressure as soon as the film reaches the ‘liquid–solid’ state.

The incorporation of CdTe particles into behenic acid films was conclusively demonstrated by recording UV/Vis absorption and photoluminescence spectra for LB films with and without CdTe

nanoparticles. Unlike the absorption spectrum of the behenic acid film without CdTe nanoparticles, the spectrum of the film with nanoparticles exhibits a shoulder (Fig. 2). This shoulder is attributed to the electronic transitions in the CdTe nanoparticles which are similar to those observed in an aqueous solution [19] except for a slight blue-shift (Fig. 2). Accordingly, the position of the excitonic photoluminescence band [19] is blue-shifted for CdTe nanoparticles in the LB film. The nature of this phenomena has been discussed in [15].

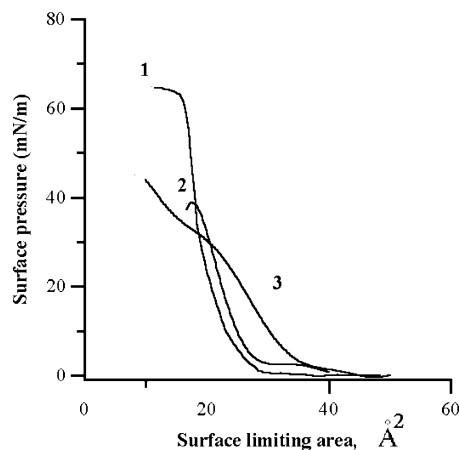


Fig. 1. Representative compression isotherms (measured at 290 K) of monolayers of behenic acid recorded on the interface of: (1) water or aqueous solution of (2) TG- and (3) TGA-capped CdTe nanoparticles.

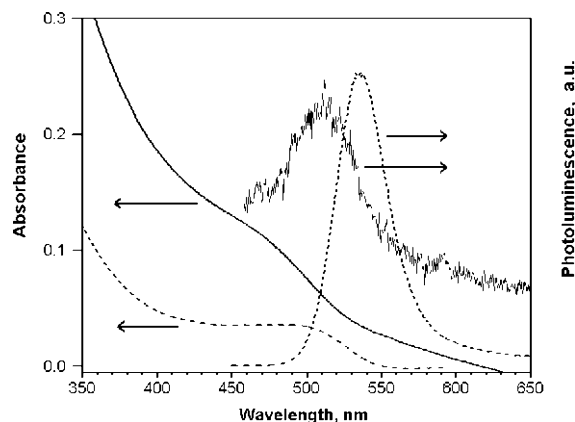


Fig. 2. Optical absorption and photoluminescence spectra of the multilayer (two-side 15 Y-type) LB film of behenic acid with incorporated TG-stabilized CdTe nanoparticles (solid lines) and of TG-stabilized CdTe nanoparticles in aqueous solution (dashed lines).

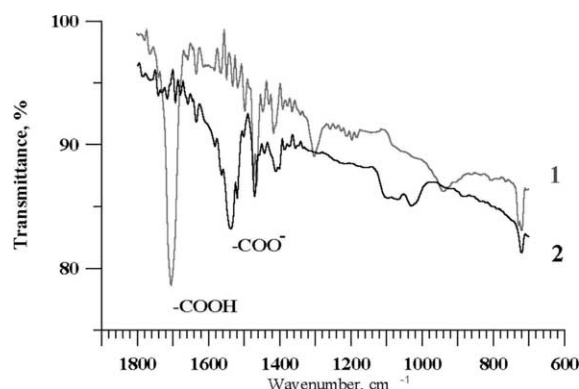


Fig. 3. FTIR spectra of multilayer LB films (10 Y-type) of behenic transferred onto silicon wafers from (1) water surface or (2) subphase with TGA-stabilized CdTe nanoparticles.

The inclusion of CdTe nanoparticles into LB films of behenic acid also results in substantial changes of their FTIR spectra (Fig. 3). The distinctive feature of pure behenic acid films is a broad band at 1708 cm^{-1} attributed to the carbonyl stretching mode of the free carboxylic groups. This band is absent in FTIR spectra of composite films where the COOH groups are converted into the ionic form. Instead, a new band at ca. 1540 cm^{-1} develops which we assigned to ν_a (COO^-) asymmetric stretching vibrations.

It is likely that in a weakly acidic subphase the dissociation of some Cd–S bonds takes place and some of the thiol molecules stabilizing the CdTe core leave the surface [15]. Moreover, in the case of TGA-stabilized CdTe nanoparticles the appearance of cations into the internal shell of thioglycolic acid may occur. In either case, the conversion of behenic acid molecules into ionic form provides ionic linkage of surface-active molecules with the surface of nanoparticles.

As suggested by Fig. 4, the morphology of composite films is also strongly dependent on the type of interfacial bonding between nanoparticles and the behenic acid monolayer. We emphasize here again that reorganization of LB films on solid surfaces is a rather common phenomenon [20]. Three-dimensional rearrangements of the composite monolayer with thioglycerol-stabilized nanoparticles prove to be destructive (Fig. 4a). On the contrary, lamella crystallites integrated into composite films with TGA-stabilized nanoparticles, possess an increased structural stability. The preferable mutual orientation of crystallites on mica is clearly seen in Fig. 4(b).

The morphology of behenic acid films with TGA-stabilized nanoparticles also depends on the method of preparation. When the films are prepared by the vertical deposition method on the graphite surface, numerous crystallites are formed (Fig. 4(c)). In contrast, monomolecular films on mica remain intact (Fig. 4(d)). Normally, the first LB monolayer would be strongly attached to the substrate. However, this is not the case with the composite film transferred to mica by the vertical deposition method. Apparently, film fragments slip off the substrate during the vertical deposition because of weak adhesive forces of mica. Consequently, the structural information about the films deposited by the vertical method may be lost.

We suggest that assemblies should be transferred to weakly adhesive surfaces such as mica by the HP method preferably.

3.2. Molecular structure of film surfaces

In the traditional vertical deposition method, films of fatty acid derivatives are formed in the salt form on the ionic subphase. Our HP method

allows the deposition of a monolayer film to be carried out on a subphase free from counter-ions (Fig. 5(a)). The film prepared by the HP method allows us to see the coexistence of two phases—solid (the brighter regions) and liquid-condensed (the darker regions). Furthermore, the HP method preserves the film structure better than the VD method, as demonstrated by molecular resolution images of solid monolayer of behenic acid on mica (Table 1). The AFM image (Fig. 5(b)) reveals arrays of rectangular face-centered cells (with two molecules per cell). AFM data for the surface area per molecule in behenic acid monolayer films on mica agree well with the value

of the limiting area derived from the π - A isotherm (Table 1). However, the observed value of parameter ' a ' is 0.53 nm, whereas typical values fall in the range from 0.48 to 0.50 nm [21]. We believe that this discrepancy is due to the disordering influence of the mica substrate.

Crystallites are only seen into behenic acid monolayer film transferred from TGA-stabilized CdTe subphase. No crystalline structures are observed in behenic acid films prepared either on pure water or salt solutions. A detailed inspection of the crystal surface reveals that it consists of parallel fibrils (Fig. 6(a)). The results of a section analysis of a film fragment with a nanocrystal

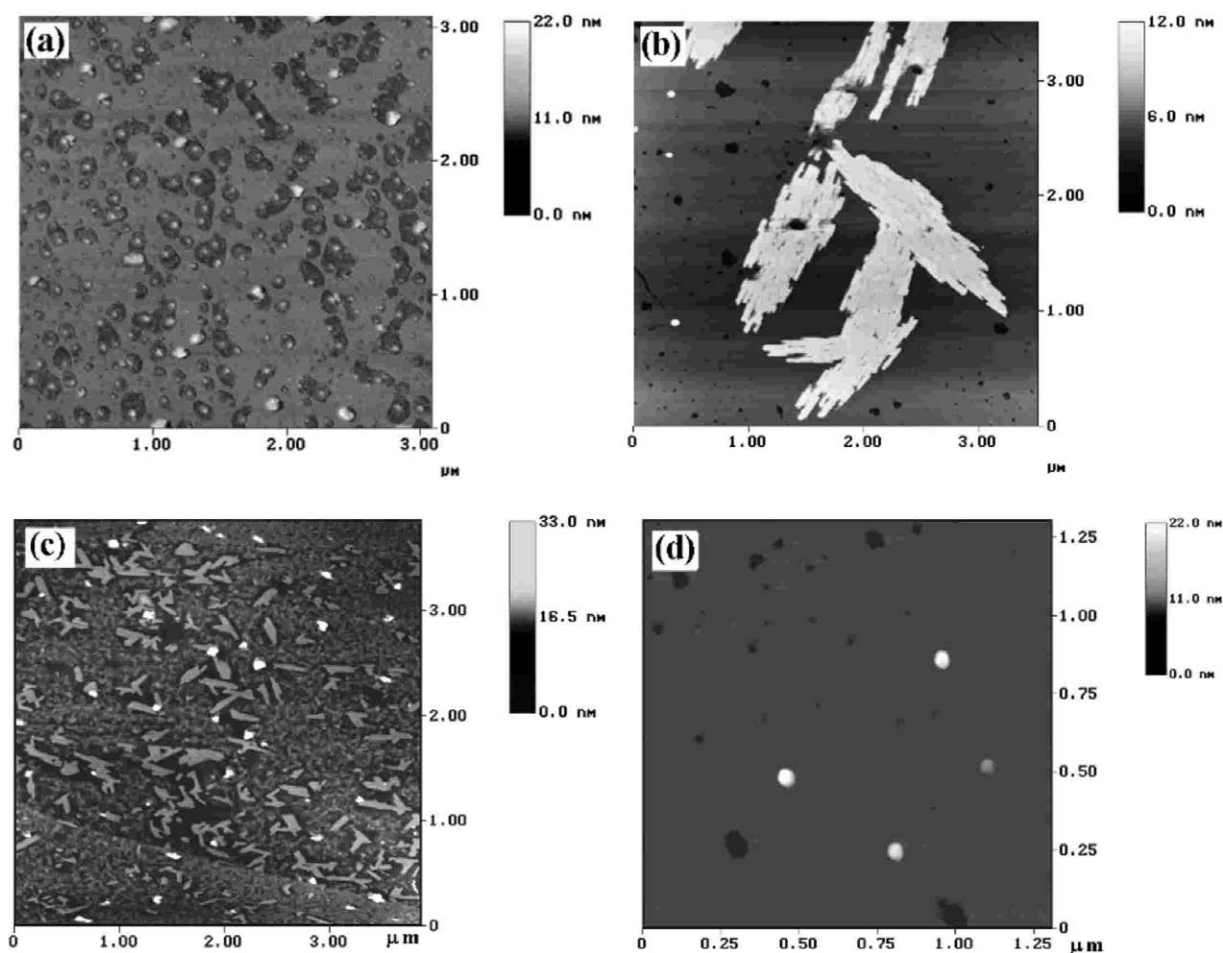


Fig. 4. AFM height images of behenic acid films transferred at $\pi = 30 \text{ mN m}^{-1}$ by (a, b) HP or (c, d) vertical method of deposition on (a, b, d) mica or (c) HOPG substrate from water solution containing (a) TG- or (b, c, d) TGA-stabilized CdTe nanoparticles.

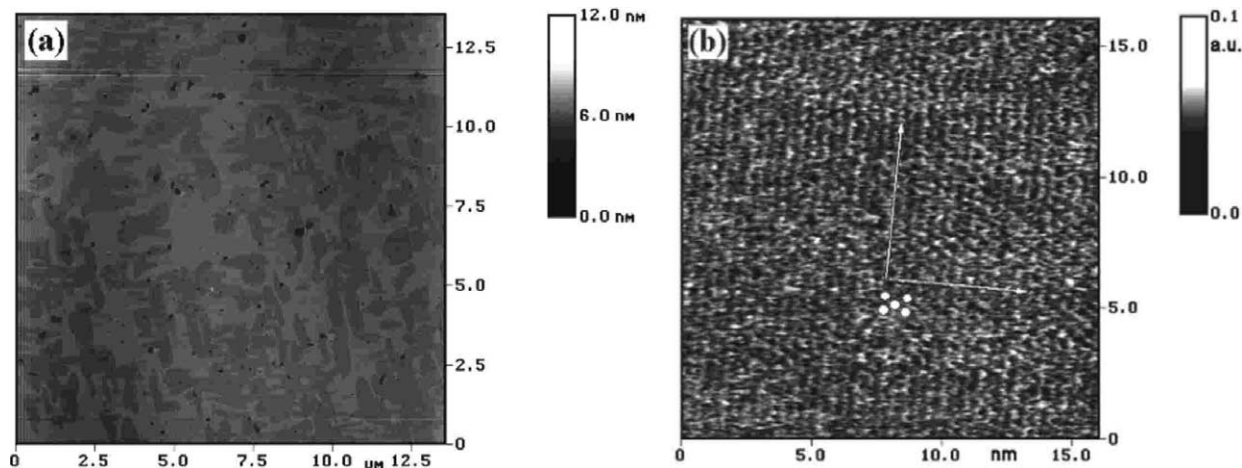


Fig. 5. (a) Large scale, (b) typical high-resolution unprocessed AFM images of behenic acid transferred by HP deposition method onto a mica substrate from water interface at 20 mN m^{-1} of surface pressure.

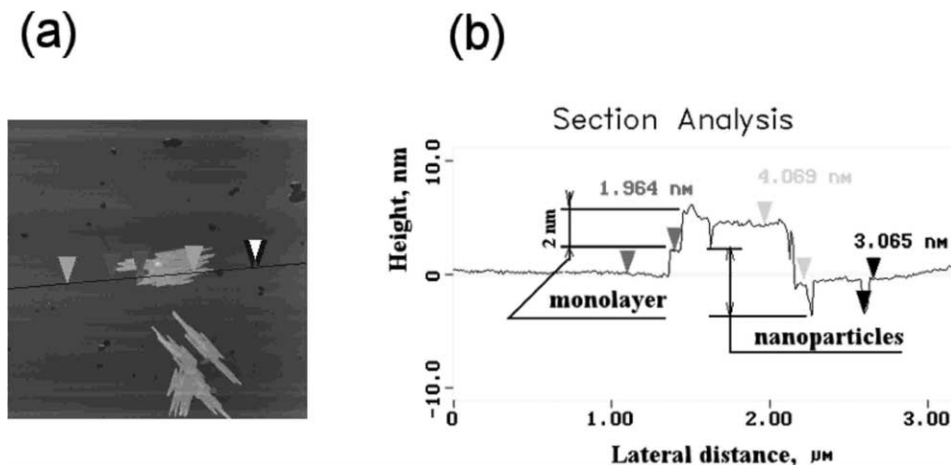


Fig. 6. (a) AFM top view and (b) section analysis of a composite monolayer transferred by HP method of deposition from water solution containing TGA-stabilized CdTe nanoparticles on mica at 30 mN m^{-1} of surface pressure.

(Fig. 6b) suggest that the crystal is built from nanoparticles with a size of ca. 5 nm and vertically stacked molecules of behenic acid (ca. 2 nm).

It was also possible to obtain molecular resolution images for lamella crystals, but not for the surrounding monolayer. The lattice parameters are comparable (Table 1) with those of fatty acid salt films [21]. These agree very well with the theoretical values of Kitaigorodsky [22] for alkyl tails packed into rectangular cell. We regard these images as direct evidence that the crystals are

covered with a layer of behenic acid molecules. This conclusion also agrees with the ionic binding model (from FTIR daTA) describing the interaction between behenic acid molecules and nanoparticles.

3.3. Reorganization of monolayers

3.3.1. The role of the substrate

The role of the substrate during the crystallization was studied on composite films of behenic

acid and TGA-stabilized CdTe nanoparticles prepared by the HP method. Such composite films undergo crystallization on graphite but not on mica. Crystallites shown in Fig. 7(a) are oriented along the crystallographic directions of graphite.

This was determined by inspecting AFM images of a small region of the film in the vicinity of an artificial defect created by applying an AFM tip pressure of about 100 nN at a slow scan speed (ca. 5 Hz). Fig. 7(b,c) show arrangements with a narrow distribution of angles between the crystallites themselves as well as between the crystallites and the crystallographic axes of HOPG. On mica substrate crystallites were preferably oriented as well, but without film reorganization.

3.3.2. Reversible transfer of crystals under the influence of the AFM tip

We repeatedly observed reversible translocations of crystallites between the substrate and the microscope tip. Indeed, because of the weak adhesion, lamellae are easily scraped off the surface by the AFM tip (Fig. 8(a)) and adsorb on a cantilever at increasing up to 100 nN the force of contact pressure of a tip on a film surface. The

holes in the film surface, seen in Fig. 8(b), are left by removed lamellae. However, as the tip pressure decreases to a few nN, lamellae return to the substrate (Fig. 8(c)) and the height of crystallites restore. Hence, the crystalline assemblies behave as a single unit.

In order to explain this phenomenon, we assume that the surface of each TGA capsule is surrounded by a layer of cations that stabilizes the CdTe core. This ionic layer should weaken adhesion of the lamellae to a hydrophobic surface of surrounding monolayer and strengthen its adsorbance to the hydrophilic surface of mica or the microscope tip depending on the force exerted by the tip on the crystal. Hence, lamellae return back into hydrophilic holes as the tip pressure decreases. Electrostatic interaction bottom shell of the positively charged assemblies and the negatively charged [23] mica surface also favors the orientation of lamella crystals along the crystallographic directions of the substrate during deposition. These assumptions agree well with the available (π -A isotherms, FTIR, AFM) experimental data.

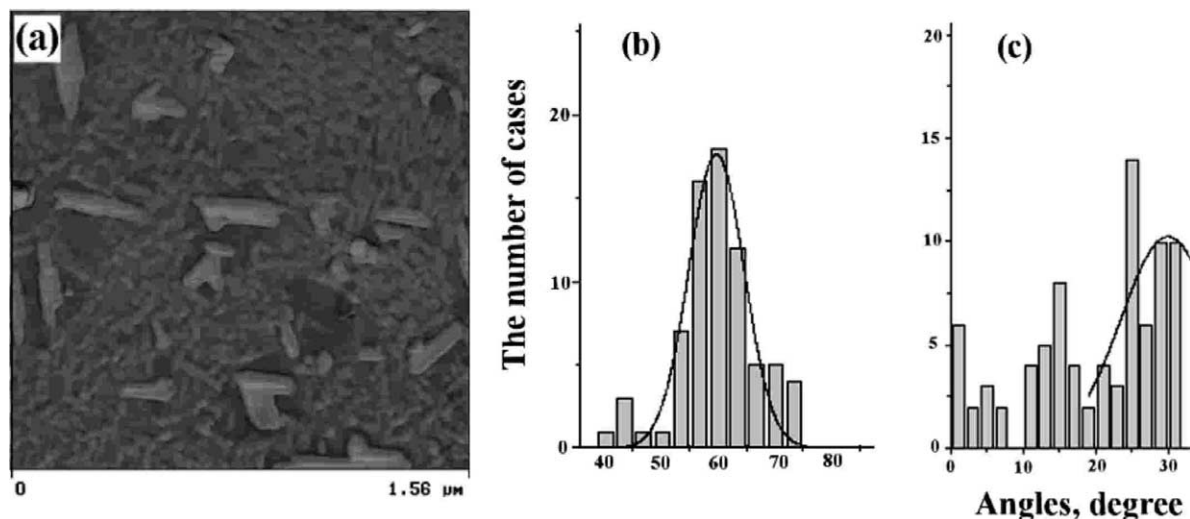


Fig. 7. (a) AFM image (phase regime) of the morphology of composite film from behenic acid and CdTe nanoparticles on HOPG surface; Histograms of distribution of angles (b) between the long axis of lamella crystals on the surface of HOPG and (c) between the lamella and the crystallographic axis of HOPG are also presented.

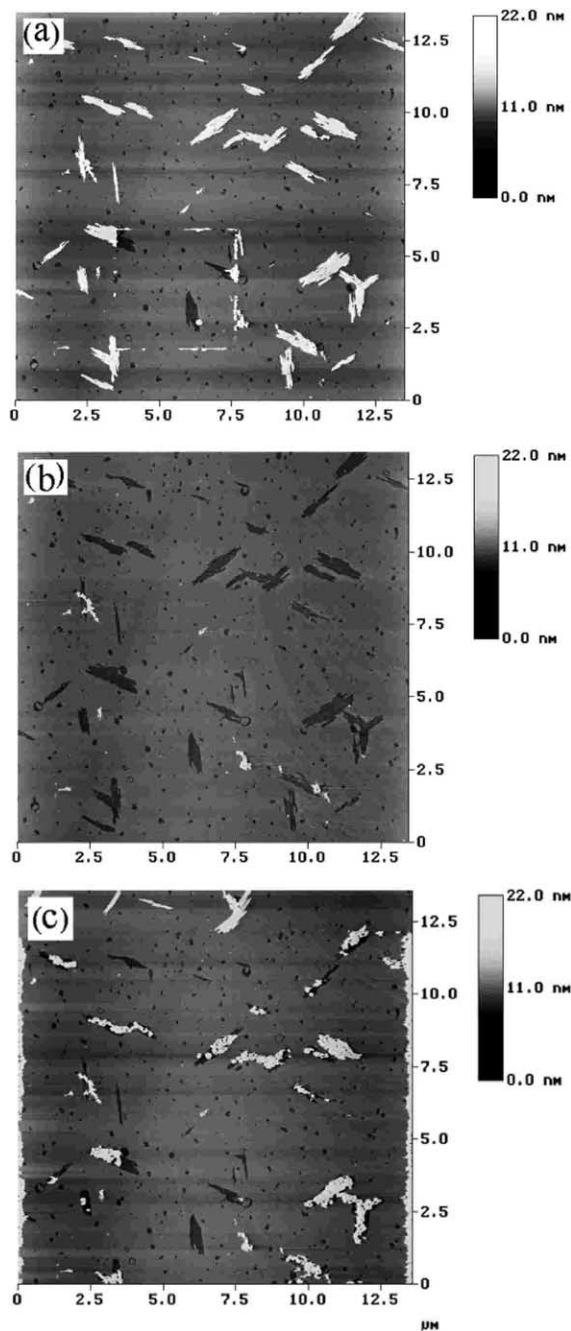


Fig. 8. AFM images illustrating reversible 'surface-tip-surface' transition of CdTe nanoparticles/behenic acid assemblies in the process of monolayer scanning: (a) the force of the surface scanning 1×10^{-9} N; (b) increase of the contact pressure up to 1×10^{-7} N; (c) decrease of the force of contact of the microscope tip down to 1×10^{-9} N.

4. Conclusions

Composite monolayer films of behenic acid and thiols-capped CdTe nanoparticles have been formed at the solution interface. Unusual properties of such films are affected by the method of preparation. The horizontal precipitation method is preferable to the traditional vertical LB technique for composite film formation. Composite assemblies of TGA-capped CdTe nanoparticles form lamella crystallites on solid surfaces. Details of the process of deposition are sensitive to the texture of mica substrate. The resulting assemblies also undergo further reorganization on the graphite surface.

The mica surface influences the preferable orientation of assemblies during the horizontal deposition. Lamellae can be reversibly transferred between the substrate and the AFM tip during the scanning.

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