



Organized planar nanostructures from ligand-stabilized nanoclusters: a route to molecular nanoelectronic devices

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Abstract

In present work, we describe the formation and deposition of mixed Langmuir monolayers composed of inert amphiphile molecular matrix and guest ligand-stabilized metal-core nanoclusters. Such approach allowed obtaining the ordered stable reproducible planar monolayer and multilayer nanocluster nanostructures on solid substrates. The use of novel polymeric Langmuir monolayers formed by amphiphilic polyelectrolytes and nanoclusters resulted in fabrication of ultimately thin monomolecular nanoscale-ordered stable planar polymeric nanocomposite films. Morphology and electron transport in fabricated nanostructures were studied experimentally using AFM and STM. The perspectives for nanoelectronic applications of organized planar nanostructures from ligand-stabilized nanoclusters are discussed.

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1. Introduction

Fabrication of new advanced technologically-useful nanostructured materials and functional nanostructures starting with atoms and molecules via cost-effective nanoscale-controlled self-assembly and self-organization processes is a basic concept of the synthetic (bottom-up) approach in nanotechnology

and nanoelectronics. The appropriate design, assembling and integration of functional nanoscale building blocks into low-dimensional and three-dimensional architectures are principal steps on the way to fundamental scientific understanding of their individual and collective, electronic, optical, magnetic and other properties, what is necessary for real advancement of nanomaterials to technologically important applications. Nanoscale conductors (dots and wires of organic and inorganic nature) exhibit novel conductive and other properties that differ considerably from those of bulk conductors, and such phenomena as

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electron tunneling, Coulomb blockade effect, quantum resistance, ballistic transport are observed at the nanoscale [1–3]. Ligand-stabilized nanocluster molecules could prove to be promising components for nanoelectronic circuits: such compounds can be chemically synthesized in macroscopic quantities with uniform size, structure and composition, and, as a result, with absolutely reproducible properties of individual clusters what is of principal importance for creation of quantum nanoelectronic devices. Stabilizing ligand shell of the cluster prevents coalescence of clusters and allows to regulate with Angstrom accuracy the inter-cluster distances in the ordered arrays of clusters. Functional groups in the nanocluster ligand shell can allow the purposeful immobilization and organization of clusters on substrate surfaces or in 3-D systems. The development of experimental methods for fabrication and characterization of organized stable structures from chemically produced nanoclusters and nanoparticles along with clear theoretical explanation of the observed electron transport effects are important for their future applications in nanoelectronics and nanotechnology.

Scanning probe microscopy techniques has been proven to be a very effective tool for investigation of morphology and conductivity of various nanostructures, as, for example, metallic clusters [4,5], fullerenes [6], and was used in the present work. Earlier, to form 2-D arrays of ligand-stabilized nanoclusters on solid substrates we have used mixed Langmuir monolayers and corresponding Langmuir–Blodgett (LB) films composed by inert surfactant molecular matrix (fatty acids) and guest ligand-stabilized metal-core nanocluster molecular compounds [7,8]. It is known that polymers are characterized by high mechanical stability, rich structural and functional variety, processability and relatively low cost what results in high potential for practical applications of polymeric-based films and composites. In present our work we were aimed to develop practically-effective synthetic and assembling approaches to fabrication of ultrathin polymeric and nanocomposite films and coatings with controlled composition and structural organization down to the nanoscale level of individual molecules. Here, we describe the formation of nanoscale-ordered polymeric quasi-crystalline monomolecular films formed by amphiphilic polyelectrolytes and the fabrication of ultimately thin monomolecular stable orga-

nized polymeric nanocomposite films containing ligand-stabilized metallic nanoclusters. The obtained nanostructures were characterized by scanning probe microscopy (STM and AFM) techniques.

2. Experimental

Stearic acid (SA) was obtained from Sigma and used as supplied. Ligand-stabilized nanocluster molecule $\text{Pt}_5(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_3]_4$ was synthesized in accordance with known procedures [9]. *N*-Alkylated derivatives of poly(4-vinylpyridine) (PVP) were exploited as amphiphilic polycations whose linear charge density as well as hydrophilic-hydrophobic balance can be easily controlled by varying the extent of *N*-alkylation and the nature of alkyl groups. Amphiphilic polycations poly(4-vinylpyridine) with 16 and 20% of cetylpyridinium groups (PVP-16 and PVP-20, correspondingly) were synthesized via the known procedures [10]. PVP with polymerization degree 1100 was prepared and then quaternized with cetyl bromide as described in [11]. Polymer composition was determined by IR spectroscopy measurements. Positive charges in PVP-16 molecules in aqueous phase at neutral pH values are due to the quaternary ammonium groups, what in combination with hydrophobic alkyl groups makes that polymer molecule water-insoluble and amphiphilic. Milli-Q water purification system was used to produce water with an average resistivity of 18 M Ω cm for all experiments. Surface pressure–monolayer area (π –*A*) isotherm measurements and monolayer deposition onto the solid substrates were carried out on a fully automatic conventional Teflon trough at 21 °C as described elsewhere [12]. Langmuir monolayers were formed by spreading a chloroform solution of amphiphile compound on the surface of the aqueous phase. Monolayers were transferred from the surface of aqueous subphase to the solid substrates at a constant surface pressure ($\pi \sim 20$ mN/m), temperature (21 °C) and dipping speed (5 mm/min) using conventional vertical or horizontal substrate dipping method to form mono- and multilayer LB films. Mica substrates were used for AFM investigations and were freshly cleaved immediately before monolayer deposition. Highly oriented pyrolytic graphite (HOPG) was used as a substrate for deposition of monolayer films for investigations by

STM. STM microtopographic images were obtained using modified Nanoscop STM device (Digital Instruments) at an ambient temperature (21 °C). The images were stable and reproducible. Single nanocluster molecules were studied spectroscopically by recording tunneling current–bias voltage (I – V) curves in a double barrier tunnel junction geometry at 21 °C, where the molecule was coupled via two tunnel junctions to the two macroscopic electrodes (HOPG substrate and the tip of STM device).

AFM measurements were performed with the use of Solver P47-SPM-MDT scanning probe microscope (NT MDT Ltd., Moscow, Russia) in a tapping mode. Silicon cantilevers NSC11 (Estonia, Mikromasch) with tip-radii of about 10 nm were used. Images were measured in air at ambient temperature (21 °C) and were stable and reproducible.

3. Results and discussion

Fig. 1 shows characteristic STM top view topographic image of closely-packed 2-D quasi-hexagonal arrangement of $\text{Pt}_5(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_3]_4$ nanoclusters in the deposited nanocluster monolayer. Corresponding characteristic I – V curve measured in the double tunnel junction configuration STM tip–nanocluster molecule–conducting HOPG substrate is presented on Fig. 1b) (curve 1). The suppressed conductivity at low bias voltage amplitudes, asymmetry and characteristic steps-like features in the curve 1 indicate to the complex character of electron tunneling through the nanocluster molecule with probable manifestation of discrete electron tunneling effects. For comparison, curve 2 on Fig. 1b demonstrates typical I – V curve recorded at the flat substrate surface areas without nanoclusters which is different substantially from those obtained above the nanoclusters.

Complex electron tunneling effects similar to that in ligand-stabilized nanoclusters were observed in STM spectroscopic studies of isolated fullerene molecules [6] and cytochrome c molecules [13] giving evidence for the similar sequential discrete electron tunneling mechanisms in such immobilized metalloprotein and nanocluster structures which can be of interest for development of bioelectronic and nano-bio-hybrid electronic systems with biological redox components integrated into synthetic structures or vice versa.

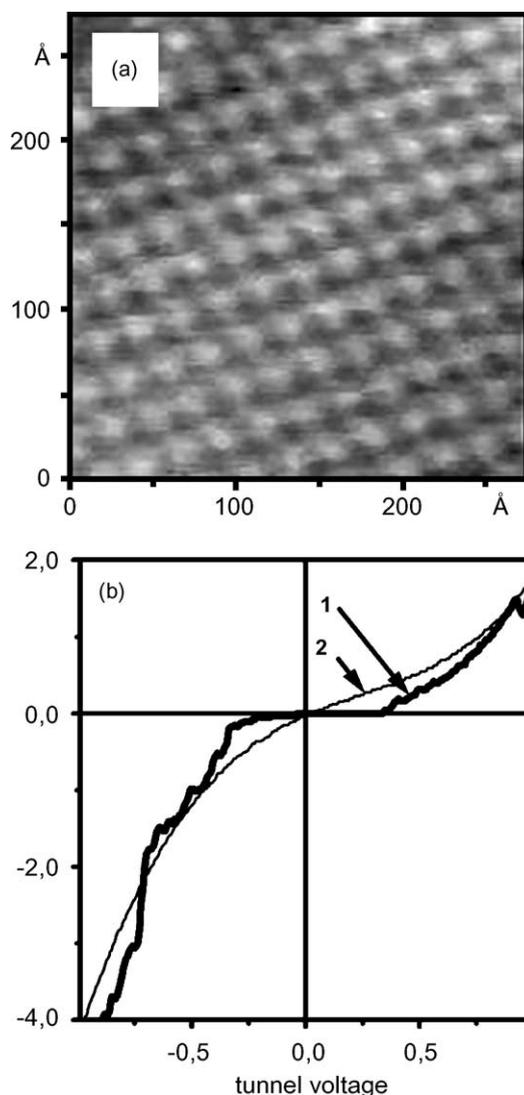


Fig. 1. Image (a) STM top view topographic image of closely-packed monolayer of $\text{Pt}_5(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_3]_4$ nanocluster molecules deposited by horizontal substrate lifting method onto the surface of HOPG substrate (black-to-white vertical color scale is 0–1 nm). (b) STM tunnel current–bias voltage (I – V) dependence in the double tunnel junction configuration: STM tip– $\text{Pt}_5(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_3]_4$ nanocluster–conducting HOPG substrate measured at the point above the nanocluster. Temperature: 21 °C.

To fabricate ordered stable planar arrays of chemically produced quantum dots (clusters and nanoparticles) in organized monomolecular polymeric matrix we have proposed an approach which is schematically illustrated on Fig. 2. In this approach, the polymeric

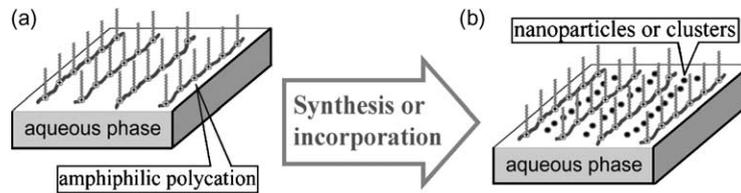


Fig. 2. Schematic diagram illustrating the approach to formation of organized planar polymeric nanocomposite film. Amphiphilic polyelectrolyte smectic liquid crystal-like monomolecular structure formed at the gas–liquid interface due to the electrostatic interactions (a) and corresponding nanoscale-ordered nanocomposite planar polymeric monolayer structure with incorporated functional nanoscopic components—clusters or nanoparticles (b).

smectic liquid crystal-like planar monolayer structure of amphiphilic polycation was formed on the surface of a liquid phase due to the intramolecular and intermolecular electrostatic interactions and served as organized stable macromolecular media for incorporation of nanosize functional and structural components. Electrostatic interactions are substantial factor for structure formation processes in that system and can be controlled easily by variations in a number of cationic groups in polymer molecules or by ionic composition of the aqueous subphase. Then, polymeric nanoscale-ordered planar nanocomposite films with 1-D and 2-D arrays of ligand-stabilized nanoclusters, metallic, oxidic or semiconducting nanoparticles can be formed via the incorporation of previously prepared inorganic components in the polymeric monolayer or via the interfacial synthesis [14] directly in the monolayer. Further deposition of such monolayer to the solid substrates allows to fabricate organized ultrathin mono- and multilayer composite polymeric quasi-crystalline films with functional inorganic nanostructures. It is possible to adsorb oppositely charged polyelectrolytes (or other compounds) from the subphase to the formed interfacial amphiphilic polyelectrolyte (or composite) monolayer what can improve stability of the film and broaden its functionality. Due to polar and charged groups in amphiphilic polyelectrolyte molecules, corresponding Langmuir monolayers should reveal good transferability to polar solid surfaces of different nature with strong binding efficiency. Multilayer planar polymeric structures with monolayer control of their composition also can be formed by this method what can be useful for fabrication of nanostructured films with advanced properties. Such approach is potentially compatible with a wide range of planar technologies

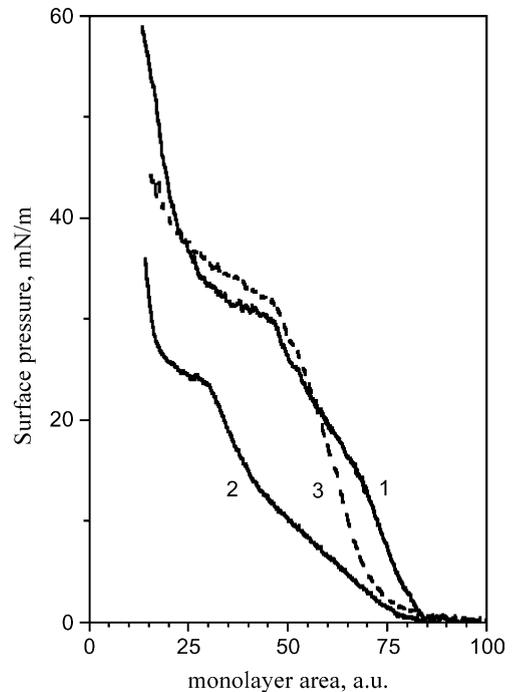


Fig. 3. Surface pressure–monolayer area isotherms. Curve 1: π -A isotherm of Langmuir monolayer formed by ligand-stabilized nanocluster molecule $\text{Pt}_5(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_3]_4$ on the water subphase, pH 6. Monolayer was formed by spreading of 192 μl of chloroform solution of nanoclusters (concentration: 10^{-4} M). Curve 2: π -A isotherm of Langmuir monolayer formed by amphiphilic polyelectrolyte PVP-20 on the water subphase, pH 6. Monolayer was formed by spreading of 192 μl of chloroform solution of PVP-20 (concentration: 3×10^{-4} M per monomer). Curve 3: π -A isotherm of the mixed Langmuir monolayer formed by molecules of nanocluster $\text{Pt}_5(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_3]_4$ and amphiphilic polyelectrolyte PVP-20 on the water subphase, pH 6. Monolayer was formed by spreading of 192 μl of mixed chloroform solution of $\text{Pt}_5(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_3]_4$ and PVP-20 (1:1 volume mixture of the initial cluster spreading solution (10^{-4} M $\text{Pt}_5(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_3]_4$) and amphiphilic polyelectrolyte spreading solution (3×10^{-4} M per monomer PVP-20)).

which are or will be used for fabrication of nanodevices.

Fig. 3 shows surface pressure–monolayer area isotherms measured with $\text{Pt}_5(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_3]_4$ monolayer (curve 1), amphiphilic polyelectrolyte PVP-20 monolayer (curve 2), and mixed Langmuir monolayer formed by molecules of nanocluster $\text{Pt}_5(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_3]_4$ and PVP-20 on the water subphase (1:1 volume mixture of the initial spreading solutions). The results of Fig. 3 indicate that in mixed Langmuir monolayer nanocluster molecules are localized predominantly two-dimensionally on the water surface.

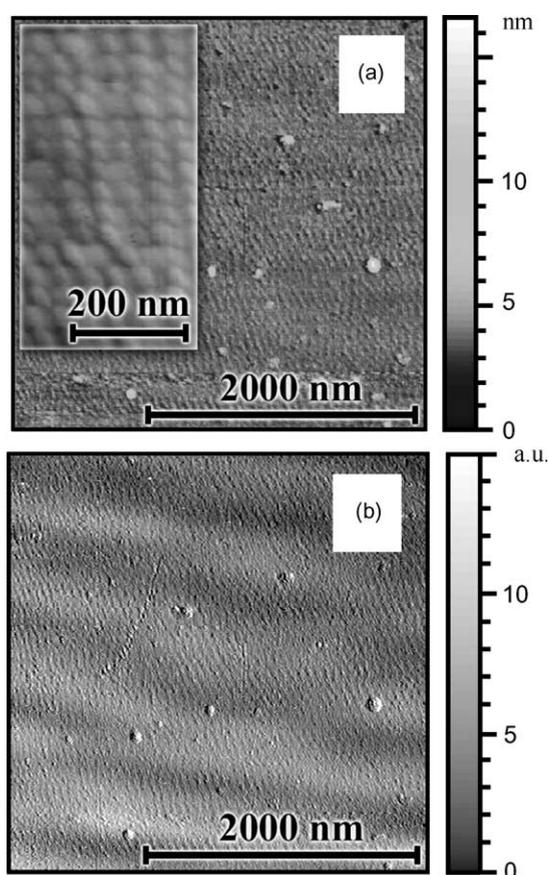


Fig. 4. AFM tapping mode images of two-layer LB film of PVP-16 deposited onto the mica substrate after 10 min incubation of the PVP-16 Langmuir monolayer at low surface pressure value ($\pi \cong 0$) on the water subphase (pH 6). (a) Top view topographic image (size: 2800 nm \times 2800 nm, black-to-white color height scale is 0–15 nm) The insert in the left upper part shows the magnified part of the image. (b) AFM phase contrast mode top view image corresponding to image (a).

Fig. 4 shows AFM tapping mode topographic image (image a) and corresponding phase contrast mode top view image (image b) of two-layer LB film of PVP-16 deposited onto the mica substrate after 10 min incubation of the PVP-16 Langmuir monolayer at low surface pressure value ($\pi \cong 0$) on the water subphase (pH 6). One can see that the film was macroscopically ordered with tightly packed and quasi-linear organized characteristic structural elements (~ 30 nm wide, 2 nm height) clearly seen from the insert in the left upper part of the image. Similar nanostructured films were obtained with PVP-20. Such amphiphilic polyelectrolyte monolayer structure can be a result of the surface micelle arrays formation which are known for LB films of diblock copolymers [15]. The tendency for linear parallel chain organization of surface micelles in PVP-16 LB films can be a result of electrostatics-driven smectic liquid crystal ordering of linear PVP-16 molecules on the aqueous surface under appropriate conditions. In the thermodynamically equilibrium state of the monolayer, the positively charged PVP-16 molecules have to be organized as planar quasi-parallel string-like structures (two-dimensional smectic

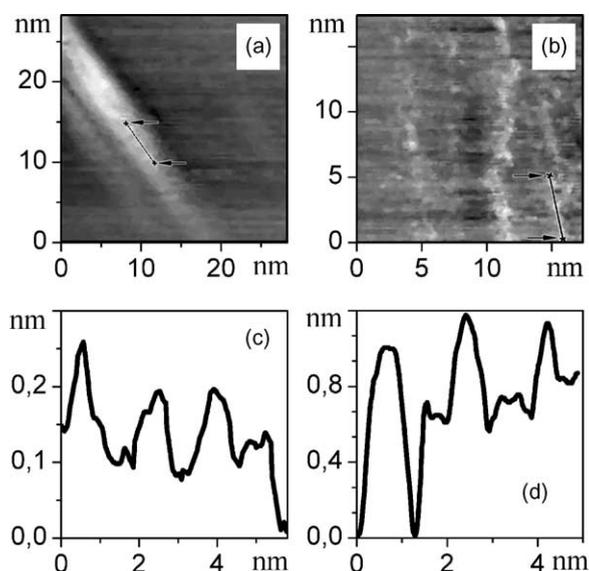


Fig. 5. Images (a) and (b): STM top view topographic images of composite PVP-16 monolayer with incorporated $\text{Pt}_5(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_3]_4$ nanocluster molecules. Monolayer was deposited by horizontal substrate lifting method onto the surface of HOPG substrate. Curves (c) and (d): characteristic cross-section profiles of the images (a) and (b), correspondingly. The positions of cross-sections are marked by the arrows.

liquid crystal) due to the electrostatic repulsive interaction between the positively-charged links and extended polycation molecules.

Fig. 5 shows STM top view topographic images of composite PVP-16 monolayer with incorporated $\text{Pt}_5(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_3]_4$ nanocluster molecules. Images (a) and (b) in this figure show STM top view topographic images of composite PVP-16 monolayer structures with incorporated $\text{Pt}_5(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_3]_4$ cluster molecules deposited on the HOPG substrate. The quasi 1-D chain structures of clusters are visible on those images. The characteristic cross-section profiles of the images (a) and (b) are presented on the pictures (c) and (d), correspondingly, and demonstrate the topographic features in the film with characteristic size ~ 1.2 nm close to the size of the cluster molecule [16].

4. Conclusions

Stable planar supramolecular nanostructures with organic ligand-stabilized metallic-core nanoclusters were fabricated using assembling nanofabrication methods based on the surface and interface interactions at the liquid–gas interface and monolayer approach. Polymeric smectic liquid quasi-crystal planar monomolecular structures were formed at the gas–liquid interface using amphiphilic polyelectrolyte, and corresponding nanoscale-ordered nanocomposite planar polymeric films with incorporated ligand-stabilized metal-core nanoclusters were fabricated successfully on a solid substrate surface. Discrete electron tunneling effects were observed in such structures at room temperature using STM which open perspectives for applications of those structures in research and development of nanoelectronic elements and devices based on the controlled SET effects.

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