

Formation and organization of planar polymeric and nanocomposite nanostructures on liquid and solid surfaces

G.B. Khomutov ^{a,*}, R.V. Gainutdinov ^b, S.P. Gubin ^c, V.V. Kislov ^d,
A.A. Rakhnyanskaya ^e, A.N. Sergeev-Cherenkov ^a, A.L. Tolstikhina ^b

^a Faculty of Physics, Moscow State University, Lenin Gory, 119992 Moscow, Russia

^b Institute of Crystallography RAS, 119899 Moscow, Russia

^c Institute of General and Inorganic Chemistry RAS, 119899 Moscow, Russia

^d Institute of Radioengineering and Electronics RAS, 101999 Moscow, Russia

^e Department of Chemistry, Moscow State University, 119992 Moscow, Russia

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Abstract

We describe a new approach to fabrication of organized planar polymeric and composite nanostructures based on synthetic reactions in organized polymeric Langmuir monolayer at the gas–liquid interface. Novel polymeric quasi-crystalline planar monomolecular structures were formed at the gas–aqueous phase interface using new water–insoluble amphiphilic polyelectrolyte molecules. Corresponding ultrathin polymeric nanoscale-ordered films and stable planar polymeric nanocomposite structures with organized inorganic nanoparticles (palladium, gold and iron oxide) grown in the polymeric monolayer were formed successfully on the solid substrate surfaces. The obtained nanostructures were characterized by atomic force microscopy and transmission electron microscopy techniques.

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1. Introduction

In recent years studies of nanoparticles and organized low-dimensional nanostructures have become a major basic and applied research area due to their novel and unique properties promising for a wide range of applications including new types of higher activity and selectivity catalysts,

chemical and biological sensors, drug delivers, high-density information storage media, electronic, magneto and optoelectronics devices, etc. [1,2]. Further advancements on the way to fabrication of new nanostructured materials and nano-devices are connected with development of new effective methods for rational assembling and integration of nanoscale functional and structural building blocks (clusters, particles, molecules, wires of organic and inorganic nature) into organized one-, two- and three-dimensional architectures, along with fabrication of nanostructures with controlled composition, organization and

* Corresponding author. Tel.: +7-95-939-3007/3025; fax: +7-95-939-1195.

E-mail address: gbk@phys.msu.ru (G.B. Khomutov).

properties. High mechanical stability, rich structural and functional variety, processability and low cost of polymers result in high potential for practical applications of polymeric-based films and composites. Cost-effective synthesis and assembling of polymeric and nanocomposite materials and films with controlled composition and structural organization down to the nanoscale level of monomolecular films and individual molecules is a challenging task now with potential for new generation of advanced functional materials and coatings.

Recently, we have fabricated novel ordered quasi-crystalline planar polymeric monomolecular films on solid substrates using amphiphilic polyelectrolytes and Langmuir–Blodgett (LB) technique [3]. We also have introduced an approach to formation of ultrathin nanocomposite polymeric films in which nanosize functional components can be incorporated or grown in the organized monomolecular polymeric matrix [4]. That approach was realized with the use of ligand-stabilized metallic nanocluster $\text{Pt}_5(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_3]_4$ incorporated in monolayer of amphiphilic polycation [4]. In present contribution we demonstrate fabrication of new organized planar polymeric and nanocomposite nanostructures via the new approach based on the method of two-dimensional synthesis of inorganic nanoparticles in a monolayer at the gas–liquid interface [5] with amphiphilic polyelectrolytes used as surfactants to form organized Langmuir monolayer matrix and to stabilize grown nanoparticles. We were interested in effects of amphiphilic polymer molecules on the morphology of generated nanoparticles and on their organization in the plain of monolayer. The obtained nanostructures were characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM) techniques.

2. Experimental details

Palladium acetate was obtained from Aldrich. Iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) was obtained from Alfa Inorganic. $\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3)\text{Cl}$ was synthesized in accordance with known procedures [6]. Water–

insoluble amphiphilic polycation poly-4-vinylpyridine (PVP) with 16% and 20% of cationic cetylpyridinium groups (PVP-16 and PVP-20, correspondingly) was synthesized via the known procedures [7]. To obtain amphiphilic polycation PVP fraction with degree of polymerization 1100 was prepared and then quaternized with cetyl bromide as described in [8]. Linear charge density as well as hydrophilic–hydrophobic balance of quaternized PVP derivatives can be easily controlled by varying the extent of *N*-alkylation and the nature of alkyl groups. 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 isotherm measurements and monolayer deposition onto the solid substrates were carried out with a fully automatic conventional Teflon trough at 21 °C as described elsewhere [9]. Langmuir monolayers were formed by spreading a chloroform solution of amphiphilic polyelectrolyte and metal–organic guest compound (polyelectrolyte concentration 10^{-4} M for monomer) on the surface of the aqueous phase. Monolayers were transferred 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. Samples for TEM measurements were prepared by nanoparticulate monolayer deposition from the aqueous subphase surface onto the Formvar film supported by the copper grid.

Iron-containing magnetic nanoparticles were fabricated photochemically as described in [5] by the UV decomposition of iron pentacarbonyl at the ambient temperature (21 °C) in a mixed Langmuir monolayer on the surface of purified water (pH = 5.6). To synthesize palladium or gold nanoparticles the mixed spreading solution of water–insoluble palladium acetate $\text{Pd}_3(\text{CH}_3\text{COO})_6$ or $\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3)\text{Cl}$ with amphiphilic polycation in chloroform was prepared (precursor/surfactant ratio was 3:1 and 1:3). Spreading solution was then deposited onto the aqueous phase containing sodium borohydride as reducing agent (NaBH_4

concentration was 5×10^{-3} M). Nanoparticles were synthesized in a mixed precursor and surfactant Langmuir monolayer formed after solvent evaporation on the surface of borohydride solution (monolayer incubation time 60 min). Nanoparticles were formed in a two-dimensional gas phase of a monolayer (at very low or no surface pressure) where in-plane diffusion of the monolayer components was allowed. The compression of a monolayer with growing nanoparticles to the monolayer condensed state and following deposition onto the solid substrate stopped the diffusion-mediated processes in the monolayer and fix effectively the synthesized nanoparticles.

AFM measurements were performed with the use of Solver P47-SPM-MDT scanning probe microscope (NT MDT Ltd., Moscow, Russia) in a tapping mode. Images were measured in air at ambient temperature (21 °C) and were stable and reproducible.

TEM images of nanoparticles synthesized in Langmuir monolayer were obtained with the use of Jeol JEM-100B microscope.

3. Results and discussion

We have found that the structure of deposited monolayers of amphiphilic polycation PVP-16 and PVP-20 were characterized by ordered planar morphology giving evidence for quasi-parallel organization of polycation molecules in plane of the film. Fig. 1 shows the characteristic AFM tapping mode topographic image (image (a)) of 2-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 characteristic structural elements (~ 33 nm in vertical direction, ~ 45 nm in horizontal direction, ~ 2 nm in height as follows from the fast Fourier transform spectrum analysis of the image (a) and cross-section profile on Fig. 1c and d, correspondingly). 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

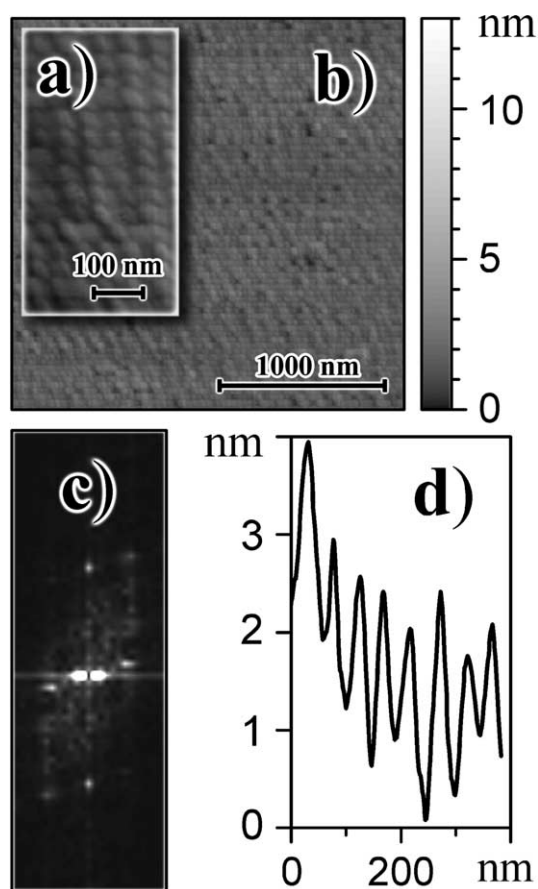


Fig. 1. AFM tapping mode images of 2-layer LB film of PVP-16 deposited onto the mica substrate after 10 min incubation of the PVP-16 Langmuir monolayer at low surface pressure value ($\pi \cong 0$) on the water subphase (pH = 6). Images (a) and (b): top view topographic images (black-to-white color height scale is 0–13 nm). Image (c): Fourier transform spectrum of the image (a). Curve (d): characteristic cross-section profile of the image (a) parallel to the X -axis.

known for LB films of diblock copolymers [10]. The tendency for linear quasi-parallel chain organization of surface micelles in PVP-16 LB films can be a result of smectic liquid crystal ordering of linear PVP-16 molecules on the aqueous subphase surface due to the effective electrostatic repulsive interaction between the links in a molecule and between extended polycation molecules in the monolayer. Also, effects of parallel organization of one-dimensional structures (wires) in Langmuir

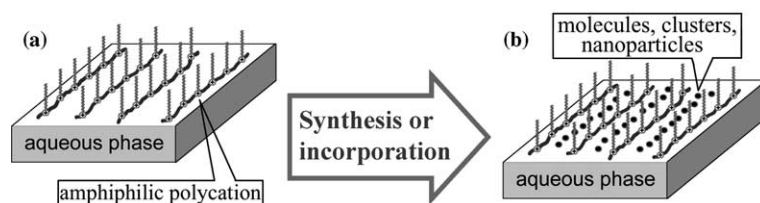


Fig. 2. Schematic diagram of the polymeric smectic liquid crystal planar monomolecular layer formed at the gas–liquid interface using amphiphilic polycation molecules (a), and corresponding nanoscale-ordered composite planar polymeric structure with incorporated functional nanoscopic components—nanoclusters or nanoparticles (b).

monolayer under compression can be involved [11].

Fig. 2 illustrates schematically the idea of our approach to create nanoscale-ordered composite planar polymeric nanostructures with incorporated or grown structural or functional nanoscopic components. First, organized polymeric monolayer structure of amphiphilic polycation molecules is formed on the surface of a liquid phase and serves as an organizing stable monomolecular media. Then, polymeric nanoscale-ordered nanocomposite film can be formed via the incorporation of previously prepared inorganic or organic functional components in the polymeric monolayer or via the interfacial synthesis of nanoparticles directly in the monolayer [5]. Further deposition of such monolayer onto the solid substrates allows fabrication of organized ultrathin mono and multilayer composite polymeric films and coatings. Such polymeric films with thickness down to a monolayer can be of use for nano-

technological applications because different functional nanosize elements (as guest molecules; ligand-stabilized nanoclusters and nanocrystals, metallic, oxide or semiconducting nanoparticles, nanorods and nanowires, etc.) can be incorporated in such films to form ultimately thin highly ordered stable planar composite polymeric nanostructures. It is possible to adsorb oppositely charged polyelectrolytes (or other compounds or colloids) from the subphase to the formed interfacial amphiphilic polyelectrolyte (or composite) monolayer what can improve stability of the film and broaden its functionality.

Fig. 3 shows palladium nanoparticles generated in mixed Langmuir monolayers with different initial content of precursor and polymeric surfactant. One can see that excess of amphiphilic polycation in the monolayer results in generation of small Pd nanoparticles (with main diameter about 3 nm) organized in quasi-linear arrays. Those results illustrate the important role of monolayer

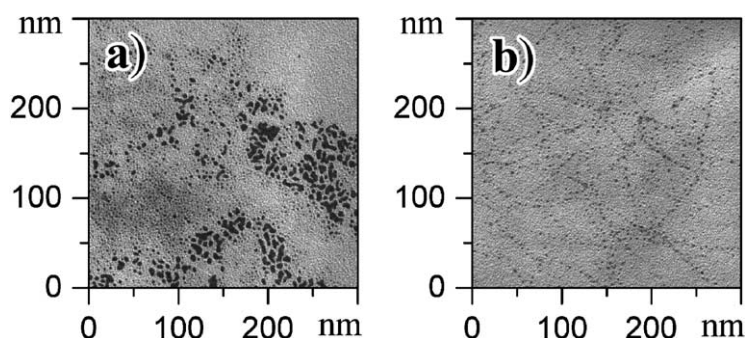


Fig. 3. Transmission electron micrographs showing Pd nanoparticles grown in Langmuir monolayer at the air/aqueous NaBH_4 solution (5×10^{-3} M) interface. Image (a): Pd nanoparticles synthesized with PdAc_2 /PVP-20 ratio 3:1, incubation time 60 min. Image (b): Pd nanoparticles synthesized with PdAc_2 /PVP-20 ratio 1:3, incubation time 60 min.

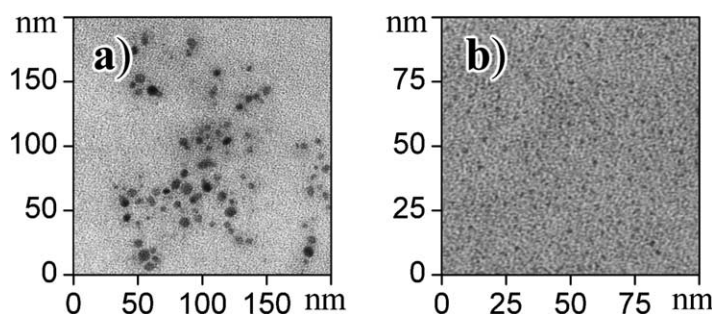


Fig. 4. Transmission electron micrograph showing Au nanoparticles. Au nanoparticles were synthesized in a mixed Langmuir monolayer (image (a): initial $\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3)\text{Cl}/\text{PVP-20}$ ratio 5:1; image (b): initial $\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3)\text{Cl}/\text{PVP-20}$ ratio 1:5) onto the aqueous sodium borohydride solution (5×10^{-3} M NaBH_4) at $\pi = 0$ and deposited onto the copper grid with Formvar coating.

composition and precursor/polymeric surfactant stoichiometry in structural organization of the mixed and nanoparticulate monolayer.

The results of similar experiments on the generation of gold nanoparticles are presented on Fig. 4. It follows from Fig. 4a that amphiphilic polycation molecules in relatively small surface concentration promote formation of large Au nanoparticles and their aggregates, as in the case with Pd nanoparticles (Fig. 3a). Under the increased concentration of polycation ultrasmall gold nanoparticles can be generated randomly localized in plain of the monolayer (Fig. 4b). Ultrasmall noble metal nanoparticles of similar size and nature demonstrate single-electron tunneling effects what makes such nanoparticles perspectives for nanoelectronic applications [12]. We also have synthesized iron oxide nanoparticles in the monolayer formed by PVP-20 and have observed formation of organized chain-like arrays of nanoparticles. Ligand exchange and substitution effects can be involved in the structure formation processes in the metal–organic precursor/PVP-20 monolayer. It is known that interaction of pyridine with tri-nuclear palladium acetate complex $\text{Pd}_3(\text{CH}_3\text{COO})_6$ results in decomposition of the complex cycle with formation of mono-nucleus complex composed by Pd, acetate and pyridine ($\text{Pd}(\text{Ac})_2[\text{Py}]_2$). Similar effects can take place when iron pentacarbonyl is present in the PVP-20 monolayer. The linear organization of Pd and iron atoms in such polymeric precursor complexes in the monolayer can be a reason for linear organization of corresponding interfacially grown Pd

and iron oxide nanoparticles. That effect is sensitive to the initial precursor/PVP-20 ratio which determines the possibilities for ligand substitution in the mixed monolayer. Linear organization of DNA molecules in DNA-templated synthesis of inorganic nanoparticles and nanowires also resulted in formation of one-dimensional inorganic nanostructures (wires and chains of metallic, semiconductor and iron oxide nanoparticles) [4,13–18]. The absence of pronounced chains in the case of monolayer with gold nanoparticles can be due to the higher stability of the used precursor $\text{Au}/\text{phenyl phosphine}$ complexes. The observed effects of amphiphilic polycation on the morphology of two-dimensionally grown nanoparticles can be also a result of specific complexing and stabilizing interactions of nucleus, growing nanoparticles and polymeric groups, along with of nonspecific electrostatic interactions of charged nanoparticles and amphiphilic polycation molecules.

4. Conclusions

New organized polymeric quasi-crystalline planar monomolecular structures were obtained using amphiphilic polyelectrolytes and monolayer technique. The formation of inorganic nanoparticles in Langmuir monolayer with amphiphilic polycation was studied. The effects of monomolecular polymeric matrix on the morphology and organization of two-dimensionally grown nanoparticles were observed and can be a result of specific ligand

substitution and nonspecific electrostatic interactions in the mixed monolayer with growing nanoparticles. The method developed can be perspective for investigation of structural organization and transformation mechanisms in poly-electrolyte complexes at the gas–liquid interface and for design and fabrication of new controlled-morphology ultimately thin highly ordered planar polymeric and nanoparticulate composite nanostructured materials, films and coatings with thickness down to a monolayer for applications in nanoelectronics and nanotechnology.

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