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The design, fabrication and characterization of controlled-morphology nanomaterials and functional planar molecular nanocluster-based nanostructures

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Abstract

New nanofabrication methods based on the monolayer techniques, biomimetic principles, interface reactions and interactions have been developed. The formation and deposition of the mixed Langmuir monolayers composed of inert amphiphile matrix and guest ligand-stabilized metal-core nanocluster molecules allowed to obtain ordered stable reproducible planar monomolecular nanocluster-based nanostructures on solid substrates. The decomposition of similar metal–organic precursor compounds in the mixed Langmuir monolayers at the gas–liquid interface resulted in the initiation of two-dimensional growth of inorganic nanoparticles in the plain of monolayer. Gold and iron-containing nanoparticles were synthesized and characterized by scanning probe microscopy and transmission electron microscopy techniques. Effect of external applied field on the shape of two-dimensionally grown magnetic nanoparticles was observed. Effects related to discrete electron tunneling were observed in the monolayer structures of nanocluster molecules and gold nanoparticles at room temperature using STM.

Keywords: Atomic force microscopy; Scanning tunneling microscopy; Scanning transmission electron microscopy (STEM); Growth; Gold; Iron oxide; Liquid–gas interfaces; Clusters

1. Introduction

Development of novel nanofabrication methods with effective control of structure, morphology and patterning at the nanometer-scale level is currently of principal importance for nanoscience and nanotechnology, advanced materials research, as well as for design of new functional nanostructures with pre-determined and unique properties. New inter-disciplinary ideas and methods can be effective and it is widely accepted that chemical and physical–chemical techniques, self-assembling and

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self-organization processes are perspective to fabricate functional nanomaterials and nanostructures [1]. Clusters and nanoparticles are currently considered as functional building blocks in nanoelectronics and nanotechnology [2–4], and the development and introduction of new methods to control effectively its structure, composition and purposeful nanoscale organization are necessary.

Earlier in our group we have introduced a bioinspired approach based on the formation of mixed biomimetic Langmuir–Blodgett (LB) films consisting of inert amphiphile molecular matrix and guest ligand-stabilized metal-core nanocluster molecular compounds to create reproducible stable planar nanostructured films in which discrete electron transport effects were observed at room temperature using STM [5,6]. The double tunnel junction (DTJ) structure "graphite substrate-nanocluster-STM tip" was studied [7] and corresponding single electron tunneling (SET)-transistor based on a single nanocluster molecule was demonstrated at room temperature for the first time [8].

A novel method for the synthesis of nanoparticles also based on the Langmuir monolayer technique has been introduced recently [9]. In that method nanoparticles were fabricated via the decomposition of an insoluble metal–organic precursor compound in a monolayer at the gas/liquid interface. The ultimately thin and anisotropic dynamic monomolecular reaction system was realized by that method with the two-dimensional growth of nanoparticles and nanostructures in the plain of a monolayer on the liquid surface. In this work we present our recent results on the fabrication and characterization of mixed monolayers with ligand-stabilized metal-core nanocluster molecules, gold and iron-containing nanoparticles. Deposited monolayers were characterized by scanning probe microscopy and transmission electron microscopy techniques.

2. Experimental

Stearic acid (SA) and arachidic acid (AA) were obtained from Aldrich/Sigma. Iron pentacarbonyl $Fe(CO)_5$ was obtained from Alfa Inorganic. $Pt_5(CO)_6[P(C_6H_5)_3]_4$ and $Au(P(C_6H_5)_3)Cl$ were synthesized by Prof. S.P. Gubin in accordance with known procedures [10]. Milli-Q water purification system was used to produce water with an average resistivity of 18 MΩ 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 surfactant and metal–organic guest compound (surfactant concentration 10^{-4} M) 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 Formwar film supported by the copper grid. Highly oriented pyrolytic graphite (HOPG) was used as a deposition substrate for investigations of monolayer films by STM.

Iron-containing magnetic nanoparticles were fabricated photochemically as described in [11] 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 gold nanoparticles the mixed spreading solution of $Au(P(C_6H_5)_3)Cl$ with AA in chloroform was prepared (precursor/surfactant ratio was 1:1). 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 30 min). Nanoparticles were formed in a 2-D 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.

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 and nanoparticles were studied spectroscopically by recording tunneling current–bias voltage (*I–V*) curves in a double barrier tunnel junction geometry at 21 °C, where the nanocluster molecule or nanoparticle was coupled via two tunnel junctions to the two macroscopic electrodes (HOPG substrate and 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. Images were measured in air at ambient temperature (21 °C) and were stable and reproducible.

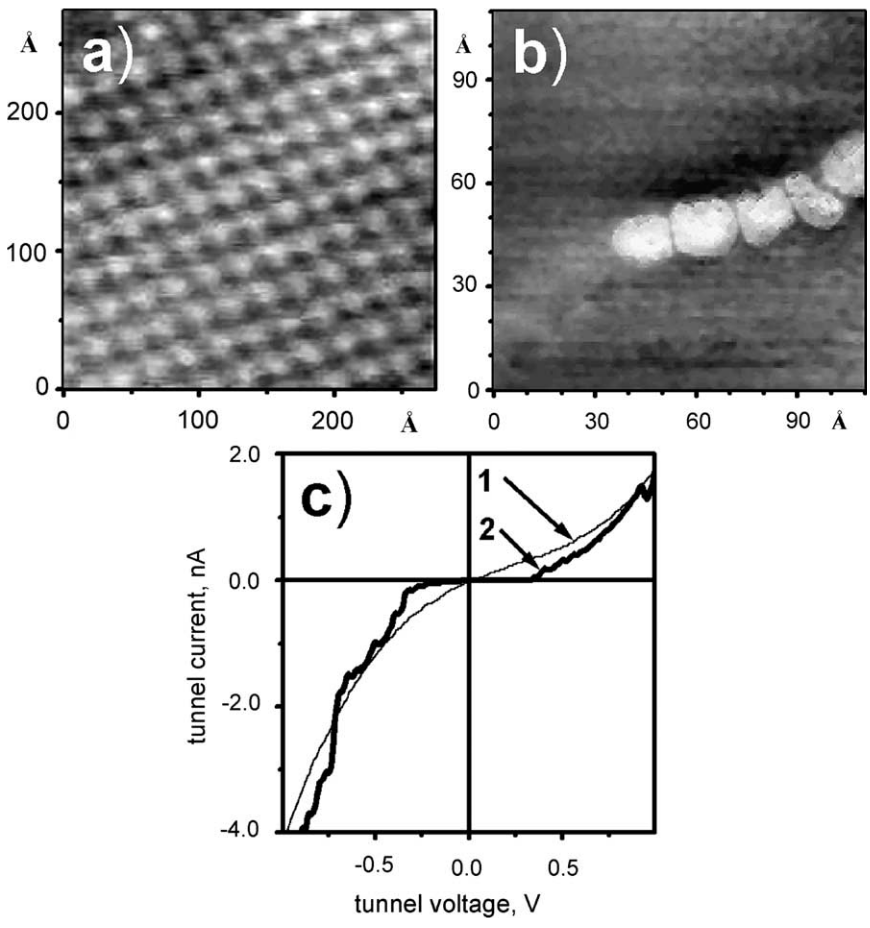

Fig. 1. STM top view topographic image of $Pt_5(CO)_6[P(C_6H_5)_3]_4$ nanocluster molecule monolayers deposited by horizontal substrate lifting method onto the surface of HOPG substrate (black-to-white vertical color scale is 0–1 nm). (a): 2-D closely packed array; (b): chain of clusters formed in a mixed monolayer composed by nanocluster and stearic acid molecules with stoichiometric ratio 1:20. (c): Curve 1: STM tunnel current–bias voltage (*I–V*) dependence in the double tunnel junction configuration STM tip—$Pt_5(CO)_6[P(C_6H_5)_3]_4$ nanocluster—conducting HOPG substrate measured at the point above the nanocluster. Curve 2: typical *I–V* curve recorded at the flat substrate surface areas without nanoclusters. Temperature 21 °C.

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

3. Results and discussion

Fig. 1 shows characteristic structures observed in the formed nanocluster monolayers using STM. Fig. 1(a) shows the STM top view topographic image of $Pt_5(CO)_6[P(C_6H_5)_3]_4$ nanocluster monolayer deposited onto the surface of HOPG substrate. One can see the ordered 2-D quasi-hexagonal arrangement of nanoclusters in the monolayer. Such chemically synthesized metal–organic nanocluster molecules are characterized by the uniform size, structure and composition, and, as a result, by absolutely reproducible properties of individual clusters what is of principal importance for creation of quantum nanoelectronic devices and makes such nanoclusters perspective building blocks for nanoelectronics and nanotechnology [7]. Stabilizing ligand shell of the clusters prevents coalescence of clusters and allows to regulate with Angstrom accuracy the inter-cluster distance in the ordered array of nanoclusters

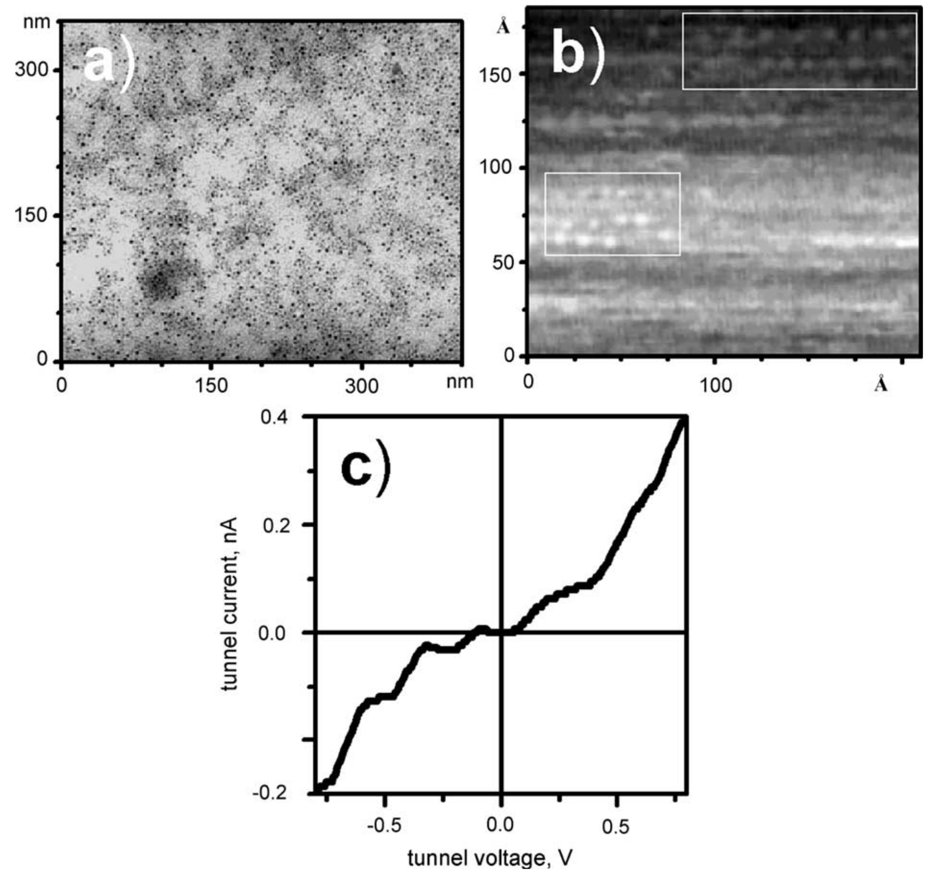

Fig. 2. Image (a): Transmission electron micrograph showing Au nanoparticles. Au nanoparticles were synthesized in a mixed Langmuir monolayer (initial $Au(P(C_6H_5)_3)Cl$/AA ratio 1:1) onto the aqueous sodium borohydride solution (5×10^{-3} M $NaBH_4$) at $\pi = 0$ and deposited onto the copper grid with Formwar coating. Image (b): STM top view topographic image of Au nanoparticles grown in Langmuir monolayer and deposited by horizontal substrate lifting method onto the surface of HOPG substrate (black-to-white vertical color scale is 1 nm). Two areas with clearly seen arrays of nanoparticles are marked by the white frames. Curve (c): STM tunneling current–bias voltage (I–V) dependence in the double tunnel junction configuration STM tip—gold nanoparticle—conducting HOPG substrate. Temperature 21 °C.

presented in Fig. 1(a). Image (b) in this figure represents the chain array of the clusters, formed in a mixed monolayer composed by nanocluster and SA molecules. Single nanocluster molecules were also observed. Such clusters are amphiphilic and ordered multilayer nanocluster structures on solid substrates can be formed using LB technique [12]. Corresponding characteristic *I–V* curve measured in the double tunnel junction configuration STM tip—$Pt_5(CO)_6[P(C_6H_5)_3]_4$ nanocluster molecule—conducting HOPG substrate is presented in Fig. 1(c) (curve 1). For comparison, curve 2 in that figure shows typical *I–V* curve recorded at the flat substrate surface areas without nanoclusters. The suppressed conductivity at low bias voltage amplitudes 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. *I–V* characteristics measured above the nanocluster molecules were substantially different from those obtained above the flat substrate areas without nanoclusters (Curve 2 in Fig. 1(c)) and exhibited rich structures resulting from a number of factors as interplay between Coulomb charging effects, discreteness of an electronic spectrum of the nanocluster molecule and strong electronic-vibrational coupling in the molecular system. Also micromechanical vibration effects were assumed to play a role in the electron transport in such nanocluster supramolecular systems [13].

The experiments with mixed monolayers of metal–organic molecules and surfactants resulted in the development of a novel approach to the synthesis of nanoparticles and nanostructures—two-dimensional synthesis at the gas–liquid interface [9,11]. Gold nanoparticles synthesized in the mixed monolayer with AA on the surface of sodium borohydride solution are presented in Fig. 2. Transmission electron micrographs (Fig. 2(a)) and STM images (Fig. 2(b)) are in good correspondence. Two areas with clearly seen arrays of nanoparticles in Fig. 2(b) are marked by the white frames. The selected area electron diffraction analyses of nanoparticles synthesized by that method indicated to the polycrystalline gold present in the sample. The main diameter of the synthesized Au

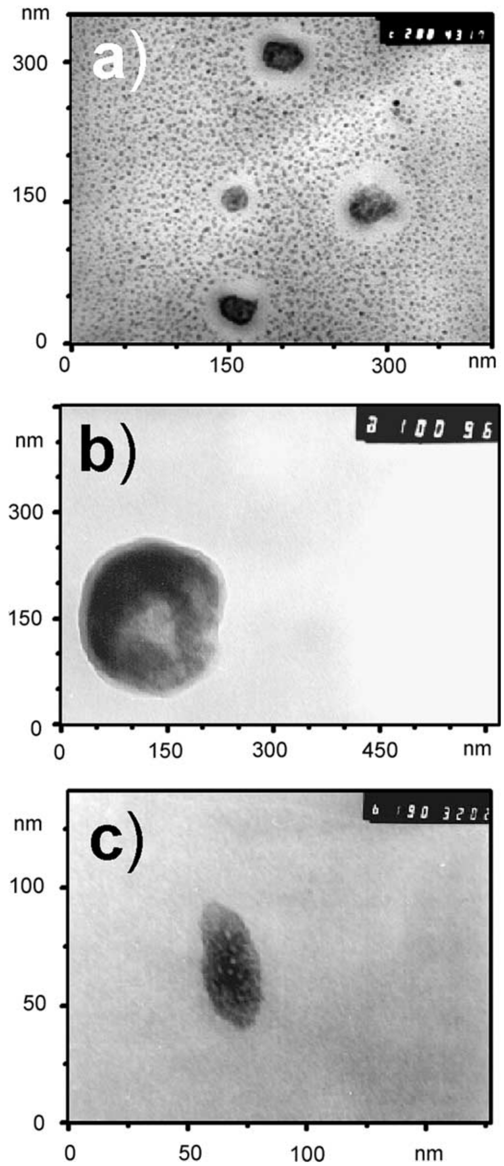

Fig. 3. Transmission electron micrographs showing iron-containing nanoparticles grown in uncompressed Langmuir monolayer and deposited onto the copper grid with Formwar coating at $\pi = 25$ mN/m. Conditions for nanoparticle synthesis for the Image (a): initial $Fe(CO)_5$/SA ratio 10:1, UV exposure time 6 s, $T = 21$ °C, subphase pH = 5.6. Conditions for nanoparticle synthesis for the Image (b) were the same as for Image (a) but with UV exposure time 4 min. Nanoparticles in Image (c) were synthesized at the same conditions as in Image (b) but in addition external magnetic field ($H = 2 \times 10^3$ Oe) parallel to the plane of nanoparticulate monolayer was applied during the synthesis of nanoparticles.

nanoparticles was about 1.5 nm what allowed the observation of the SET effects with those nanoparticles at room temperature using STM. The characteristic steps-like features are clearly visible in the corresponding *I–V* curve (Fig. 2(c)). Similar effects were observed at room temperature with nano-sized gold [2,3,14] and Co [15] nanoparticles. Such effect makes the monolayer planar arrays of interfacially grown Au nanoparticles perspective for potential applications in SET devices.

Figs. 3(a) and 4(a) show the initial stages of formation of iron-containing nanostructures photochemically generated in Langmuir monolayer under short UV illumination regime. It is clearly seen from Fig. 3(a) that every such nanostructure is surrounded by an area with exhausted small nanoparticles and nucleus. The characteristic plate-like nanoparticle formed under relatively long UV irradiation time (4 min) is shown in Fig. 3(b), and AFM image of corresponding nanoparticulate monolayer is present in Fig. 4(a). One can see from Fig. 4(a) that the nanoparticles have substantially flatten shape—about 100 nm in diameter and only ∼2 nm in the height. Self-organization effect and formation of quasi-1-D chains of nanoparticles via dark incubation after the

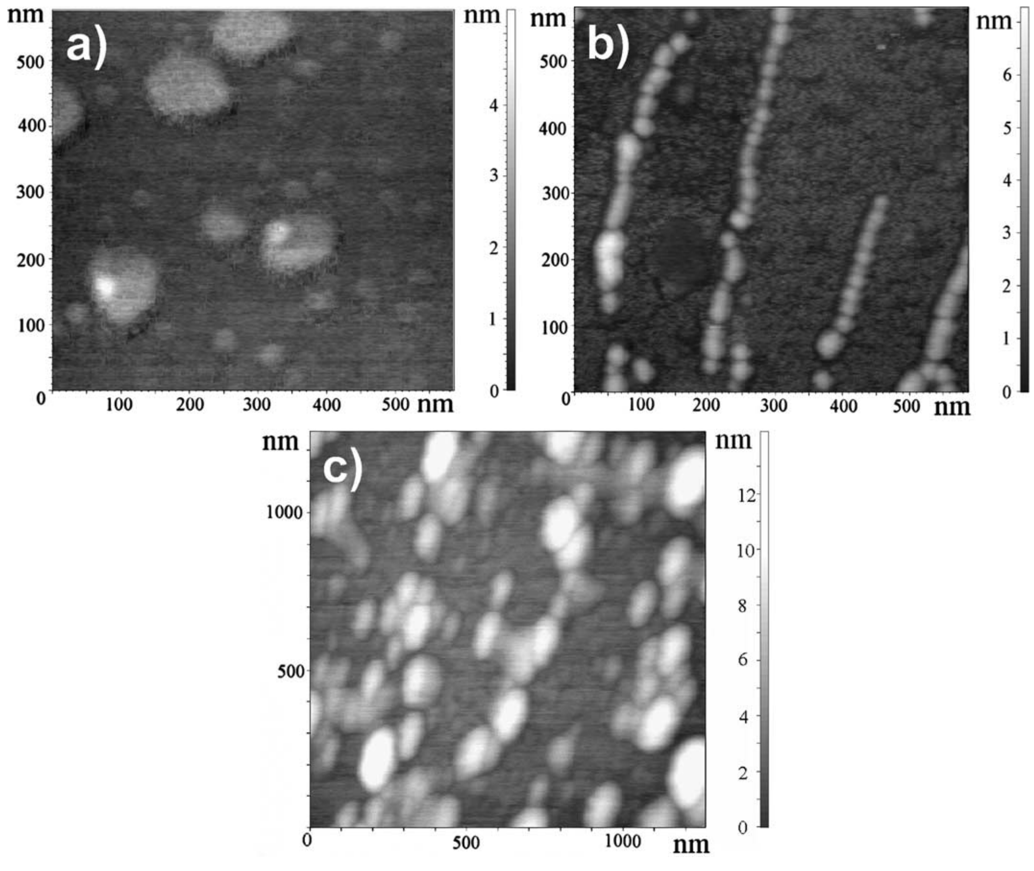

Fig. 4. AFM tapping mode topographic images of iron-containing nanoparticles synthesized in uncompressed Langmuir monolayer (at $\pi = 0$) and deposited onto the mica substrate at $\pi = 25$ mN/m using vertical substrate lifting method. Image (a): initial $Fe(CO)_5$/SA ratio was 10:1, UV exposure time 4 min, $T = 21$ °C, subphase pH = 5.6. Image (b): dark incubation of the nanoparticulate monolayer for 4 min after the UV illumination for 6 s. Image (c): nanoparticles were synthesized in Langmuir monolayer under applied external magnetic field ($H = 2 \times 10^3$ Oe) parallel to the plane of monolayer; other conditions for nanoparticles synthesis were the same as in the Image (a).

generation of nanoparticles under short UV illumination conditions is illustrated by Fig. 4(b). Formation of chain aggregates is characteristic for the systems with colloid magnetic particles [16]. Chains of self-organized magnetite nanoparticles are present also in magnetotactic bacteria and play important physiological role in their space orientation [17]. Figs. 3(c) and 4(c) demonstrate the effect of external magnetic field applied during the nanoparticles synthesis on the shape of resulted nanoparticles. The shape of substantial part of nanoparticles was changed from circular plate-like and ring-like to the field-aligned ellipsoidal and needle-like when external magnetic field parallel to the plane of particulate monolayer was applied during the synthesis. The evident correlation between the direction of the applied field and the long axis of anisotropic nanoparticles grown and deposited under the applied field was observed. These AFM and TEM results are in good agreement with STM data obtained earlier in our group on the effects of applied fields on the morphology of magnetic iron-containing nanoparticles [18] and with literature data [19].

4. Conclusions

Nanocluster-containing stable planar molecular nanostructures with high structural order and reproducibility were fabricated by the interface monolayer approach. Discrete electron tunneling effects were observed in that structure at room temperature using STM. The data presented illustrate the possibilities of 2-D synthesis method to produce in a controllable way anisotropic inorganic nanoparticles and self-organized planar nanostructures with various morphologies. Interfacially grown small gold nanoparticles reveal Coulomb charging effect at room temperature and thus can find applications in research and development of nanoelectronics elements and devices based on the single-electron tunneling effects.

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References

[1] S. Roth, M. Burghard, G. Leising, Curr. Opinion Solid State Mater. Sci. 3 (1998) 209.
[2] D.L. Klein, P.L. McEuen, J.E.B. Katari, R. Roth, A.P. Alivisatos, Appl. Phys. Lett. 68 (1996) 2576.
[3] T. Sato, H. Ahmed, D. Brown, B.F.G. Johnson, J. Appl. Phys. 82 (1997) 696.
[4] G. Schmid, Y.-P. Liu, M. Schumann, T. Raschke, C. Radehaus, Nanoletters 1 (2001) 405.
[5] A.A. Zubilov, S.P. Gubin, A.K. Korotkov, A.G. Nikolaev, E.S. Soldatov, V.V. Khanin, G.B. Khomutov, S.A. Yakovenko, Tech. Phys. Lett. 20 (1994) 195.
[6] G.B. Khomutov, E.S. Soldatov, S.P. Gubin, S.A. Yakovenko, A.S. Trifonov, A.Yu. Obydenov, V.V. Khanin, Thin Solid Films 327–329 (1998) 550.
[7] S.P. Gubin, Yu.V. Gulayev, G.B. Khomutov, V.V. Kislov, V.V. Kolesov, E.S. Soldatov, K.S. Sulaimankulov, A.S. Trifonov, Nanotechnology 13 (2002) 185.
[8] E.S. Soldatov, V.V. Khanin, A.S. Trifonov, S.P. Gubin, V.V. Kolesov, D.E. Presnov, S.A. Yakovenko, G.B. Khomutov, JETP Lett. 64 (1996) 556.
[9] G.B. Khomutov, A.Yu. Obydenov, S.A. Yakovenko, E.S. Soldatov, A.S. Trifonov, V.V. Khanin, S.P. Gubin, Mater. Sci. Eng. C 8–9 (1999) 309.
[10] S.P. Gubin, Chemistry of Clusters, Nauka, Moscow, 1987.
[11] G.B. Khomutov, Colloids Surf. A 202 (2002) 243.
[12] A.Yu. Obydenov, S.P. Gubin, V.V. Khanin, S.N. Polyakov, A.N. Sergeev-Cherenkov, E.S. Soldatov, A.S. Trifonov, G.B. Khomutov, Colloids Surf. A 198–200 (2002) 389.
[13] L.Y. Gorelik, A. Isacsson, M. Jonson, B. Kasemo, R.I. Shekhter, M.V. Voinova, Physica B 249–251 (1998) 197.
[14] R.P. Andres, T. Bein, M. Dorogi, S. Feng, J.I. Henderson, C.P. Kubiak, W. Mahoney, R.G. Osifchin, R. Reifenberger, Science 272 (1996) 1323.
[15] C. Petit, T. Cren, D. Roditchev, W. Sacks, J. Klein, M.-P. Pileni, Adv. Mater. 11 (1999) 1198.
[16] A.T. Skjeltorp, J. Appl. Phys. 57 (1985) 3285.
[17] R.B. Frankel, R.P. Blakemore, R.S. Wolfe, Science 203 (1979) 1355.
[18] G.B. Khomutov, S.P. Gubin, Yu.A. Koksharov, V.V. Khanin, A.Yu. Obidenov, E.S. Soldatov, A.S. Trifonov, Mater. Res. Soc. Symp. Proc. 577 (1999) 427.
[19] T. Prozorov, R. Prozorov, Yu. Koltypin, I. Felner, A. Gedanken, J. Phys. Chem. B. 102 (1998) 10165.