Molecular Nanocluster Electronics: Organized Superstructures at Nanoscale and New Functional Nanomaterials

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ABSTRACT

We report on a number of new effects of self-organization at nanoscale, leading to creation of new functional nanomaterials, including carbon and carbon-metal nanotoroids and nanodiscs and self-assembling of magnetic nanoparticles into helices and chains. We also extensively used a new approach of biopattern nanoengineering to create DNA-based complexes with metal or CdSe/ZnS core-shell nanorods (22 x 4.5 nm) which possess strongly linearly polarized photoluminescence due to unidirectional orientation of nanorods along DNA filaments. Optical, electrical and topology (geometrical) properties of such complexes were investigated. This work is a result of a coherent effort (since 1980's) of a consortium of Russian research groups in Nanotechnology (INTC – Interdisciplinary Nanotechnology Consortium) aimed at creating molecular electronic devices based on individual and collective properties of specially designed and fabricated nanoclusters.

Keywords: nanoclusters, nanoelectronics, carbon, nanotoroids, nanotubes.

1 INTRODUCTION

We consider a concept of Molecular Nanocluster based Electronics (**MNC-Electronics**) – where all components are completely reproducible, technologically compatible and have specific pre-designed functional properties. Molecular nanoclusters proved to be very promising objects for applications in electronics not only because they have absolutely identical chemical structure and allow for "from bottom to the top" approach in constructing new electronic devices, but it is also possible to design and create great variety of such functional nanoparticles with specific properties. A broad spectrum of metalorganic nanoclusters, containing normally a metal core surrounded by an organic ligand shell has been investigated [1, 2]. Most extensive studies performed within INTC activities included nanoclusters containing following metals: *Pt, Pb, Fe, Au*, etc. with number of metal atoms in the core from 3 to 101 and typical sizes up to several nanometers as well as nanoclusters, containing semiconductor core (CdS, CdSe) for optical applications [3]. This required complete technological cycle of nanocluster design, fabrication, deposition, formation of organized nanostructures (nanorods, chains), characterization, etc. [1].

2 MOLECULAR CLUSTER MATERIALS

In the present work the systematical research of so-called "small" clusters (with a number of metal atoms from 3 up to 101) is carried out. Various molecular clusters were synthesized and purified by routine chemical techniques. Their chemical properties and IR spectral characteristics were in accordance with the well-known standard data.
The main properties of cluster molecules can be described as follows:

1. Clusters as any molecular compound may be purified by routine chemical methods and after purification all molecules of the sample are strictly identical both in composition and structure. Hence, the parameters scattering of cluster nanostructures caused by elements dissimilarity will be appreciably less then in case of using traditional technologies.

2. The size of clusters is very suitable for the production of tunneling molecular nanostructures. The tunnel barrier of the basic molecular cluster may be noticeably less than for any element formed by methods of modern nanolithography and elements are absolutely identical. Thus, it will allow to essentially increase circuit complexity of elements and, hence, to increase the information volume.

3. The currents passing through tunneling nanostructures from a cluster element are sufficiently small and the time of switching of such an element (time of tunneling) is also very small ~ 10^{-12} sec. Therefore, the power consumption of one element will be sufficiently low so that even at very high integration level of elements the electrical nanocircuit will be not destroyed.

4. The chemical and physical properties of clusters are already quite well investigated. Now there are various technologies to deposit cluster molecules on a substrate not only by physical (sedimentation, including field-induced, LB-technique), but also by chemical methods.

Therefore, such cluster molecules can be supposed to be among the most preferable candidates for a role of the simple basic "elements" for fabrication of the nanostructures for the purposes of future molecular electronics.

The structures containing the isolated cluster molecules of platinum, palladium, iron cluster, cluster chains, two- and three- dimensional structures of clusters were obtained on the HOPG surface. Depending on deposition conditions (the surface pressure at the moment of monolayer transferring, cluster concentration in a solution) it was possible to obtain separate cluster molecules on a substrate surface, as well as the ordered structures. The cluster size on graphite was determined by STM methods and was compared with the X-ray data of monocrystals of the same compounds.

3 ELECTRONIC PROPERTIES OF MOLECULAR NANOSTRUCTURES

The single-electron devices (analogue of the diode and the transistor) having individual molecular nanoclusters as their basis working at room temperatures were fabricated [1]. The series of control characteristics (i.e. dependence of a tunnel current through a double-junction tunnel nanostructure on a voltage of control electrode at the fixed tunnel voltage on the double-junction structure) were recorded after the CVC measurements. It has been shown that the current through the investigated molecular transistor structure changes periodically at monotonous change of the control electrode voltage with different period for various clusters (Fig. 1.). The estimate of electrometric sensitivity of the system from the maximal slope of the control characteristic and experimentally observed noise (amplitude about of ~150 pA at a bandwidth of 30 kHz and a time of CVC measurement of 3 ms) gives the value of $\sim 7*10^{-4}$ e/√Hz. This value approaches the typical values for traditional thin-film single-electron systems. Obviously the recorded noise was caused mainly by mechanical vibrations in STM.

Typical steps-like I-V curves were observed (Fig. 2.) for various cluster's structures.

Theoretically calculated in our work [1, 4] CVC's for single nanocluster's level case and their dependence on the profile of metal cluster and ligand shell (size of barrier) are in good agreement with experimental results for tunnel current at room temperature through molecular nanoclusters obtained earlier [1, 2, 5, 6].

In present work a fabrication of three-dimensional and planar molecular nanostructures as well as experimental and theoretical investigation of an electron transport in them are considered. Very high sensitivity of molecular tunneling systems to the electric charge allows for a number of effects in structures when the behaviour of those structures will depend on external electromagnetic field. This means that this technology can be very promising not only for development of nanoelectronic devices, but also for detecting and processing of external electromagnetic signals.

4 ORGANIZED SUPERSTRUCTURES AT NANOSCALE AND NEW FUNCTIONAL NANOMATERIALS

We report experimental observation (by AFM, STM and HRTEM methods) of nanotoroids for both carbon and carbon-metal superstructures produced by methods of arc discharge and laser ablation. Size of superstructures is ~ 10 nm for carbon and ~ 30 nm for carbon-metal (outer diameter), with inner diameter ~1/3 of the total.

Initial observations of toroids were made for pure carbon, but gradual increase of metal to some optimal concentration dramatically increased the yield of toroidal structures [8, 9]. The influence of pressure, humidity and temperature was also investigated. Also effects of reversible transition of topology (sphere - toroid) (Fig. 3.a - 3.c.) on the same sample, were observed depending on external parameters [8].

The possibility of such structures was discussed earlier [10, 11], but we also discovered carbon-metal nanocapsules among toroids (Fig. 3.c.), with shapes like nanodiscs, reminiscent of human erythrocytes. Changing concentrations and metals (Mo, Cr, etc) leads to difference in shapes and sizes of superstructures. Therefore, new types of topologically closed carbon and carbon-metal nanostructures are discovered, with the theoretical model presented elsewhere [12]. We also discuss technological aspects of the growth of such nanostructures and their applications as new functional nanomaterials.

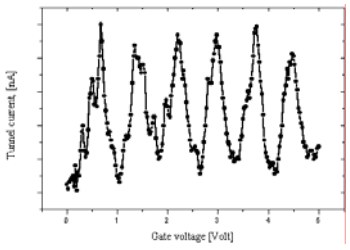
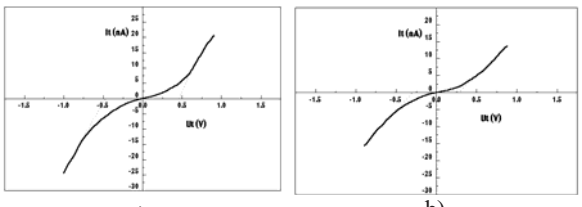


Fig. 1. The control characteristic of tunneling structure "STM tip- cluster- substrate"



a) b)

Fig. 2. CVC for the nanocluster structures
a). $Pd_3(CO)_3[P(C_6H_5)_3]_4$, b). $Pd_{10}(CO)_{12}(PBu_3)_6$.

We also present new experimental results on self-assembling (Fig. 4.) and electrical properties of a number of carbon-metal (including Au_{101}) molecular nanoclusters,

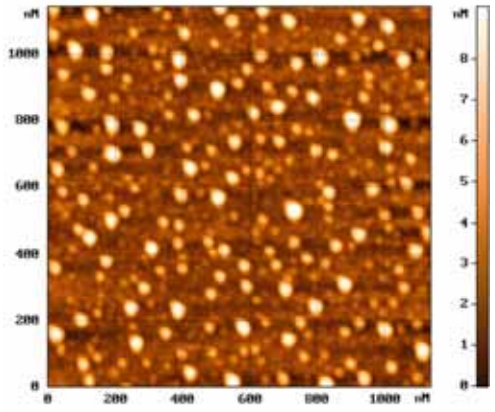


Fig. 3.a.

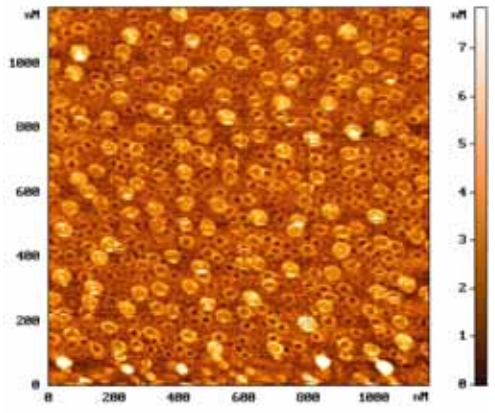


Fig. 3.b.

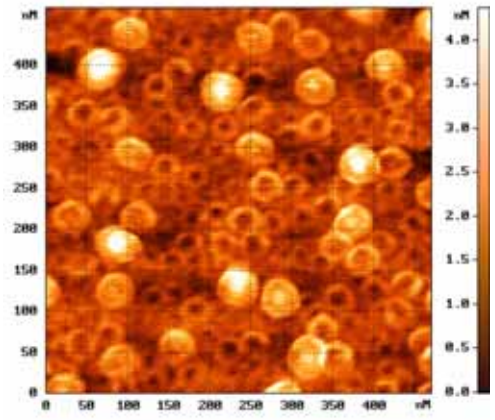


Fig. 3.c.

Fig. 3. AFM Images of reversible topological transition from spheres (a) to toroids (b, c)

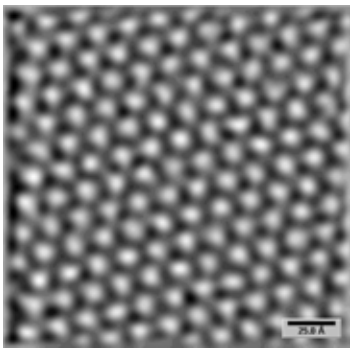


Fig. 4. self-assembling Au_{101} – monolayer

typical size of few nanometers, clearly demonstrating

Coulomb blockade and single-electronic properties, as presented by us earlier for other systems [1].

Self-organization of magnetic nanoparticles (Ni, size ~ 2.5 nm) on very smooth (gold on HOPG) surfaces is also discussed, including formation of chains, double chains, helices and nanotubes [8-10] of magnetic nanoparticles (Fig. 5.a – 5.c.).

These self- organization effects can also lead to new applications in magnetic nanomaterials, particularly for

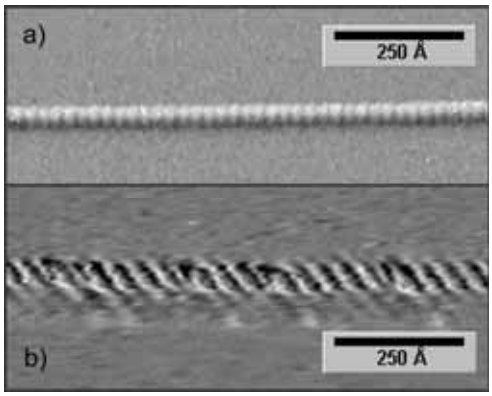


Fig. 5. Self-assembled chain a. and helices b. of Ni nanoparticles

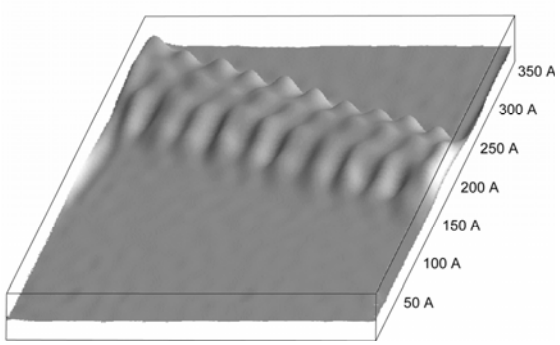


Fig. 5.c. Self-assembled nanotube-like superstructure of Ni nanoparticles

topologically closed superstructures [16].

We introduce also a new approach of biopattern nanoengineering, using biological molecules, and in particular, DNA molecules as building blocks and nanotemplates for controllable fabrication of various bioinorganic nanostructures due to their unique physical-chemical properties and recognition capabilities.

We have synthesized novel DNA complexes with positively charged, highly luminescent CdSe nanorods that can be self-organized into filamentary, netlike or spheroidal nanostructures. CdSe/ZnS core – shell nanorods (22 x 4.5 nm) produce room-temperature photoluminescence (PL) band centered around 580 nm with PL quantum yield above 30% and are arranged into collinear strings or filaments of micrometer length. DNA-CdSe nanorod filaments possess strongly linearly polarized PL due to unidirectional orientation of nanorods along the filaments and can be extensively used as new bioinorganic nanomaterials (biomarkers, sources of polarized light, ets.) [3].

5 CONCLUSIONS

In our opinion the new prospective approach of modern nanoelectronics is connected with choosing of optimal objects – future nanoelectronic elements – and providing their reproducible work at room temperature. Self-organization processes for nanoclusters and biopattern engineering reported in this communication may form the basis for custom-designed technology of creating such optimal nanoelectronic elements.

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