

FORCED ORGANIZATION OF MAGNETIC QUASI-ONE-DIMENSIONAL IRON-ORGANIC NANOSTRUCTURES ON INORGANIC MATRICES

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Abstract. The magnetic properties of nanostructures based on quasi-one-dimensional iron-organic “brushes” attached to silica are studied for the first time. The non-compensated antiferromagnetism is established at the chemical constructing of iron-organic nanostructures on silica surface. The data obtained indicate the perspectives of such structures for spin electronics.

1. INTRODUCTION

It is known [1] that structural organization of a compound (arrangement of relative position of its structural units) proceeds either during self-organization or forced organization processes. Forced organization of structural units in the defined order is performed instead of spontaneous organization (that takes place while crystallization process runs) in extra-fine chemical synthesis [2,3] – so pre-defined composition and structure can be realized.

Depending on the temperature and other conditions of chemical construction, it is possible to change the density of stacking of structural units. The infinite number of the more complicated structures beyond the crystalline ones could be created. The use of such a methodology for synthesis of new solid matters is the most promising.

In the past decade, the investigations were realized in the field of spin (electronic spin states) management. This is a scientific field with an official name spintronics (or spin transport electronics). Spintronics also deals with magnetic nanostructures. The main feature of spintronics is

an application of magnetic moment of an electron as a tool for matter properties regulation; this provides additional possibilities for regulation of physical properties [4,5].

The traditional objectives of spintronics are molecular ferromagnetics – organic paramagnetic molecules or complexes where metal ions as magnetism holders are coated with ligand shell consisted of organic molecules [6,7]. It is worth to note that these molecular ferromagnetics of different structure and spin density have a meaningful disadvantage due to the features of organic molecules – low spin density and a lot of chemical ballast. So, it is important to get the spintronics objects with high spin density by means of directed chemical constructing of metal-organic structures for spin stabilization.

In the present paper, the possibility to create the ordered state of magnetic spin systems by means of chemical constructing of nanostructures of different spin density on the basis of quasi-one-dimensional iron-organic nanostructures (brush-like) attached perpendicularly to inorganic matrix is shown for the first time.

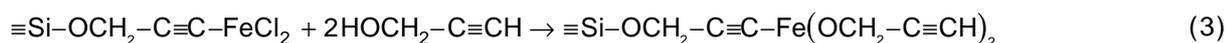
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2. EXPERIMENTAL

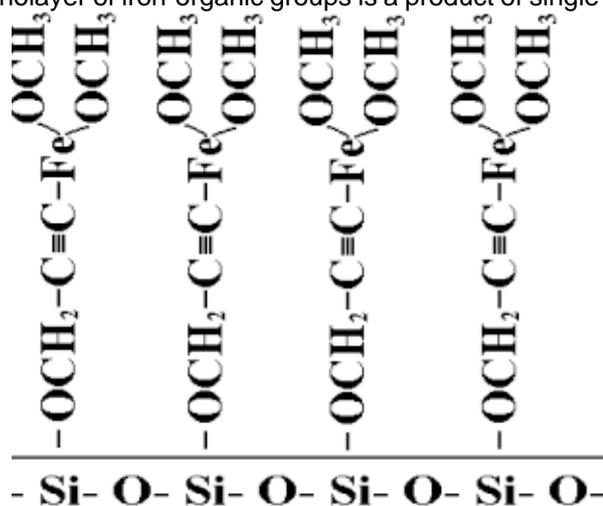
The study of conditions giving the opportunity to get structural inhomogeneities of determined length on silica surface and investigation of their magnetic properties has been done on the example of brush chains on silica surface from organic groups including Fe^{3+} ions forming the chains $\equiv\text{Si}-(\text{R}-\text{Fe}-\text{R})_n$, where R is propargyl group $[-\text{O}-\text{CH}_2-\text{C}\equiv\text{C}-]$, n is number of $\text{R}-\text{Fe}-\text{R}$ chains attached. The synthesis of iron-organic groups on the support surface (i.e. on silica or silicon) has been performed by the molecular layering (ML-ALD) method introduced in 1970s by St. Petersburg (Leningrad) scientific school [2,3]. As a support, dispersed silica (silochrom, SCh-120 with specific surface of $120 \text{ m}^2/\text{g}$ and pore diameter of 35.0 nm , specific magnetic susceptibility of $-0.348 \cdot 10^{-6} \text{ cm}^3/\text{g}$) has been used. Silicon samples with nanostructures attached were used for the atomic force microscopy study.

The topography of silica surface with nanostructures attached was investigated by the scanning probe microscope Solver P47 Pro (NT-MDT, Russia) has been used. This study was performed by atomic force microscopy in tapping mode in air; the study was carried out in 4-5 points on the sample surface.

Gas-phase synthesis has been performed at $200 \text{ }^\circ\text{C}$ in the flow of purified argon; samples with different length of organic chains were synthesized. The length of chains has been regulated by the number of cycles of surface reactions (1–3):



Silica with a single monolayer of iron-organic groups is a product of single reaction 3 (see scheme 1).



Scheme 1. Single iron-organic monolayer on silica

The multifold treatment of surface can lead to longer quasi-one-dimensional structures.

Magnetic susceptibility of the synthesized samples was measured by the Faraday method in the temperature range of $90\text{--}293\text{K}$ at four values of magnetization within the range $4100\text{--}8280 \text{ Oe}$. Mössbauer spectroscopy has been applied to control the iron content in synthesized nanostructures; these measurements were carried out at 293K in the absorption mode using ^{57}Co isotope as a source of γ -quants.

3. RESULTS AND DISCUSSION

Mössbauer spectra of the samples with (a) single monolayer or (b) four monolayers of iron-organic groups are depicted in Fig. 1. The doublet in spectrum (1) indicates that no phase formation takes place on the surface. The spectrum of the sample with 4 monolayers (Fig. 1b) is more complicated. Doublet, as well as sextet can be revealed in this spectrum and its parameters meaningfully differ from the parameters characterizing bulk iron oxide. Taking into account Fe-C bonds, their presence could be described by the spectrum showed in this figure. The Mössbauer data allow proposing the growth of amorphous iron-organic chains.

Пропускание

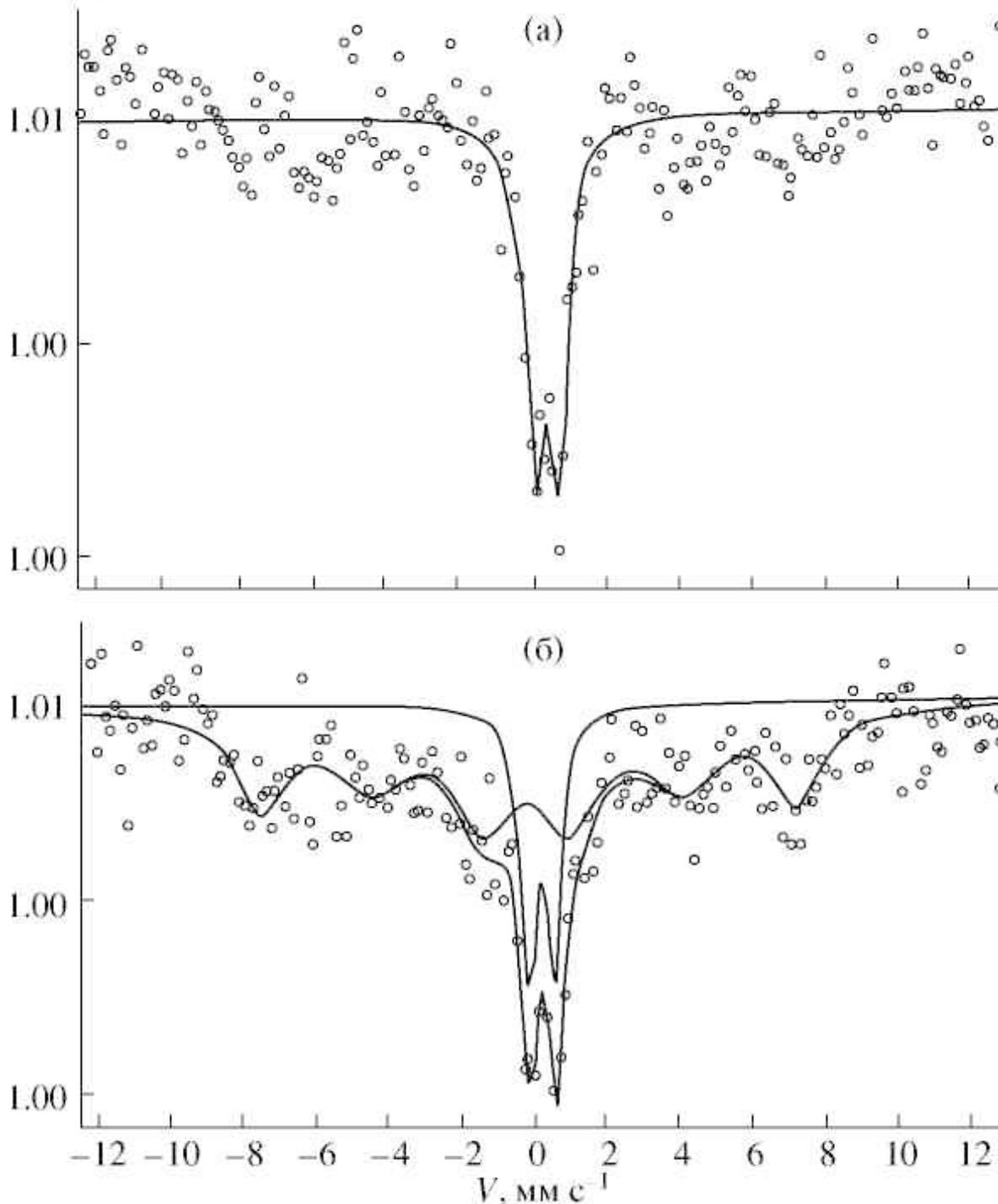


Fig. 1. Mössbauer spectra of silicon samples with one (a) and four (b) monolayers of iron-organic groups.

AFM study of the samples containing iron-organic structures after 30 cycles of reactions 1–3 (Fig. 2) confirmed the presence on silicon surface isolated nanostructures as high as ca. 30 nm. It is close to the predicted value for nanostructures syn-

thesized. At the same time, the diameter of these structures reaches 500 nm and does not satisfy the model of growth proposed (Fig. 3a).

It can be considered that non-controlled reactions of polymerization and condensation take place

Table 1. The values of χ and content of iron ions in iron-organic groups on silica gel.

Sample	Fe ³⁺ mmol/g	Fe ²⁺ mmol/g	T, K	$\chi^*10^6(\text{cm}^3/\text{g})$				μ_{eff}
				H_1	H_2	H_3	H_4	
No.1 Sample with single monolayer of organic (R) groups (R = O-CH ₂ -C≡CH)	–	–	90	0.345	0.458	0.110	0.143	
			140	-0.186	-0.223	-0.220	-0.179	
			200	-0.212	-0.200	-0.236	-0.215	
			240	-0.266	-0.235	-0.259	-0.233	
			273	-0.212	-0.223	-0.267	-0.239	
			293	-0.425	-0.282	-0.299	-0.263	
No.2 Sample after 1 cycle of surface reactions (R = OCH ₃)	0.30	0	90	5.77	4.37	4.04	3.85	2.89
			140	4.99	3.71	3.35	3.19	
			200	4.40	3.25	2.97	2.82	
			240	3.98	2.95	2.76	2.65	
			273	3.81	2.84	2.65	2.54	
			293	3.63	2.74	2.56	2.38	
No.3 Sample after 1 cycle of surface reactions (R = O-CH ₂ -C≡CH)	0.28	0	90	9.09	6.75	6.20	5.83	
			140	8.70	6.45	5.90	5.57	
			200	8.27	6.13	5.63	5.28	
			240	8.08	5.97	5.49	5.17	
			273	7.88	5.85	5.36	5.06	
			293	7.85	5.80	5.32	5.00	
No.4 Sample after 2 cycles of surface reactions (R = O-CH ₂ -C≡CH)	0.89	0	90	34.9	30.1	30.0	30.3	
			140	21.8	18.9	19.0	19.2	
			200	16.0	13.8	13.8	13.7	
			240	14.4	12.2	12.0	11.9	
			273	12.6	10.7	10.7	10.6	
			293	12.0	10.1	10.0	9.9	
No.5 Sample after 4 cycles of surface reactions (R = O-CH ₂ -C≡CH)	1.49	0.10	90	138.3	85.9	79.6	71.6	4.57
			140	133.6	90.1	76.8	68.6	
			200	127.4	85.2	72.7	65.3	
			240	124.3	82.8	70.9	63.2	
			273	119.6	80.4	69.0	61.5	
			293	120.4	79.7	67.9	60.8	

at the temperature of synthesis (200 °C) leading to the agglomeration of single iron-organic groups into bigger aggregates (Fig. 3b).

Summarized data on the magnetic properties of quasi-one-dimensional iron-organic nanostructures are presented in Table 1.

The magnetic susceptibilities (χ_{sp}) measurements of the initial propargyl alcohol and silica, treated with this alcohol indicate their diamagnetism. The values of magnetic susceptibilities are equal to $-0.4 \cdot 10^{-6}$ and $-0.1 \cdot 10^{-6} \text{ cm}^3/\text{g}$, respectively.

Sample 1, chemically synthesized and containing 1 monolayer of organic groups is less diamagnetic. If the temperature decreased to 90K, the sample becomes paramagnetic and the dependence of magnetic susceptibility on magnetization is appeared. This effect can be attributed to re-distribution of electron density of surface organic groups due to triple bonds present. The increase of the layer's number leads to the increase in magnetic susceptibility; its dependence on magnetization appeared.

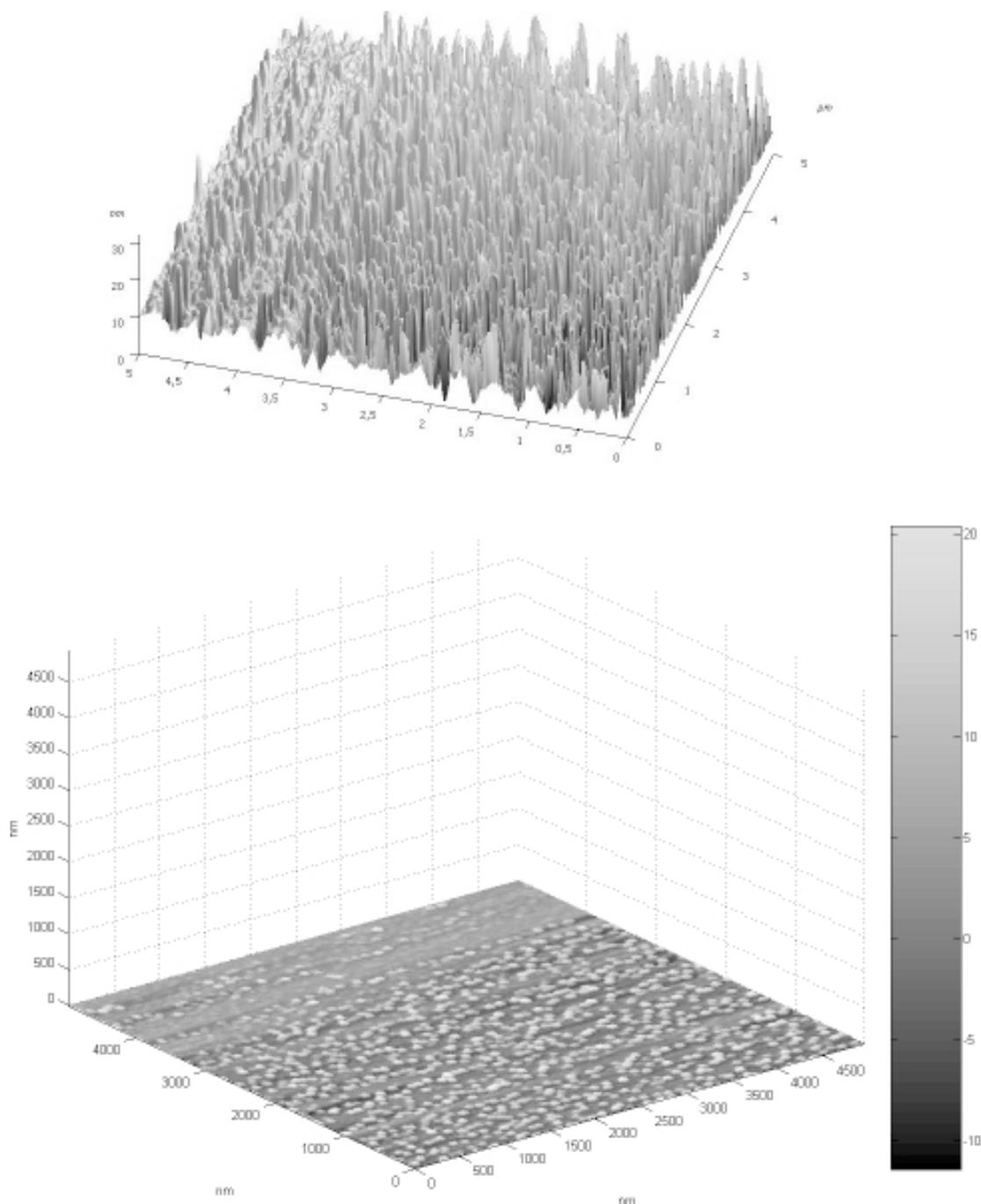


Fig. 2. 3D reconstruction (AFM-microcopy) of silicon containing iron-organic nanostructures after 30 cycles of surface reactions (2, 3).

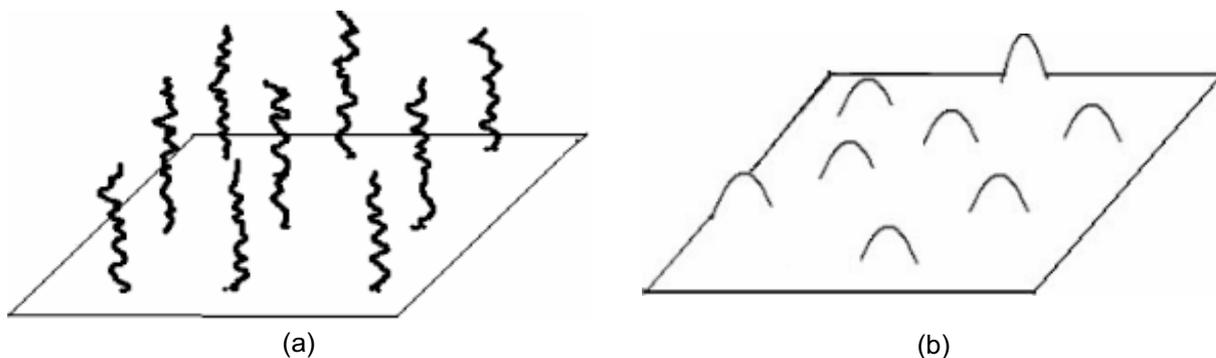


Fig. 3. The model of structure of silicon surface with iron-organic groups (a, b): a – predicted growth of iron-organic groups; b – experimental (according to AFM in Fig. 2) growth of iron-organic groups.

The preliminary calculations of the effective magnetic moment (right column in Table 1) based on the susceptibility values and the data of chemical analysis, indicate their increase with temperature. It means that the interactions are antiferromagnetic within the layer as well as between the layers.

It could be proposed that these effects are due to the features of spin density distribution of organic groups included into nanostructures attached. The difference of magnetic behavior of two and four monolayers is evident. In the first case, the interactions are antiferromagnetic. In the second case, the non-compensated antiferromagnetism appeared; it is indicated by the significant dependence of c on the magnetic field direction. Probably, antiferromagnetic exchange parameter is different within the limits of layer and between layers, because compensation of magnetic moments of layers takes place and susceptibility, as it can be seen from Table 1, does not depend on the field. When the number of layers is increasing, the influence of triple bond on the distribution of electronic density should be increased. It does not allow complete compensation of magnetic moments and leads to non-compensated antiferromagnetism.

4. CONCLUSIONS

In conclusion, non-compensated antiferromagnetism is revealed for the iron-organic groups of

the defined length attached to silica surface. The data indicate that spintronics is promising for the study of nanostructures attached to the support.

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