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Patterned arrays of magnetic nano-engineered capsules on solid supports

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Abstract

The aim of the present work is to develop a method for the patterning of the nanocapsule arrays immobilized on solid surfaces applying electron beam treatment to the formed layers of nanoparticles with magnetic materials in the cavity or in the shell. The successful patterning was demonstrated by optical microscopy, while morphology and structure of the formed system were analyzed by atomic force microscopy.

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1. Introduction

Nano-engineered polymeric capsules (NPC) are new perspective objects allowing to provide space confinement of different materials [1]. NPC are usually produced by polyelectrolyte self-assembling of polymer multilayers onto spherical templates with successive removal of the template by varying the environmental conditions such as pH or ionic strength of the solvent. Currently, NPC with the diameter within 100–5000 nm and the shell thickness of 5–50 nm were produced [2]. It is possible to grow some inorganic crystals inside the capsule cavity or in the shell region. The possibility to grow particles with magnetic properties in NPCs was already demonstrated [3]. Scheme of the NPC with magnetic core is illustrated in Fig. 1. Successive diminishing of the capsule sizes can allow the formation of capsules with single magnetic domains in them, what can be very useful for practical applications.

Further steps toward practical applications demand the development of the methods, allowing to immobilize these objects on solid supports and to perform their patterning, in order to realize desirable features, necessary for the device realization, such as pixels for the memory systems.

The aim of the present work was the deposition of the arrays of NPC with magnetic materials onto solid supports, testing of their local magnetic properties by magnetic force microscopy and the development of the lithography processes on these layers. Electron beam treatment was chosen for the lithography as it had already demonstrated its applicability for patterning thin organic layers and nanoparticle arrays [4].

2. Materials and methods

Nano-engineered capsules used in this work (namely poly allylamine hydrochloride (PAH)/poly styrene sulfonate (PSS) (Fe_3O_4)) consist of PAH/PSS capsules inside which magnetic Fe_3O_4 nanoparticles were synthesized. The difference in pH between capsule interior and surrounding solution, described in Ref. [5], and the

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Fig. 1. Scheme of magnetic particle containing NPC.

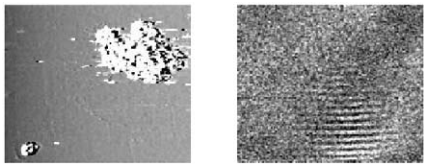

Fig. 2. Images of the NPC at solid support. Left image—noncontact AFM; right image—magnetic force image. Image size is 50×50 μm.

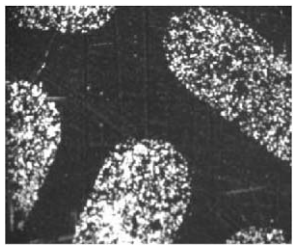

Fig. 3. Optical microscope image of patterned layer of NPC on glass support. Image size is 0.4×0.4 mm^2.

presence of inner PAH complex cause spontaneous precipitation of the magnetic Fe_3O_4 nanoparticles exclusively inside the capsules. At first PAH/PSS capsules were exposed to the 0.01 M NaOH for 4 h. Then they were washed and 3 ml of 0.66 M $FeSO_4$ + 0.62 M $Fe_2(SO_4)_3$ solution were added to 200 μl of 5% v/v aqueous suspension of PAH/PSS capsules for 6 h. During this time combined precipitation of both Fe (II) and Fe (III) ions and the formation of the magnetic Fe_3O_4 were observed. After synthesis the excess of Fe (II) and Fe (III) ions was removed from bulk solution by repeated magnetic decantation.

Lithography was performed by electron beam irradiation with a home-made electron gun through masks with different geometry (characteristic sizes of the mask features were of about 0.1 mm). Acceleration voltage of the electron beam was 2 kV and the exposition time was 10 min, providing the radiation dose of 3×10^{-3} C/cm^2. Development of the features was performed in the Tween solution (25%) for 3 min under sonification.

Morphology of the samples was studied by AFM in noncontact mode ($v = 170$ kHz, Autoprobe CP-R, Thermomicroscope). MFM images were acquired with a magnetic cantilever ((Co) NSG-01, NT-MDT) that was scanned well above the surface probing only the stray field from the magnetic core and not the Van der Waals forces.

3. Results and discussion

Images of the NPC with magnetic core are presented in Fig. 2. Large corrugated area (left image) corresponds to the aggregate of capsules. The presence of magnetic material in the capsules is in agreement with previous measurements [5] and it was identified by magnetic force measurements (corrugated area in the right image). Difference in the position of NPC aggregate zone can be explained considering that not only the tip but whole cantilever is magnetic. Therefore, the strongest magnetic interaction takes place not when the tip is located over the object. When empty or non magnetic capsules were imaged, no features were registered with the magnetic cantilever.

Optical image of the NPC layer on glass substrate after lithography is presented in Fig. 3. Capsules in the zones, irradiated with electron beam were fixed at the support surface, while that in the zones, closed with the mask, were completely removed during the development process. As the lithography was performed through contact masks, minimum feature size reached in this work was 80 μm. Better resolution can be obtained using scanning electron beam lithography machines.

4. Conclusions

The possibility of the deposition and patterning of layers of nano-engineered polymeric capsules onto solid supports was demonstrated. These arrays can be used for the formation of magnetic devices, such as memory systems. Diminishing of the capsule size will allow to form objects with single magnetic domains. The developed lithography process will allow to pattern them in a desirable way.

This innovative technology is competitive for the formation of thin magnetic coatings useful both for memory systems and for head reading devices.

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