Macromolecules **2003,** *36,* 6493−6496

Deposition and Patterning of Polymeric Capsule Layers

Tatiana Berzina,[†] Svetlana Erokhina,[‡] Dmitry Shchukin,[§] Gleb Sukhorukov,[§] and Victor Erokhin*,[†]

Department of Physics and INFM, University of Parma, Parco Area delle Scienze 7A, 43100, Parma, Italy; DISTBIMO, University of Genoa, Corso Europa 30, 16132 Genoa, Italy; and Max-Planck-Institute fuer KGF, Am Muehlenberg 1, 14476, Golm bei Potsdam, Germany

Received May 19, 2003; Revised Manuscript Received July 9, 2003

ABSTRACT: Nanoengineered polymeric capsules of different types were deposited on solid supports by the solution casting technique. Patterning of these layers was performed with an electron beam. Electron beam irradiation of such layers resulted in the significant increase of the capsule adhesion to the substrate. Development of the patterns was carried out in detergent solutions under sonication. Capsules in the nonirradiated areas of the samples were washed out, while those in irradiated zones remained on the substrate surface. The possibility of two-step lithography on successively deposited layers of capsules of different types was demonstrated.

Introduction

Current developments of techniques for the formation of nanoengineered polymeric capsules have attracted great attention due to their interesting application perspectives.[1] A recent technique is based on the self-assembling of polymeric shells on spherical (or any other shape) precursors by electrostatic interactions and/or by the method of surface-controlled precipitation. After the shell is formed, it is possible to remove the precursor varying the environmental conditions. (In most of the cases, pH variation resulted in the solubility of the precursor nuclei.) Thus, hollow polymeric capsules can be formed. An important feature of these capsules is the smart nature of the shell which may change its properties as a response to the environmental condition variations.[2]

It is also possible to manipulate the intercapsule content varying the environmental conditions. The possibility has been demonstrated to grow space-confined organic[3] and inorganic crystals,[4] to insert and to deliver biomolecules (such as proteins),[5] to perform selective metallization,[6] etc.

Most of the possible applications of nanocapsules are considered for the liquid phase. In fact, specific features of the objects, such as shell pores of the fixed diameter and, moreover, the possibility to open and close reversibly these pores when it is necessary, together with the possibility to insert some receptors in the shell surface, allowing the attachment of the capsules to specific areas, provide perspectives for intelligent drug delivery.

Nevertheless, there are applications that require strongly the immobilization of the capsules onto solid support surfaces. These applications are connected to the fabrication of sensitive elements of multipurpose sensors and regular distribution of space-confined materials. The last can be illustrated by the formation of capsule-confined magnetic granules on a flat surface. In fact, adequately chosen precursors can provide the desirable confinement of the magnetic particle growth. If it will be small enough, it is possible to expect the growth of a single magnetic domain in each capsule. Realization of this idea will allow to construct a new generation of magnetic media based on such phenomena as tunneling[7] or ballistic[8] magnetoresistance, realized with rather simple and low-cost technologies.

However, all interesting applications of nanocapsules (preferentially, filled with some materials), immobilized on solid support surfaces, can be taken into serious consideration only if a method can be developed for their in-plane patterning. In fact, if we consider the applications, mentioned above, namely, magnetic media and sensor arrays, the necessity to have the possibility of 2-D manipulation with immobilized arrays becomes clear. In the case of capsules with magnetic domains, pixel arrays must be formed as the elementary units of information storage. In the case of multiuse complex sensor systems it is necessary to arrange capsules with different enzymes, receptors, DNA, or other sensitive molecules in the desirable patterns on the surface of transducer substrate. Therefore, it is possible to claim that effective utilization of filled capsules immobilized on solid surfaces requires the development of the 2-D pattern formation process. Moreover, in the most of cases it will be necessary to apply the lithography procedures several times in order to realize the desirable mutual arrangement of capsules filled with different functionally active molecules or crystals.

From this point of view, we recall that the method of the patterning of organic layers with electron beam irradiation is well-known.[9] Microelectronics is based on the use of electron beam resists, negative or positive, where the electron beam irradiation results in the polymerization of monomers or in the destruction of polymers in the mask layers. In any case, the result is the variation of the solubility and stability of the irradiated areas with respect to nonirradiated ones. After a proper developing process, which consists of the treatment with solvents, 2-D features in the layer plane are formed. Concerning nanometer-scale objects, the method was successfully applied for the patterning of Langmuir−Blodgett films.[10] Possible mechanisms of the electron beam action on different organic object, different to polymerization, will be discussed in the other paper.

† University of Parma.
‡ University of Genoa.
§ Max-Planck-Institute fuer KGF.
* Corresponding author: tel +39 0521 905251; fax +39 0521 905223; e-mail erokhin@fis.unipr.it.

10.1021/ma0346557 CCC: $25.00
Published on Web 07/31/2003

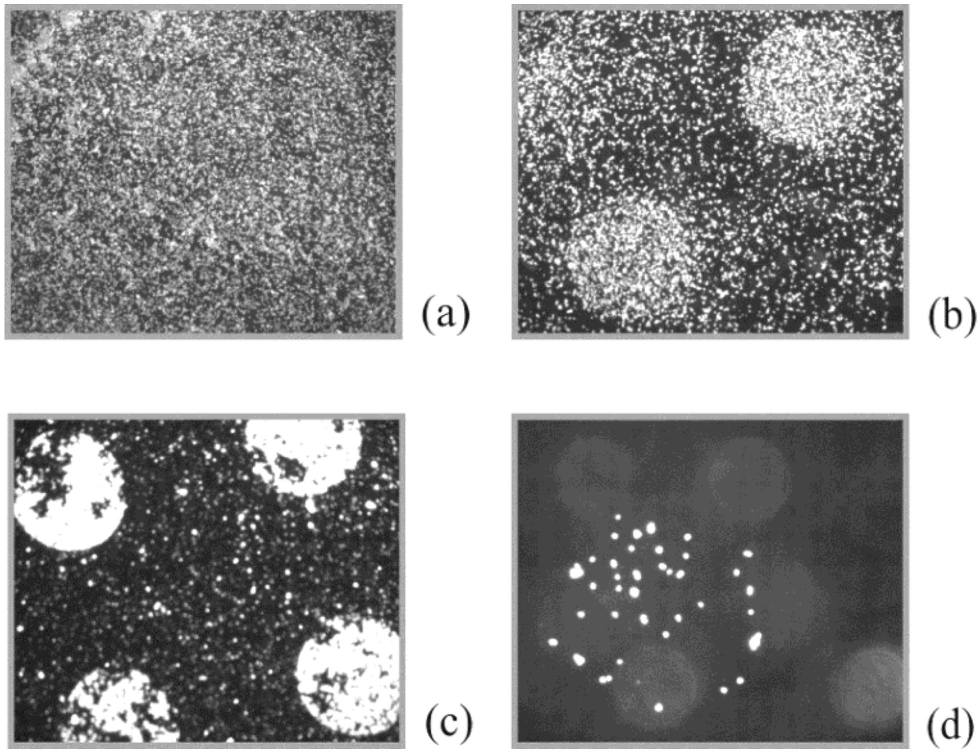

Figure 1. Layer of nanoengineered polymeric capsules at solid surface after electron beam treatment before the development (a); underdeveloped (b) 1 min in detergent solution under sonification; developed (c) 5 min in detergent solution under sonification; overdeveloped (d) 20 min in detergent solution under sonification. Image size is 0.4 × 0.4 mm.

In the present work we present a generalization of the electron beam irradiation approach to the patterning of the nanoengineered polymeric capsule layers immobilized on solid surfaces. In this case the objects are much more complex because they contain polymeric shells independent of the fact that they are empty or filled with some compounds.

Experimental Section

Two types of capsules were used in this work. The first one (namely PAH/PSS) is a poly(styrenesulfonate) (PSS, MW ~ 70 000)/poly(allylamine hydrochloride) (PAH, MW ~ 50 000) polyelectrolyte capsules containing 0.1 M of PAH monomers inside. These capsules were prepared by controlled precipitation of PAH complex with citric acid on the $MnCO_3$ template particles of 3.2 μm diameter followed by layer-by-layer assembling PAH/PSS multilayers on the top of formed core/shell particles.[2,11] After removal of $MnCO_3$ template core (which dissolves at pH = 1), the resulting capsules are composed of two shells: the inner one is formed by the PAH/citrate complex, and the outer shell is the PAH/PSS complex. A more detailed description of the synthesis can be found elsewhere.[2,12,13] The other type of nanocapsules (namely PAH/PPS (Fe_3O_4)) consists 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 14, and the presence of inner PAH complex cause spontaneous precipitation of the magnetic Fe_3O_4 nanoparticles exclusively inside the capsules.[4,15] 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 was 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.

Microscopy images were acquired with the optical microscope Axiotech (Zeiss, Germany).

Hydrophilic glass slides were used as substrate for the deposition. A glass surface treatment was performed in concentrated sulfuric acid (10−15 min) under heating to 80−100 °C. After that, the glass slides were carefully washed in distilled water. Because of such a treatment, strongly hydrolyzed surfaces were obtained.

PAH/PSS capsules were used for the single lithography, while PAH/PSS (Fe_3O_4) as the first layer and PAH/PPS as the second layer were employed for the double lithography.

The pattern formation process on the samples consists of several steps. During the first step the solid substrates were covered with capsule layers by means of a solution casting method. Before casting, capsule solutions were shaken for 1−2 min to avoid capsule aggregates. After drying in air at room temperature, the samples were placed into the vacuum chamber and vacuumed until 10^{-5} Torr. Electron beam irradiation (step 2) was performed with a homemade electron gun[16] through masks with different geometry (characteristic sizes of the mask features were about 0.1 mm). The acceleration voltage of the electron beam was 2 kV and the exposition time was 3 min, providing the radiation dose of 3×10^{-3} C/cm^2. Development of the exposed samples was tried in different solvents, namely, chloroform, ethanol, and detergent solutions. It appeared that chloroform and ethanol do not provide any apparent action on the sample. On the contrary detergent solutions resulted in the removal of the capsules from the nontreated areas of the sample. The best results, i.e., that practically all capsules in irradiated areas remained on the sample surface, while from nonirradiated areas were removed almost completely, were reached when the development process was performed with the 20% solution of Tween 20 for 3−5 min under sonication. The resultant sample contained immobilized capsules only in the exposed areas, while in the nonexposed ones were washed out during the detergent treatment step.

Some samples were prepared by repeating the lithography process two times for the formation of patterns with two different types of capsules. In this case, the already patterned sample was covered with the other nanocapsule layer (step 4), formed by solution casting. Then the sample was placed again into the vacuum chamber (10^{-5} Torr) and exposed to the electron beam (step 5) as done in step 2. The electron beam irradiation was performed through a mask with different geometry in order to to distinguish 2-D features formed during the first and the second lithography processes. The exposed sample was again developed in the detergent solution in ultrasonic bath (step 6), leaving at the support surface areas formed during the first and the second lithography processes.

Results and Discussion

Solution casting allows to realize rather uniform coating of solid substrates with nanocapsule layer. However, close regular packing of capsules was not reached probably due to the rather low concentration of the stock solutions and empty nature of the capsules. The last fact can be responsible for the shape variation of the objects during drying process, resulting in the transformation of the initially monodisperse objects into polydisperse ones that cannot form regular packing. The photograph of the solution casting formed layer after drying is shown in Figure 1a.

Electron beam irradiation of the sample did not change its morphology (image not shown), indicating that both vacuum and electron beam treatment did not induce visible (macroscopic) variation of the capsule structure. Initially, chloroform and then ethanol were tested for the development of these electron beam irradiated samples. No effect was recorded even for rather long time intervals, such as 30 min (the resulting morphology is similar to that in Figure 1a). Simple washing with detergent solution did not provide any changes in the sample as well. The effect of the development becomes visible only when the treatment was performed with detergent solution in the ultrasonic bath. The morphology of the sample after such development for 1 min is shown in the Figure 1b.

As is clear from the image, exposed regions begin to be less soluble in detergent solutions with respect to nonirradiated ones. However, capsules in nonexposed zones were not completely removed from the support surface. Therefore, we have increased the developing time. The morphology of the sample after the ultrasonic bath treatment with detergent solution for 5 min is shown in Figure 1c. As is clear from the image, the treatment had resulted in the practically complete removal of the capsules in nonirradiated zones, leaving practically the same coating in areas exposed to the electron beam action.

Further treatment with the detergent solution (20 min) resulted in the complete removal of capsules in nonexposed areas and significant reduction of their concentration in exposed zones (overdevelopment phenomenon). The morphology of the sample is shown in Figure 1d. The capsule distribution on the surface is still concentrated in circles, corresponding to the irradiated zones. However, the number of these capsules is much less than before, and they are not in contact with each other. The fact that not contacted capsules are still better attached to the substrate surface indicates that the mechanism of the electron beam action differs significantly from that in the case of organic layers, where the exposition provides cross-linking of adjacent molecules. In the present case, instead, it is more likely that the electron beam exposition procedure activates molecules of the capsule shell. This activation results in the formation of bonds between the capsules and the substrate surface. In fact, energy of the electrons (3 keV) is absolutely enough for penetration through whole shells (about 2 nm) in the case of hollow capsules.[16] Irradiation results in breaking of some bonds in the polymer molecules. When the irradiation is stopped, these bonds are linked with adjacent molecules and OH groups at the glass surface. In the case of filled capsules, the electron beam, of course, cannot penetrate the whole capsule volume (about 3 μm diameter). However, the activation in this case can be due to the backscattering of electrons from the substrate surface. Being randomly distributed, these scattered electrons can activate the whole capsule surface, even that faced to the support surface.

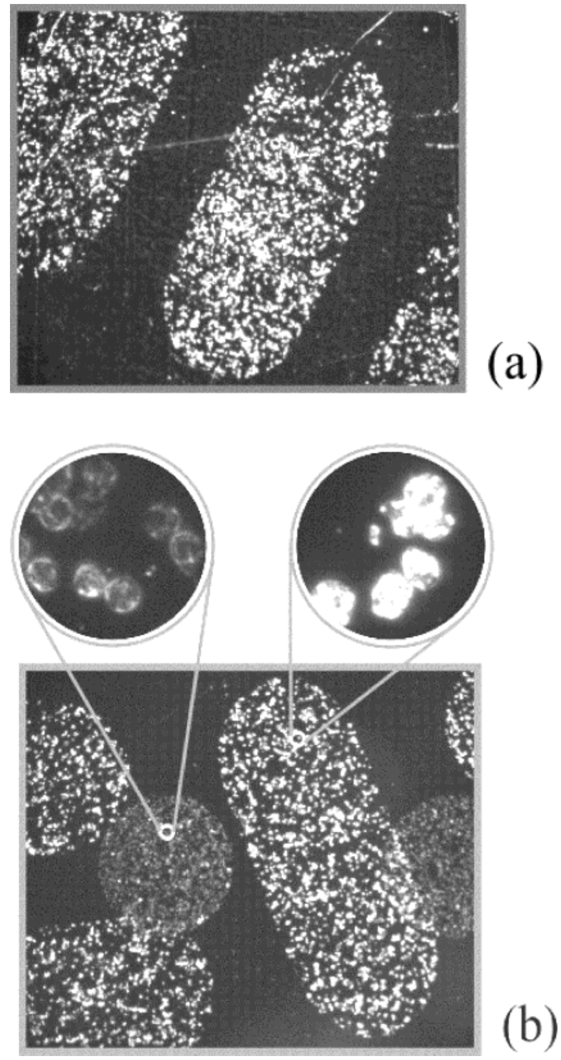

Figure 2. Image of the sample after first lithography (a) and after second lithography (b). Image size is 0.4 × 0.4 mm. Insets show different capsules used during the first and second lithography.

From the application point of view, it is very important to demonstrate the possibility of multistep lithography on nanocapsule arrays, as it can provide the way to produce 2-D macromolecular architectures on solid substrates. Therefore, two-step lithography process on layers of different capsules was performed. Initially, a mask with beanlike windows was used for the exposition of layer of hollow capsules. The morphology of the sample after the development is shown in Figure 2a. The second layer of capsules with Fe_3O_4 inside was deposited onto this sample by solution casting. Then it was exposed to the electron beam radiation through the mask with circular windows and developed in the detergent solution. The image of the sample prepared in such a way is shown in Figure 2b. The performance of the second lithography resulted in the overlapping of a new picture, formed by nanocapsules, with the old one. It is very important that the second lithography (irradiation and development) did not destroy the picture formed during the first lithography process, demonstrating the real applicability of the developed method for the realization of patterns composed from different capsules. Insets to Figure 2b represent images of different areas of the samples with higher magnification, allowing to distinguish clearly the different nature of capsules used in the first and second lithography processes.

Conclusions

A method of the 2-D patterning of capsule layers on solid supports is reported. The method is based on the electron beam irradiation of preformed nanocapsule layers and their successive development in detergent solutions in an ultrasonic bath.

The developed method allows to obtain a desired geometry of the nanocapsule attachment to solid supports. It is important to note that the lithography process can be repeated several times (in the present work, it was done twice) in order to obtain patterned features of different capsules in 2-D plane. Thus, it provides the possibility to organize necessary mutual 2-D arrangement of encapsulated reagents and/or nanocrystals that can be driving engines for molecular manipulating machines, such as catalytic reactors, sensors, or quantum devices based on space-confined inorganic elements.

Details of the lithography mechanism are not yet clear. The available data allow to suggest that the main effect of the electron beam irradiation is in the activation of the capsule shell molecules, resulting in the better adhesion of capsules to the solid support surface, probably through binding to OH groups on glass surface. The main reason for such conclusion is connected to the fact that the initial layers of capsules are not densely packed. Therefore, the irradiation effect cannot be attributed to the cross-linking of the adjacent capsule shells, but to the activation of the shell molecules and successive binding to the substrate surface.

Acknowledgment. The authors thank Prof. M. P. Fontana and Dr. L. Musa for helpful discussions. The present work was supported by MIUR under the grant “Molecular nanodevices”. One author also thanks Nanoworld Projects Europe S.p.a. Strambino (TO), Italy.

References and Notes

(1) Donath, E.; Sukhorukov, G. B.; Caruso, F.; Davis, S.; Möhwald, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2202−2205.
(2) Sukhorukov, G. B. In *Novel Methods to Study Interfacial Layers*; Möbius, D., Miller, R., Eds.; Elsevier Science B.V.: Amsterdam, 2001; p 384.
(3) Sukhorukov, G. B.; Dähne, L.; Hartmann, J.; Donath, E.; Möhwald, H. *Adv. Mater.* **2000**, *12*, 112−115.
(4) Shchukin, D. G.; Radtchenko, I.; Sukhorukov, G. B. *J. Phys. Chem. B* **2003**, *107*, 86−90.
(5) Antipov, V.; Shchukin, D.; Fedutik, Y.; Zanaveskina, I.; Klechkovskaya, V.; Sukhorukov, G.; Möhwald, H. *Macromol. Rapid Commun.* **2003**, *24*, 274−277.
(6) Voigt, A.; Buske, N.; Sukhorukov, G. B.; Antipov, A. A.; Leporatti, S.; Lichtenfeld, H.; Bäumler, H.; Donath, E.; Möhwald, H. *J. Magn. Magn. Mater.* **2001**, *225*, 59−66.
(7) Wulfhekel, W.; Ding, H. F.; Kirschner, J. *J. Magn. Magn. Mater.* **2002**, *242*−*245*, 47−52.
(8) Garcia, N.; Munoz, M.; Osipov, V. V.; Ponizovskaya, E. V.; Qian, G. G.; Saveliev, I. G.; Zhao, Y.-W. *J. Magn. Magn. Mater.* **2002**, *240*, 92−99.
(9) Groves, T. R.; Pickard, D.; Rafferty, B.; Crosland, N.; Adam, D.; Schubert, G. *Microelectron. Eng.* **2002**, *61*−*62*, 285−293.
(10) Lvov, Y. M.; Troitsky, V. I.; Feigin, L. A. *Mol. Cryst. Liq. Cryst.* **1989**, *172*, 89−97.
(11) Sukhorukov, G. B.; Donath, E.; Lichtenfeld, H.; Knippel, M.; Budde, A.; Möhwald, H. *Colloids Surf. A* **1998**, *137*, 253−266.
(12) Voigt, A.; Lichtenfeld, H.; Sukhorukov, G. B.; Zastrow, H.; Donath, E.; Baumler, H.; Mohwald, H. *Ind. Eng. Chem. Res.* **1999**, *38*, 4037−4043.
(13) Radtchenko, I. L.; Sukhorukov, G. B.; Leporatti, S.; Khomutov, G. B.; Donath, E.; Möhwald, H. *J. Colloid Interface Sci.* **2000**, *230*, 272−280.
(14) Sukhorukov, G. B.; Brumen, M.; Donath, E.; Mohwald, H. *J. Phys. Chem. B* **1999**, *103*, 6434.
(15) Shchukin, D. G.; Radtchenko, I.; Sukhorukov, G. B. *Mater. Lett.* **2003**, *57*, 1743.
(16) Troitsky, V. I.; Matveeva, N. K. *Thin Solid Films* **1998**, *327*−*329*, 659−662.

MA0346557