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NANO- AND MICROPARTICLE DISTRIBUTION ON SOLID AND FLEXIBLE SUBSTRATES – PART II

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ABSTRACT. By using the self-assembling process, it is possible to generate a large number of various structural organizations in which individual elements get together into regular patterns under suitable conditions. Two-dimensional self-assembled networks placed on solid and flexible substrates were obtained from solutions containing nano- and micro sized polymer spheres by evaporating the solvent in proper environmental conditions. The entire procedures are uncomplicated and they had been demonstrated as readily reproducible. The parameters used during of the process are as well very easy to control.

Key words: *nanotechnology, self-assembly, nano/microparticles*

INTRODUCTION

Many materials properties change radically at small length scales, because the phenomena, that occur at the nanoscale level can lead to the creation of materials which may display new properties in comparison to the properties they exhibit on a macro scale level. Numerous research fields are able today to study and develop different categories of materials that demonstrate distinctive properties due to their small dimensions. A large interest is focused today on the colloid science, which has given the opportunity to enlarge the number of materials with practical relevance in the field of nanotechnology. Some of the most common nanotechnological applications of different types of nano- and micro scaled materials consist of particle insertion in cosmetics, food products, paints and different categories of plastic materials, which can be used for instance in food packaging, cloth making or for coating various surfaces and furthermore for producing various types

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of surfaces, fuel catalysts and also disinfectants [1, 2]. Within this paper are presented several methods, which were used to obtain two-dimensional self-assembled networks placed on flexible substrates from solutions containing nano- and micro sized polymer spheres.

RESULTS AND DISCUSSION

Self-assembly is considered the basic principle which generates spontaneous and reversible structural organizations, in which fractions or disordered components of a primary system form organized structures or patterns. The colloidal particle integration sequence into defined flexible constructions is also based on the self-assembly approach. The mimicking procedure of molecular self-assemblies and as well the integration of nanoparticles into clusters are based in general on van der Waals forces [6], electrostatic interactions [3], hydrogen bonding [3], dipole–dipole interactions [3] and capillary forces [4].

The transfer of polystyrene microbeads to the PDMS (polydimethylsiloxane) film has generated a non-closely-packed monolayer on the PDMS surface, showing good results for relatively large-sized microspheres (1-3 µm), due to the fact that the spheres sink into the polymer film during the process (Figure 1).

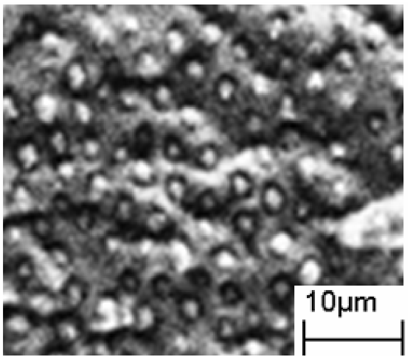

Figure 1. Polystyrene microbeads partially sunk into the PDMS film

This technique however did not yield good results when using small-sized microbeads (200-800 nm), because they do not behave in the same manner. These beads also sink into the PDMS film, but are incapable of maintaining a homogenous plane level (Figure 2).

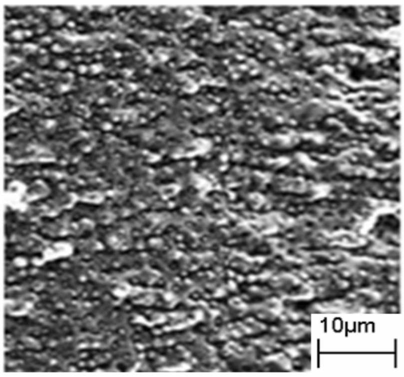

Figure 2. Polystyrene nanospheres transferred onto the PDMS film

A major disadvantage for this approach is that the stability of the spheres is relative, even for large-sized microbeads sunk into the PDMS film. Particularly when the structure is bent, some of the microbeads jump off the film leaving the surface filled with holes (Figure 3).

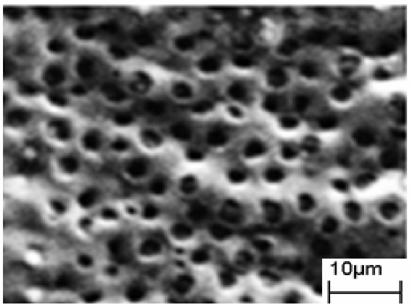

Figure 3. Polymer surface filled with holes after microbeads jumping

Through the dipping technique, a well-distributed monolayer of highly ordered, hexagonal closely-packed microbeads can be generated. The dipping speed has a strong influence over the monolayer formation and as a result a high dipping speed may lead to a multilayer deposition over the substrate, while a lower dipping speed might not be adequate enough for generating a close-packed monolayer. The main disadvantage of this process is that it requires a relatively long time (few hours) to complete for larger flexible probes (40-50 cm foils) and large volumes (depending of the sample characteristics) of suspensions. Another drawback to this technique is that the microspheres will deposit themselves along both sides of the substrate and not only on the substrate itself, as well as on the walls of the beaker, leading to a waste of material, especially problematic for expensive suspensions.

For the situation of particle self-assembling by means of suspension evaporation within the heating oven, the structure of the self-assembled aggregate depends on the rate of solvent evaporation. A slow evaporation of the solvent leads to ordered colloidal crystals. By tilting the substrates, the gravity acts as an additional force affecting the template and influencing the arrangement of the particles. Temperature plays as well a significant role in the monolayer formation process. As temperature decreases, the preference of the surface for the microbeads increases, due to the diminution of the thermal disorder in the forming monolayer. As a result, a cold liquid suspension was used to ensure a good distribution and a proper formation of the monolayer assembly. All substrates free of impurity were used immediately after they were cleaned.

CONCLUSIONS

Two-dimensional self-assembled networks and configurations made of nano- and micron-sized polymer spheres may be simply obtained from a solution which contains the polymer microspheres. Ordered configurations were obtained after the solvent evaporation under proper experimental conditions, or by transferring the spheres onto a thin flexible polymer film. The self-assembly procedure can be easily influenced by several parameters (e.g. temperature, dipping speed, vibrations) and as a consequence the sensitivity to environmental perturbations may lead to visible changes in the final structure or even compromise it. By using small amounts of materials and uncomplicated mechanical setups, these methods are very easy to use and the experimental parameters simple to control without requiring special working conditions. The substrate immersion into the colloidal solution is considered the best technique for generating a well ordered monolayer.

EXPERIMENTAL SECTION

The nano- and microparticle distribution onto flexible substrates was possible by using several experimental techniques. The first method used was the microbead transfer from a solid substrate to a flexible substrate.

1. The microbead transfer technique to a polymer (PDMS) film

For generating a non-closely-packed monolayer, the lift-up soft lithography technique [5] was used, in which a single layer of microspheres was transferred from a normal glass substrate onto the surface of a PDMS (polydimethylsiloxane) polymer film [6] (Figure4).

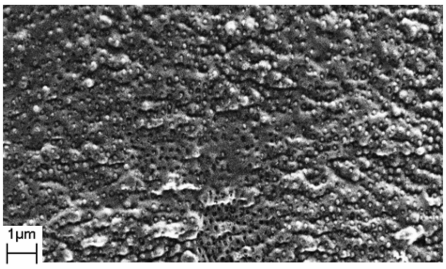

Figure 4. Microbeads transferred to a PDMS film

2. Substrate immersion inside a colloidal solution

Another way to generate the monolayer is to dip the flexible substrate into a colloidal solution and then remove it at a constant speed. In such a case, a perfect, well-distributed monolayer of highly ordered, hexagonally packed microbeads is formed over the surface (Figure 5).

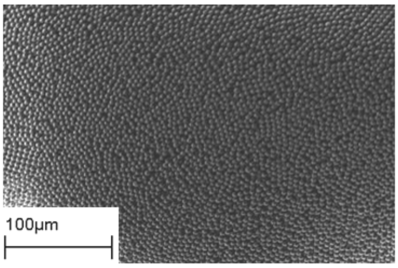

Figure 5. Uniform monolayer of polymer microbeads

3. The microbead deposition to a flexible polymer foil

For generating a two-dimensional monolayer on the flexible substrate (polymer foil), the solvent first was evaporated by using a heating oven (60℃ for 10h). The results can be seen in figure 6.

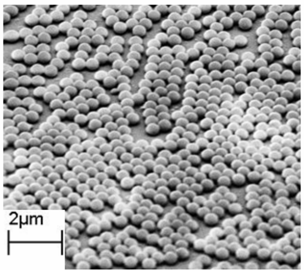

Figure 6. 2-D monolayer on a flexible polymer substrate by evaporating the solvent in a heating oven

Next was applied a solvent evaporation at room temperature (24h) by tilting the flexible substrates at a small angle (2-15°) between the normal surface and to the gravity, to induce particle arrangement (Figure 7). In this case to prevent the foil curving, the flexible material was held on a solid support (glass microscope slide or a polystyrene Petri dish).

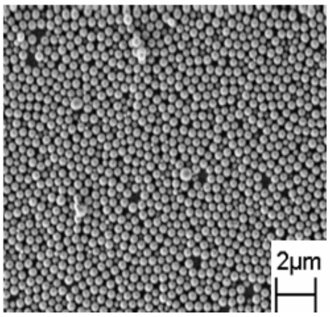

Figure 7. 2-D monolayer on a flexible polymer substrate by evaporating the solvent at room temperature

For the previous mentioned techniques, the following materials were utilized: microscope slides: 76x26 mm; cover-slips: 20x20mm; 24x24mm; 24x50mm; solvent: toluene; polyester (PET) foil; nanobeads and microspheres made of: poly (MMA), 200 nm, poly(styrene-co-MMA), 200 nm with 80% MMA and 20% styrene, polystyrene 1µm and polystyrene microspheres (Polysciences Inc.) with the following dimensions and concentrations presented in the table bellow (Table 1). The glass transition temperature for the polystyrene spheres it is in the temperature range of 95 ℃ – 1 05 ℃. [7]

Table 1. Polystyrene microspheres used during experiments

Diameter µm	**Concentration %**		
0.202	2.56	2.61	2.67
0.465	2.62	2.65	
0.477	2.69		
0.495	2.66		
0.987	2.54		
0.989	2.60	2.69	
1.091	2.76		
1.826	2.70		
5.658	2.65		

REFERENCES

1. H.M. Peter, B.H. Irene, V.S. Oleg, *J. Nanobiotechnology*, **2004**, *2*, 12.
2. F. Buentello, D. Persad, B. Erin, M. Douglas, S. Abdallah, P. Singer, *PloS Medicine,* **2005**, *2*, 300.
3. Y. Xia, G.M. Whitesides, *Soft lithography, Annual Review of Material Science*, **1998**, *28*, 153.
4. M.J. Madou, Fundamentals of microfabrication, CRC Press, New York, 2nd Ed., **2000**, 20, ISBN: 0849394511.
5. D. Manciula, Nano- and micro-structured polymer surfaces, Combined Faculties for the Natural Sciences and for Mathematics of the Ruperto- Carola University of Heidelberg, Germany, PhD thesis, 4th April, **2007**, 10.
6. J. C. McDonald, D.C. Duffy, J.R. Anderson, D.T. Chiu, H. Wu, O.J. Schueller, G. M. Whitesides, *Electrophoresis*, **2000**, *21*, 27.
7. D. Manciula, I.O. Marian, B.R.H. Mişca, *Studia Universitatis Babeş-Bolyai, Chemia*, **2008**, *1*, 48.