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In memoriam prof. dr. Liviu Oniciu

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

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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 procedure is uncomplicated and it has been demonstrated as readily reproducible. The parameters used for the duration of the process are as well very easy to control.

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

INTRODUCTION

Nanotechnology represents a large scientific domain and moreover a multidisciplinary field which combines varied concepts from different areas, such as supramolecular chemistry, applied physics, functional devices, materials and colloidal science [1]. Moreover, this area is mainly centered on the study, synthesis, design, and characterization of nanoscale materials, which are close related to many modern technologies in use today. Developments in the field of nanotechnology also serve as useful tools in other research fields such as biology, chemistry and physics [2-6]. Many materials properties change radically at small length scales. The phenomena, which occur at the nanoscale level, can lead to creation of materials that may display new properties in comparison to the properties they exhibit on a macro scale level. Many research fields are able today to study and develop different

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categories of materials that demonstrate distinctive properties due to their small dimensions. Carbon nanotubes [7], nanoparticles [8], nanorods [9], and various nanoscale materials [10] that can be successfully used for bulk and for medical applications, especially in nanomedicine [11] and microelectronics [12] give some common examples of such materials. In addition, a large interest now is focused on the colloid science, which has given the opportunity to enlarge the number of materials with practical relevance in the field of nanotechnology and numerous examples of nanotechnology in modern use can be mentioned today. Some of the most common nanotechnological applications of different types of nano- and micro scaled materials, consists of particle insertion in cosmetics, food products, paints and different category 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 of surfaces, fuel catalysts and also disinfectants. [13,14]. In this paper are presented several methods, which were used to obtain two-dimensional self-assembled networks placed on solid substrates from solutions containing nano- and micro sized polymer spheres.

RESULTS AND DISCUSSION

Self-assembling during solvent evaporation is a simple and low cost technique, frequently used for 2D and 3D assembly of colloidal crystals. It is possible to grow millimeter-sized arrays and to control the thickness of the array by varying the initial concentration of the suspension for each method used. The particle distribution results for each method used are presented next. The outcome generated by using the spin casting of the liquid suspension is depicted in figure 1. Good results were obtained for spheres of smaller sizes (200-500 nm) using this technique.

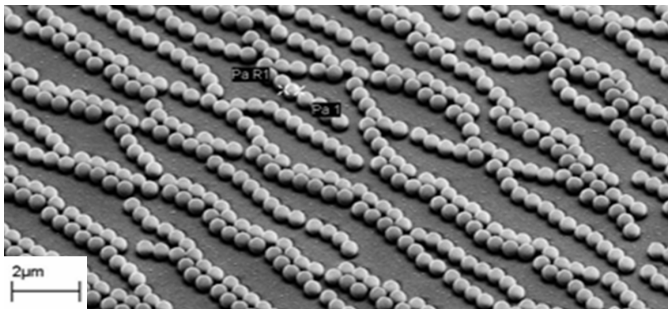

Figure 1. Polymer bead layer prepared by spin coating on glass substrate.

For the fabrication of a two-dimensional monolayer, the solvent was evaporated in two modes, either by using a heating oven (65℃ for 8h), or at room temperature (24h) by tilting the substrates at a small angle (2-20°) between the normal surface and gravity, to induce particle arrangement. Substrates free of impurity were used immediately after they were cleaned. 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 (figure 2).

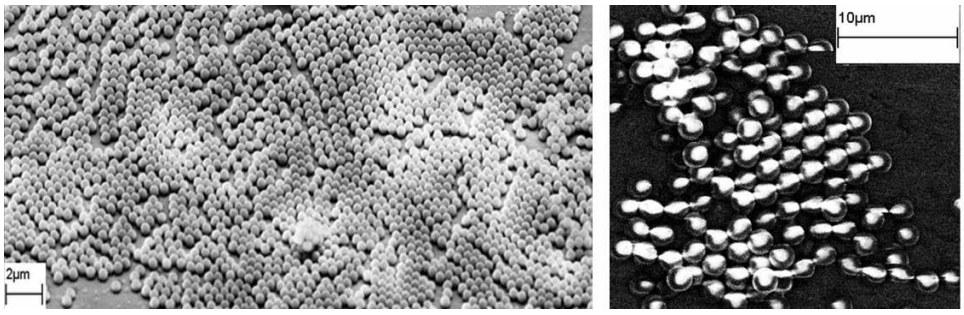

Figure 2. Monolayer formation following the suspension evaporation on glass (left) and polystyrene (right).

By tilting the substrates, the gravity acts as an additional force affecting the template and influencing the arrangement of the particles (figure 3).

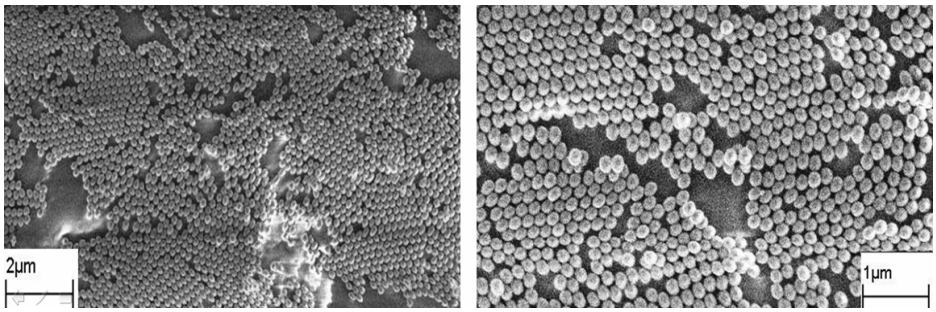

Figure 3. Monolayer formation following the suspension evaporation on tilted glass (left) and polystyrene (right).

The spacing and the distribution of the micro spheres are influenced by the sizes and deposition times of the micro beads. Longer deposition times lead to a close agglomeration of the beads, especially for spheres of

smaller sizes (200-500nm), without generating a monolayer of highly ordered hexagonal closely-packed micro-beads, while for spheres with wider diameters (3-5μ) an ‘‘island’’ agglomeration is generated. A shorter deposition time is responsible for increased space between the spheres on the substrate. The higher the tilting angle is, the more defects seen during the distribution, along with the multilayer formation. A high concentration of the suspension may also lead to defects in multilayer formation. Therefore, a small value (max. 2% solid content in the aqueous solution/suspension) has been chosen for substrate deposition via solvent evaporation.

By using the dipping technique, a well-distributed monolayer of highly ordered, hexagonal, closely packed micro beads can be generated (figure 4). To achieve a good distribution, particles must be monodispersed and must be absorbed onto the substrate. Several other conditions must also be met, such as a good suspension quality, a stable atmosphere around the cell and a good substrate quality. The dipping speed has a strong influence over the monolayer formation. 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.

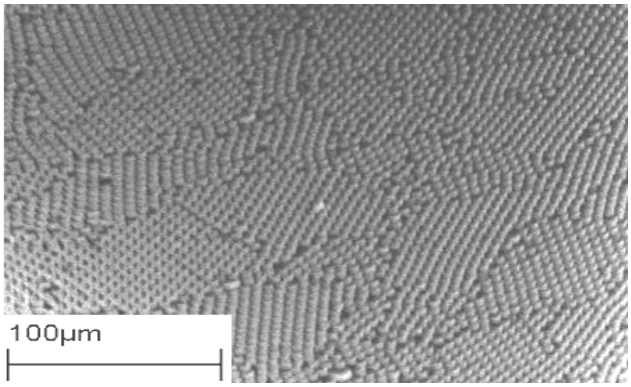

Figure 4. Particle monolayer produced on glass
by means of dip-coating process

The interactions of the particles that were deposited onto the surface can be attributed to electrostatic and lateral capillary forces that are able to influence adjacent particles and cause them to be attracted to each other, forming two-dimensional arrays of dense hexagonal packing. To form fine particle monolayer on large-sized areas, the quality of the suspension has to be also considered. After forming and drying, the micro-sized monolayer particle arrays display a radiant iridescent coloring when illuminated in white light.

CONCLUSIONS

Two-dimensional self-assembled networks and configurations made of nano- and micro-sized polymer spheres may be simply obtained from a solution containing the polymer spheres. Ordered configurations are obtained by means of solvent evaporation under proper experimental conditions. The driving force of the process is the capillary interaction, but the basic condition for having a superior self-assembled structure into an ordered pattern is the simultaneous presence of long-range repulsive and short-range attractive forces. The self-assembly procedure can be easily influenced by external parameters and therefore the sensitivity to environmental perturbations may lead to visible changes in the final structure or even compromise it. The solvent evaporation rate must not unfold too rapidly, to avoid generating instabilities and defects that may arise within the array. Particle concentrations and solvent composition may also play an important role in determining particle deposit morphologies. The substrate immersion within the colloidal solution was considered to be the best methods for preparing a high quality and well ordered monolayer.

EXPERIMENTAL SECTION

As solid substrates during the experiments, microscope glass slides and polystyrene Petri dishes were used. For preparing the substrates, which holds the micro bead monolayer, several consecutive steps were followed. A substrate clean up has been completed in the beginning of the experiment. All glass substrates were cleaned with a solution consisting of 3:1 mixture of sulfuric acid and 30% hydrogen peroxide, for 3h and then rinsed with de-ionized water and dried. The Petri dishes were made from clear polystyrene and were clean and sterilized. Several procedures were afterward tested to the successful distribution of the micro beads onto the substrates.

A two-dimensional monolayer of polymer beads (1μm) was prepared first by spin casting the liquid suspension onto the glass substrate at 1700 rpm for 20 seconds. The next effort for the fabrication of a two-dimensional monolayer array consists of accumulating the nano/micro spheres into a closely packed arrangement, onto both a cleaned glass surface and a dirt free polystyrene substrate (Petri dish) by evaporating the suspension into a heating oven at 65^{o}C for 8 hours. The suspension evaporation was also completed by tilting a glass substrate at room temperature at a small angle between the normal surface and gravity. Nano- and micro particle monolayer can also be obtained by using the particle self-assemble procedure on vertical substrates, by means of solvent evaporation as the driving force behind the fabrication process.

During the experiments, the following equipments and materials were used: inverted Axio Observer microscope (Zeiss), scanning electron microscope (SEM) Gemini 1530 (Zeiss), microscope slides (76x26mm), cover-

slips (24x50mm); polyMMA micro beads (BASF): particle size 200nm and solid content of 24.5%; polystyrene-co-MMA (BASF): particle size 200nm, 80% MMA, 20% styrene and 24.6% solid content; polystyrene (BASF): particle size 1µm, solid content: 9.4%; polystyrene micro spheres (Polysciences, Inc.). The concentrations of the polystyrene micro sphere solutions used for the duration of experiments are presented in table 1.

Table 1.

Polystyrene nano/micro spheres used during experiments

Diameter (µ)	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		

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