Influence of the Application of Von Kármán-Like Flows on the Colloidal Crystallization of Polystyrene Particles

M. Yoldi†, W. González-Viñas†, R. Sirera*, M.C. Arcos*
*†Dept. of Physics and Applied Mathematics // *Dept. of Chemistry and Edaphology*
Universidad de Navarra. Irunlarrea s/n, E-31080 Pamplona, Spain
e-mail: wens@fisica.unav.es

ABSTRACT
Self-assembled methods for the preparation of inverted opals is nowadays an important way to obtain 3D photonic crystals, since they offer some advantages as important as reduced costs. The main drawback of these techniques is the domain size achieved. We report a novel method of colloidal particles arrangement which reduces the formation of defects and increases the domain sizes. This method consists on assisting, by a von Kármán-like flow, the electrophoretic deposition of polystyrene particles. In this paper we study the effects caused by the application of such flow.
Keywords: colloidal crystalization, electrophoresis, flows, long-range order, defects.

1. INTRODUCTION

The concept of energy band is one of the most important in solid-state physics, since it allows to understand the properties of the materials from a microscopic point of view. Also, it permits the appearance of quasi-particles like electrons and holes, whose density of states is zero in the forbidden band. The energy gap corresponding to these forbidden band is the known band-gap. Although the periodicity of a material (so we have a crystalline material) is not a necessary condition to find energy bands, the translational invariance of the crystal is the key to a set of band properties very interesting ([1], [2]) for applications, through the Bloch theorem [3].

Photonic crystals are the counterpart of the electronic crystals, if the Bloch theorem is extended to consider magnetic fields in periodically changing refractive index materials. In this case, it is possible to obtain photonic band-gap materials [4].

In the last years, a great deal of attention has been paid to the fabrication of photonic crystals by self-assembled methods such as the inverted opals one. This method consists on the preparation of the colloidal crystal by ordering uniform colloidal particles, a subsequent deposition in the interstices of the material whose properties want to be reinforced in the scale imposed by the particles, and the removal of the colloidal particles.

Several techniques of arrangement have been used to obtain ordered arrays of colloidal particles [5]-[14], but none of them avoided enough the formation of defects to obtain colloidal crystals useful in the preparation of photonic crystals.

2. EXPERIMENTAL SET-UP

In this paper we report the preparation of arrays with particle size of 975 nm using an electrophoretic deposition assisted by hydrodynamic von Kármán-like flows [15]. This has been made in the cell showed in Fig. 1, in an aqueous-ethanolic medium (2:1 ethanol/water) with pH=10, (adjusted by adding aqueous ammonium hydroxide) and 0.33% PS w/V, using 5x5 mm glass slides covered by Indium Tin Oxide (ITO) thin film as substrates [16].
In this work, we characterize the rate of deposition and the domain size obtained in the growth of colloidal crystals assembled using simultaneously a constant applied voltage and a hydrodynamic flow.

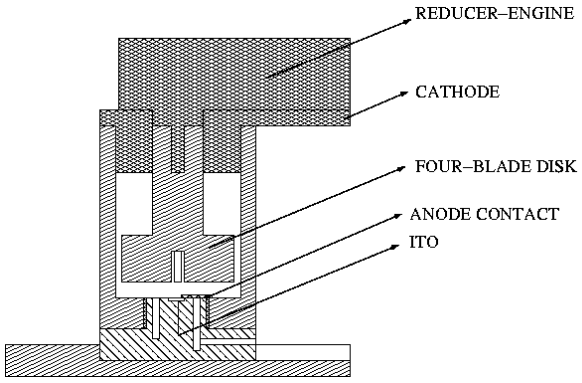

Figure 1. Sketch of the deposition cell.

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When the colloidal crystal was formed, a higher voltage during a shorter time was applied to partly coagulate the colloidal crystal obtained [17]-[19].
Smaller colloidal particles are of interest for nano-fabrication while larger ones allow to shift the stop-band in NIR and IR region. They have also the advantage to be easily visualized by optical microscopy, in case the number of layers is smaller than 5. Otherwise, their characterization is made by SEM. By image processing, the structure and order of the samples were determined from their optical and S.E.M. micrographies. Domains with hcp structures were observed, with negligible number of point defects and dislocations. Planar defects, which consisted on domain boundaries and cracks formed in the drying stage, were observed (Fig. 2).

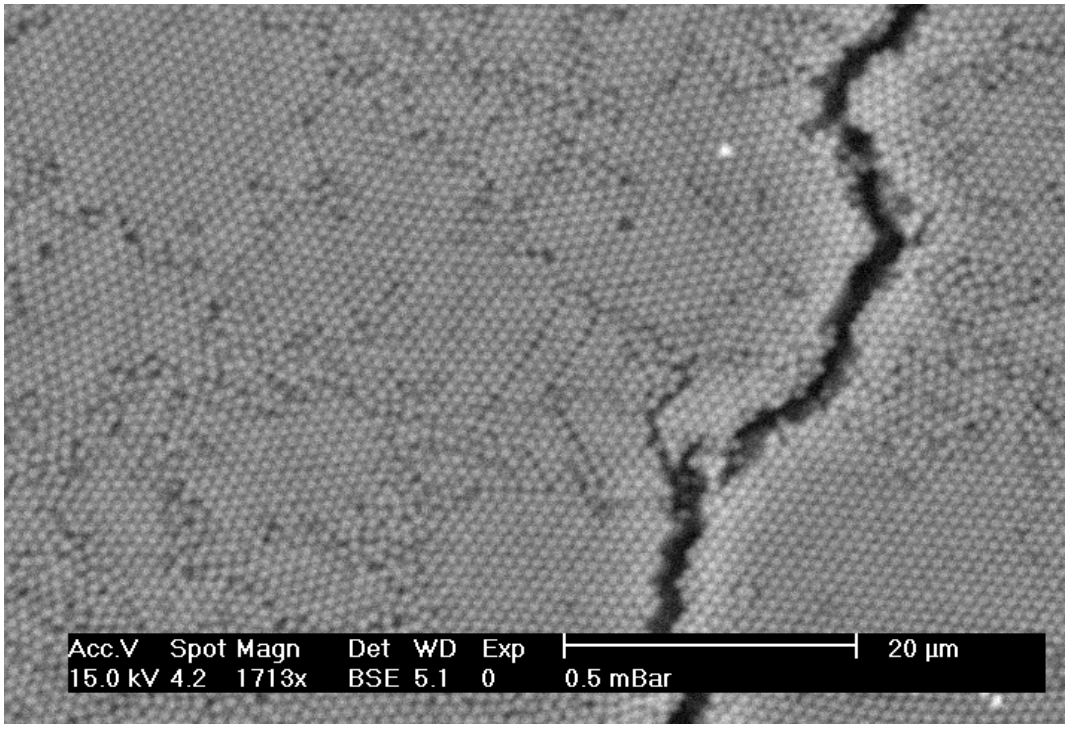

Figure 2. SEM typical image, with cracks and smaller crystallites.

According to Petukhov et al.[20], the capillary forces generated during the drying process destroy the long-range order and break the domains into smaller crystallites with slightly different orientations. As the misorientation angle between crystallites is small, we will consider them to be the same domain.

3. RESULTS AND DISCUSSION

In a previous paper [21] has been stated that the average size of domains <N> increases as the applied voltage does or the flow rate does. In this way, we can say that assisting the electrophoresis with hydrodynamic von Kármán-like flows carries to important quantitative improvements if the experiments with or without flows are compared

Cross-section micrographies of the samples were made to determine the number of deposited layers. The weight of a monolayer was also measured to calibrate a method based on weights as an easier way to the determination of the number of layers. Figure 3 shows the deposition rate versus the non-dimensional time of deposition at 10 V.

As it can be expected, the number of deposited layers increase with the time of deposition, but the higher flow rate, the smaller increase. This is a very interesting result, because we have realized that the screening effects of the adsorbed colloidal layers imposes an end to the electrophoretic deposition. This critical time (used to adimensionalize the times involved in the process) can be easily detected by the different rate of increase between the electrophoretic mechanism (faster) and the residual one, which consists on a natural sedimentation forced by the repulsion which carries out the negative electrode to the colloidal negative-charged particles. In this way, more time is needed to obtain the same number of layers if an hydrodynamic Von Kármán-like flow is applied, but bigger domain size is obtained.

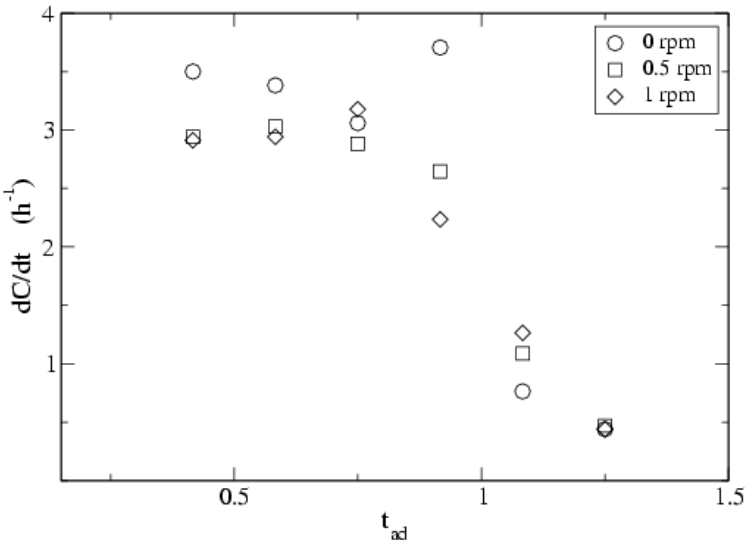

Figure 3. Rate vs. time of deposition.

The domain size was also determined at different deposition times. Results reveal how the average size of the domain is constant until a critical time (in our case around 12 h) from which it starts to decrease. This confirms the change in the mechanism of deposition. The typical size of domain in the electrophoretic stage, and the critical time have been used to obtain non-dimensional results. Figure 4 shows non-dimensional domain size versus the time of deposition. The inset shows the average size of domain in the electrophoretic stage.

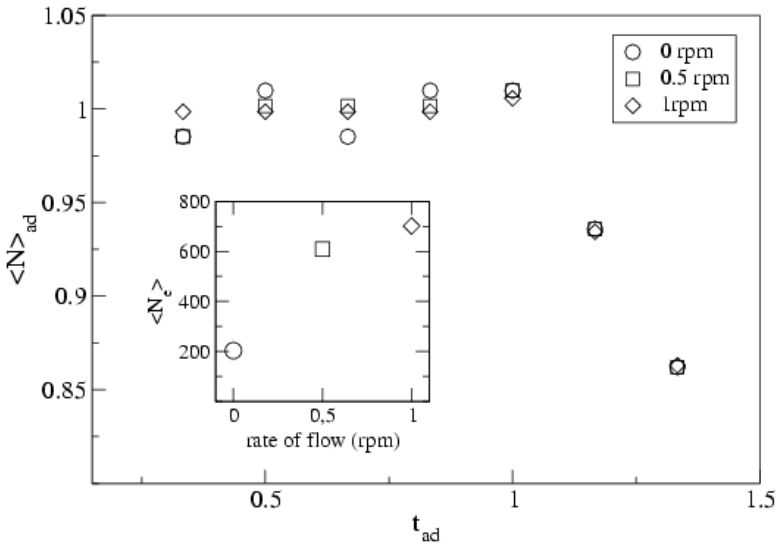

Figure 4. Non-dimensional average domain size. Inset: Average size of domains in the electrophoretic stage.

As it can be seen, in the electrophoretic stage, the rate of deposition is around three layers per hour and the order remains almost constant, meanwhile after the critical time the rate of deposition diminishes to less than one layer per hour, and the order is much smaller than before.

4. CONCLUSIONS

In this paper it has been shown that assisting an electrophoretic deposition by hydrodynamical flows, increases appreciably the long-range order in the colloidal crystal. The order acchieved is a major improvement to the non-templated colloidal crystallization of particles around 1 □m of diameter. In spite of this one can observe the

appearance of smaller crystallites and, also, of cracks both formed in the drying stage of the colloidal crystallization. We also have stated the fact of the existence of a critical time for the order. Actually, this time is also seen in the number of deposited layers, as an indirect confirmation of a change in the mechanism of colloidal crystallization.

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