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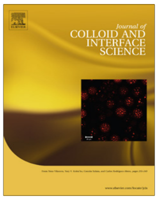

Short Communication

Wet formation and structural characterization of quasi-hexagonal monolayers

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ABSTRACT

We have presented a simple and efficient method for producing dense particle monolayers with controlled surface coverage. The method is based on particle sedimentation, manipulation of the particle–substrate electrostatic interaction, and gentle mechanical vibration of the system. It allows for obtaining quasi-hexagonal structures under wet conditions. Using this method, we have produced a monolayer of 3 μm silica particles on a glassy carbon substrate. By optical microscopy, we have determined the coordinates of the particles and surface coverage of the obtained structure to be 0.82. We have characterized the monolayer structure by means of the pair-correlation function and power spectrum. We have also compared the results with those for a 2D hexagonal monolayer and monolayer generated by random sequential adsorption at the coverage 0.50. We have found the surface fractal dimension to be 2.5, independently of the monolayer surface coverage.

Two dimensionally (2D) ordered arrays of colloidal particles are of large significance because they exhibit unique pattern-dependent properties. They also show promising application in a variety of technologically important areas such as photonics, electronics, optoelectronic devices, biological and chemical sensing, surface wetting, and energy conversion [1–3].

There are different methods for producing hexagonal-close-packed (hcp) monolayer. They can be divided into a few typical strategies: dip-coating, spin-coating, drop-coating, and self-assembly at the gas–liquid interface [1,4]. Also, there are many lithographic methods for producing patterned surfaces at micro- and nanoscale [5–7]. However, a relatively high cost and low throughput contribute to their low popularity. Also, to form a hexagonal structure of particles on a solid substrate, all the methods require drying the synthesized particle monolayer, which is not always possible or easy. What is more important, drying leads to the formation of a compressed structure with particles contacting each other, essentially making it impossible to control the particle–particle distance or surface coverage.

In this work we have proposed a simple technique for producing quasi-hexagonal monolayers with controlled surface coverage. The approach, in contrast to the above-mentioned, allows obtaining such layers under wet conditions. Consequently, the method is suitable for the preparation of quasi-hexagonal monolayers of non-contacting particles. By controlling the electrostatic particle–particle interaction, we can adjust monolayer parameters such as the surface coverage and mean distance between particles. We believe that the simplicity and low cost will allow for further modifications and improvements of the technique. In this paper, we have described just the basic experimental protocol, which we hope to be useful for a further development of the method. Moreover, we have characterized our formed structure by means of the pair-correlation function and power spectrum.

Our technique can be divided into four key stages shown in Fig. 1. In what follows we have assumed that the charge on the substrate can be reversed, particles are surface charged, and they sediment in a reasonable time.

In the first step, we have let the particles sediment to the substrate surface. To achieve that at a reasonable time, the ratio of the particle to solution density has to be large enough. Also, to prevent the formation of a multilayer structure or aggregates, the amount and concentration of the particle suspension need to correspond to the amount of the particles in the monolayer at the desired coverage. At this stage, we have to prevent localized adsorption of the particles in the ballistic regime that would result in a non-hexagonal structure of a relatively low coverage [8,9]. Therefore, we have maintained the same polarity on the particles and substrate. In our system, we have achieved that by adjusting the solution pH and ionic strength. As a result, the gravitational and electrostatic forces acting on the particles have balanced out at a distance from the substrate surface (see Fig. 1(a)).

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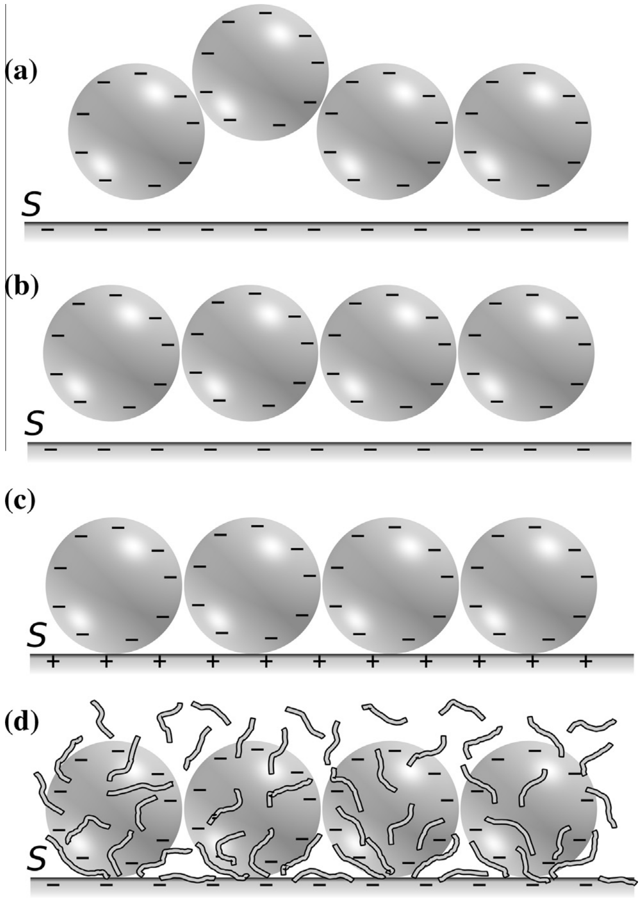

Fig. 1. Main steps in production of quasi-hexagonal monolayer: (a) particle sedimentation and initial packing, (b) monolayer packing after gentle tapping, (c) electrostatic immobilization of particles at substrate, and (d) polymeric stabilization of monolayer. Solvent molecules and counterions are omitted for clarity.

After the first step, because of the substrate surface heterogeneity, the particles can be adsorbed at different distances from the substrate or even form a locally multilayered structure. Therefore, in the second step, we have had to redistribute them into a quasi-hexagonal monolayer. For that, we have stimulated our system mechanically by gentle tapping with tweezers. The resulting structure is schematically presented in Fig. 1(b).

Once the quasi-hexagonal monolayer has been formed, we have adsorbed it irreversibly on the substrate surface. We have done that in two steps. First, we have electrostatically immobilized the particles. That has prevented the structure disintegration in the next step, i.e., the polymeric stabilization of the monolayer on the substrate surface. To immobilize the particles, we have reversed the polarity of the substrate surface (see Fig. 1(c)) to remove the electrostatic energy barrier for their irreversible adsorption. In our system, we have done that by applying a potential difference between the substrate and a platinum wire counter electrode immersed in the solution.

In the last step, we have stabilized the immobilized structure. We have done that by adding to the solution a binding agent. In our system, we have used a cationic polyelectrolyte (see Fig. 1(d)). Soon after the addition of the binding agent, typically after 2 min, we have reversed the polarization of the substrate again to enhance adsorption of diffusing polyelectrolyte molecules on it. Obviously, they have also adsorbed on the negatively charged particles, binding them to the substrate. Let us remark that the potential difference and time of its application cannot be too large. Otherwise, depending on the solution chemistry and catalytic properties of the substrate, nanobubbles of hydrogen can be formed at the substrate and disturb the monolayer structure.

In our experiments, we have used monodisperse silica particles of the diameter $2a = 3.02$ μm (supplied by microParticles GmbH) and density 1.85 g/cm^3, functionalized with carboxylate groups. To verify the particle size we have deposited particle monolayer on a glassy carbon (GC) disk. Then, we have dried it out and recorded its micrographs by means of a scanning electron microscope. We have determined the diameter to be 3.00 ± 0.01 μm, in good agreement with the supplier data.

As a substrate in our experiments, we have used a GC electrode of the diameter and surface area equal 3,00 ± 0.01 mm and 7.065 mm^2, respectively. We have characterized its surface after mechanical polishing [10] and rinsing with distilled water, by means of the atomic force microscopy. The root-mean-square roughness of the prepared surface has been relatively small, less than 5 nm. Therefore, we can assume that the substrate roughness is negligible in the scale of the particle size.

During our experiments, we have maintained a steady temperature of 298 K and pH = 5.8. We have carried out particle deposition in the cell presented previously [10]. This system allowed the use of a small amount of particle suspension and to reverse the GC potential. As described above, the amount and bulk concentration of the silica particle suspension were adjusted in such a way to prevent the formation of multilayer sediment and particle aggregates. In the case of 3.02 μm particles with the density 1.85 g/cm^3, the sedimentation speed in water is about 5 μm/s. Therefore, after a few minutes all the particles have settled down. To form a dense monolayer, we have gently tapped the cell several times. Then, we have applied a positive potential to the GC electrode (1 V with respect to the Pt electrode) to immobilize the particles on the substrate. To permanently fix the monolayer, we have added into the cell 0.15 M KCl solution with poly(diallyldimethylammonium chloride) (PDADMAC, Aldrich) at the concentration 500 ppm. Next, we have reversed the electric potential to let the cationic polymer adsorb on the electrode surface and to bind the particles to it. Finally, after about 20 min, we have rinsed the GC electrode with ultrapure water.

After particle deposition, to characterize the adsorbed layer, we have captured its microscopic images, using an inverted optical microscope (Nikon, Japan). To obtain a representative sample, we have taken seven digital images of the layer, with the total number of particles equal 18,000. During the microscopic examination, the GC substrate with the monolayer of silica particles has been under wet conditions. Next, we have analyzed the optical microscope images of the monolayer to determine the particle positions and surface coverage of the layer, $\theta = \pi a^2 N/S$, where N and S are, respectively, the number of identified particles and analyzed surface area. For that, we have used the Loco's Shire program, v. 2.8.24.0, with minor manual corrections. The coverage of the obtained monolayer has been $\theta = 0.82$. It is worth to mention that the surface coverage of such dense particle monolayers can be also determined from electrochemical measurements [10,11]. We have processed the collected particle coordinates with our Fortran codes to calculate the pair-correlation function [12] and power spectrum. To achieve a sufficient accuracy, we have analyzed more than 13,000 and 18,000 particles, respectively.

We have presented results of our calculations in Figs. 2–4. For a comparison, we have also presented pair-correlation functions and power spectra calculated for hexagonal [13] and random particle monolayers. We have obtained the latter from random sequential adsorption (RSA) simulations [12,14] at the coverage $\theta = 0.50$. Let us remind that in case of a hexagonal monolayer, the pair-correlation function exhibits a series of infinite peaks at definite distances. Therefore, for the sake of comparison, we have calculated a finite difference counterpart of the function, for thin rings