Fabrication of Ordered 2D Colloidal Crystals on Flat and Patterned Substrates by Spin Coating

by

Meneka Banik and Rabibrata Mukherjee*

Instability and Soft Patterning Laboratory, Department of Chemical Engineering,

Indian Institute of Technology Kharagpur, West Bengal, Pin 721302, India

Corresponding author: *rabibrata@che.iitkgp.ac.in
S1.0 Surface Charge of the colloids:

The PS particles and synthesized silica particles show a net negative surface charge, because of which an anionic surfactant (SDS) was added to the colloidal dispersion. Apart from SDS, a non-ionic surfactant (Triton-X) was also used for stabilizing the particles. However, the colloidal dispersion was rendered unstable on addition of a cationic surfactant (HTAB). This is attributed to coulombic binding of the positively charged head group of HTAB onto PS and silica particles; both of which have negative surface charge, as verified by measurement of zeta potential.

![Zeta Potential Distribution](image)

**Figure S1.** (A) The surface charge of PS particles was found to be -38.9 mV (B) Surface of silica particles was found to be -18.6 mV.

S2.0 HCP array formation by PS and Silica colloids on different surfaces:

Large-area HCP formation by colloidal particles depends on various factors; spin coating condition and dispersion concentration being the dominant ones. These factors have been optimized for different type (PS, silica) and size of particles (300, 600, 800 nm). Also, the nature of the surface governs the quality of the array formed and the dispersion concentration and RPM has to be modulated for obtaining large-area HCP ordering. The FESEM images for HCP formation by PS and silica colloids on different surfaces is shown in Figure S2, S3, S4 and S5.
Figure S2. HCP array formation by PS colloids \(d_D = 300 \text{ nm}\) on (A) glass (B) silicon wafer (C) PS film (D) PMMA film (E) PDMS film. Scale bar of each image is 1 µm.

Figure S3. HCP array formation by PS colloids \(d_D = 600 \text{ nm}\) on (A) glass (B) silicon wafer (C) PS film (D) PMMA film (E) PDMS film. Scale bar of each image is 1 µm.

Figure S4. HCP array formation by PS colloids \(d_D = 800 \text{ nm}\) on (A) glass (B) silicon wafer (C) PS film (D) PMMA film (E) PDMS film. Scale bar of each image is 1 µm.
Figure S5. HCP array formation by Silica colloids ($d_D = 350$ nm) on (A) glass (B) silicon wafer (C) PS film (D) PMMA film (E) PDMS film. Scale bar of each image is 1 µm.

S3.0 Morphology of Patterned Substrates

The AFM morphology of the PS, PMMA and PDMS films, patterned using the same stamps, is shown below in Figure S6. The grating patterns obtained with a DVD foil had a periodicity $\lambda_P \approx 750$ nm, groove width $l_P \approx 350$ nm and groove depth $h_P \approx 100$ nm. The films patterned with a CD foil had a periodicity of $\lambda_P \approx 1.5$ µm, groove width $l_P \approx 750$ nm and groove depth $h_P \approx 250$ nm. The patterns on all the three type of films was identical.

Figure S6. Morphology of patterned PS, PMMA and PDMS surfaces with Type 1 Geometry (patterned with DVD foil). For the replicated patterns, periodicity $\lambda_P \approx 750$ nm, groove width $l_P \approx 350$ nm and groove depth $h_P \approx 100$ nm.
**Figure S7.** Morphology of patterned PS, PMMA and PDMS surfaces with Type 2 Geometry (patterned with CD foil). For the replicated patterns, periodicity $\lambda_p \approx 1.5 \mu m$, groove width $l_p \approx 750$ nm and groove depth $h_p \approx 250$ nm.

### S4.0 Synthesis of silica colloids:

During the silica synthesis process two main reactions are involved:

1. **Formation of silanol group by hydrolysis**
   
   \[
   \text{Si}-(\text{OR})_4 + \text{H}_2\text{O} \leftrightarrow \text{Si}-(\text{OH})_4 + 4\text{R}^-\text{OH}
   \]

2. **Formation of siloxane bridges by condensation polymerization reactions**
   
   \[
   2\text{Si}-(\text{OH})_4 \rightarrow 2(\text{Si}^-\text{O}^-\text{Si}) + 4\text{H}_2\text{O}
   \]

Ethanol was first taken in a beaker and kept in a sonication bath, to which a pre-calculated amount of TEOS was added. After 20 minutes of sonication, 28% ammonium hydroxide was added as a catalyst to promote the condensation reaction. Sonication was continued for another 60 min to get a white turbid suspension. All the steps were conducted at room temperature. The silica suspension was allowed to stand for an hour and then dried and calcined to obtain silica powder. The average size of the silica particles was found to be $d_p \approx 350$ nm. The silica powder was re-dispersed in methanol.

### S5.0 Fractional Coverage of Surface with Colloids ($F_s$)

Fractional coverage ($F_s$) at a particular location is defined as the area occupied by the ordered colloidal domains relative to the total area of the region. Conceptually, this is similar to the term occupation factor introduced by M. Pichumani and W. Gonzalez–Vinas.\(^1\)

$F_s$ was determined using Pico Image Basic (Version 5.1), an integrated AFM and SPM imaging and analysis software package. The “Slice” feature of the software was used to render and further analyse the rendered AFM images. Here as an example we demonstrate three cases for fractional coverage measurement from 10\(\mu m\) x10\(\mu m\) area 2D AFM image
using the software. The first case is of a perfect monolayer HCP array where $F_s$ is equal to 1. The second case is of a partially filled monolayer, where $F_s$ is less than 1. And the third case is of a multilayer array. Here the $F_s$ obtained from the software is added to 1 and hence the net $F_s$ is greater than 1.

When a uniform monolayer HCP array is obtained over the entire surface, $F_s$ is equal to 1 (Figure S8).

![Figure S8: (A) 2D AFM image (B) Fractional coverage ($F_s = 0.99$) as calculated using the software.](image)

When a scattered array is obtained on the substrate, $F_s$ is less than 1 (Figure S9).

![Figure S9: (A) 2D AFM image (B) Fractional coverage ($F_s = 0.23$) as calculated using the software.](image)

When a multilayer is obtained, the bottom layer is considered as a uniform layer and the area covered by the top layer is calculated from the software. This is then added to 1 to get the fractional coverage (Figure S10).
Figure S10: (A) 2D AFM image (B) Fractional coverage ($F_s = 1.25$) as calculated using the software.

References:
1. Pichumani, M.; González-Viñas, W. Spin-coating of dilute magnetic colloids in a magnetic field. *Magnetohydrodynamics* **2011**, *47*, 191–199.