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Structure and physical properties of colloidal crystals made of silica particles

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ABSTRACT

The relationship between the particles size distribution of colloidal crystals and the structure and physical properties of the resulting 2D colloidal crystals is presented in this work. The colloids were constituted of silica sub-micron spheres with different size distributions comprised between 150 and 520 nm, synthesized by the Stöber method and assembled in one monolayer through the Langmuir–Blodgett technique. Optical and wetting properties of the resulting crystals were studied by different techniques – UV–visible spectrometry, spectroscopic ellipsometry and contact angle measurements. They were related to the crystal structure which was analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The conservation of orientational and translational orders over a large area is found for crystals with narrow particle size distribution. Optical interference bands in the transmittance spectra are linked to the crystal periodicity and the presence of optical anisotropy is attributed to distortions in the film generated by the deposition process. Moreover, large particle size distribution results in the most hydrophobic crystals. Thus the physical properties of the colloidal crystals can be tailored or tuned by controlling the particle size distribution and the deposition parameters.

1. Introduction

Photonic crystals (PhCs), which are defined by a refractive index periodicity in the sub-micrometer to micrometer length scale, have been broadly studied and developed in the last few years [1–3] and a peak in the number of publications was reached in 2008. Because of the easiness of production and the presence of either incomplete or full photonic gap, PhCs with a periodicity in 1 [4] or 3 dimensions [5,6] are the most common ones. Nevertheless 2D PhCs [7] encounter also a growing interest because they represent an intermediary state between 1 and 3D PhCs from a theoretical point of view. In addition, the so-called 2D PhCs are intrinsically related to the concept of "surface" and therefore, this topic deals with optical phenomena, but also with all kind of interactions as those treated in surface science in which the crystalline order plays a specific role, such as tribology (friction and wear), contact angle, surface chemistry and filtering. Also, we can find 2D PhCs in nature with different optical effects – iridescent Morphos butterfly wings [8], feathers [9], and beetles – and different purposes (defense, camouflage, mimesis, communication, alert, sun protection, etc.). They are imitated in nature-inspired devices [10] or biomimetic tools like structural colour inks [11], vapour sensors [12], self-cleaning surface such as lotus leaves [13] and anisotropic tribological coatings [14].

Artificial 2D PhCs are usually made by lithography [15] and self-assembly methods [16] and are used in many applications like lenses [17], large displays [18], 2D grating [19], polarizers [20], polarimeters [21], in photovoltaics [22] and as support for biosensors [23,24]. Ordered holes in high refractive index materials [15], colloidal crystals [25,26] also called crystal monolayers [27] or Self Assembled Monolayers (SAMs), and 2D colloidal gratings [28] constitute the various categories of PhC slabs, which consist in structures with 2D periodicity but with finite thickness [29].

In particular, SAMs made of particles with a narrow size distribution are fabricated by different techniques: Langmuir–Blodgett technique [30–32], dip-coating [33], vertical deposition [34,35] and spin-coating [27,28,36]. SAMs are characterized by their degree of structural arrangement which can be scaled from disordered to highly ordered one, from non-close-packed (NCP) [37] to random hexagonal close-packed one (RHCP) (mixture of fcc and hcp) [38] and finally from hexagonal non-close packed (HNCP) [39] to hexagonal close packed one (HCP).

In this work, we studied the structural effects of 2D crystals of silica particles on their physical properties. First, the influence of the particles size distribution on the final arrangement was studied. Mainly, three particle size distributions were synthesized and consisted of batches of bimodal polydisperse particles, multimodal polydisperse particles and unimodal monodisperse particles. Then samples representative of the three different batches were selected

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and characterized in order to establish the relationship between the physical properties and their structure.

2. Experimental details

Silica particles were synthesized by a simple sol–gel process based on the Stöber method [40]. Ethanol and distilled water were first mixed together and a small quantity of TEOS was added to the solution. Upon a critical concentration of NH_4OH, the solution turned white due to the size of the particles, which becomes comparable to the wavelength of the visible light.

By changing the experimental parameters, three batches of different particle size distributions ranging from 150 to 520 nm were synthesized. The molar proportions in $TEOS:NH_4OH:H_2O:EtOH$ reactants were chosen so that batch 1 had an excess of ammonia and a lack of water (1:57:0:192), batch 2 and batch 3 had the same quantity of ammonia but batch 2 presented an excess of water (1:18:28:126 for batch 2 and 1:18:9:126 for batch 3). Finally amino-propyl-triethoxysilane surfactant (APTS) was introduced in the solution and the mixture was warmed up on a hot-plate at $70 \pm 5\,^\circ C$ for one hour. The same molar ratio of APTS:TEOS = 1:1 was applied in the three different recipes in order to ensure a complete coverage of the particles surface with the hydrophilic $-NH_2$ amine group coming from the surfactant and to further facilitate the fabrication of crystal monolayer through the Langmuir–Blodgett technique.

Substrates of about $4\,cm^2$ area made of commercial glass or cut from monocrystalline silicon wafers were cleaned in a Piranha solution (mixture of H_2SO_4 75 vol.% and H_2O_2 25 vol.%), rinsed with Milli-Q water and immersed vertically inside the Langmuir–Blodgett trough (KSV Minitrough) filled with Milli-Q water. The synthesized sub-micron particles were diluted in a mixture of ethanol and chloroform (batch 1) or methanol and chloroform (batch 2 and 3) in a proportion of (1:3) and sonicated for 1 h before spreading the solution on the water surface in the Langmuir–Blodgett trough by dropping solution aliquots from a Hamilton syringe. The Brewster Angle Microscopy (BAM) device and the control of the surface pressure permitted to verify that the water surface was uniformly covered with a particle monolayer. After this step, the barriers were brought closer, with a constant rate of 10 mm/min up to a surface pressure of $5\,mN\,m^{-1}$. The substrate was lifted from the trough with a speed of $2\,mm\,min^{-1}$ at constant pressure [21,41], dragging on its surface a monolayer of silica sub-micron particles. Particles representative of the different batches were assembled in colloidal crystals and the resulting samples were called SAM1, SAM2 and SAM3, the index referring to the respective batch (see Table 1).

The morphology and size of the silica sub-micron particles and the assembly structure deposited on glass were observed with an environmental Scanning Electron Microscope Quanta 200 FEI which ensures a non-destructive characterization since no conductive coating modification of the sample is necessary. An accelerating voltage of 15 kV was applied and the emission current was set to 100 μA. The pressure inside the chamber was adjusted to 0.64 Torr.

The characterization of the surface topography was carried using a XE-70 AFM system from Park Systems. The measurements were conducted in non-contact mode, which allows the characterization of the samples by minimizing the particle-tip interaction. The samples were scanned over an area of 5 μm × 5 μm, at a frequency of 0.20 Hz.

The optical characterization consisted in measuring the transmittance spectra and the optical anisotropy of the samples.

The transmittance was measured with a UV-2101 PC UV–Vis Scanning Spectrophotometer (Shimadzu), between 200 nm and 800 nm in normal incidence using non-polarized light. The reference for each sample was the bare glass substrate.

We used a standard phase modulated ellipsometer in transmission mode, working in the UV–Visible range, to complete the optical characterization by measuring the linear birefringence (*LB*) and the linear dichroism (*LD*) of the sample. In the case of small anisotropy, the Mueller matrix M for a non-depolarizing and linearly anisotropic uniaxial sample at normal incidence with its principal axis at $\phi = 0^\circ$ reduces to [42]:

$$M = \begin{pmatrix} 1 & -LD & 0 & 0 \\ -LD & 1 & 0 & 0 \\ 0 & 0 & 1 & -LB \\ 0 & 0 & LB & 1 \end{pmatrix} \qquad (1)$$

where

$$LB = LB_{\max} = \frac{2\pi d \cdot (n_O - n_E)}{\lambda} \qquad (2)$$

and

$$LD = LD_{\max} = \frac{2\pi d \cdot (\kappa_O - \kappa_E)}{\lambda} \qquad (3)$$

n_O and n_E are the ordinary and extraordinary refractive indices, and κ_O and κ_E are the ordinary and extraordinary extinction coefficients, d is the thickness of the sample and λ is the wavelength.

In the setup, the sample could be rotated in its plane (azimuthal angle, ϕ), describing a complete circle, with a minimum step of 1°. The anisotropy axes of the samples were evaluated by performing several spectral measurements of *LD* and *LB* for different azimuthal angles of the sample. Thus, by rotating the sample and performing a scan over a wavelength range between 280 and 750 nm, the values of $LB_{\max}$ and $LD_{\max}$ could be determined. More details of the transmission ellipsometer setup can be found elsewhere [43].

The measurements of contact angle of water drop on the sample surface were realized in dynamic advancing mode a short time after the sample preparation. The surface of the SAMs, a silica substrate and APTS coated silicon wafer were investigated. An average drop volume of deionised water of 30 μl was added at a rate of 0.6 μl/s at the air-sample interface, at a temperature around 25 °C and humidity about 48%. The evolution of the contact angle of the water drop in contact with the sample surface was recorded every second.

3. Results and discussion

3.1. Langmuir films

The film formation at the water surface of the Langmuir trough (Fig. 1), shows different structures when the lateral pressure Π increases, depending on the particle batch. BAM images correspond to surface area of about $3850\,\mu m^2$. At this magnification, when Π is close to zero, SAM1 looks quite homogeneous SAM2 shows large white stripes, probably due to layers overlapping and SAM3 clearly presents particle domains with different contrasts. Just before lifting the substrate, SAM1 surface has changed and show contrasted lines over a uniform background which may indicate layers overlapping (the pressure may be too high), and the domains are still visible on SAM3. The interpretation of the BAM images can lead to improper conclusion. Indeed, the absence or presence of high contrasted regions is not related to the quality of the layer. The homogeneity of SAM1 and SAM2 surfaces observed from BAM images is better than SAM3 one but it has no signification about the crystallinity of the layers. The order level in the layer will be determined from SEM images in Section 3.2.2.

According to BAM images, the domains in SAM3 are about 550 to $2200\,\mu m^2$. The formation of particle domains [44] occurs during the deposition of solution drops on the water surface and depends