



Fabrication of stabilized colloidal crystal monolayers



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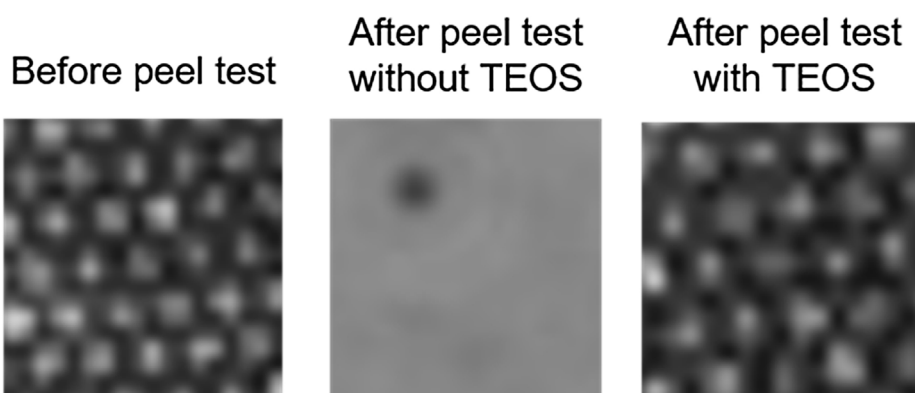
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HIGHLIGHTS

- We developed a simple method to make colloidal crystal monolayers more mechanically robust using the sol-gel reaction of tetraethylorthosilicate.
- The method was found to be applicable to silica particle layer-by-layer films.
- The desirable properties of the film are unaltered by the treatment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 August 2016

Received in revised form 2 November 2016

Accepted 22 November 2016

Available online 23 November 2016

Keywords:

Colloidal crystal

Microspheres

Tetraethylorthosilicate

Monolayer

Robust

layer-by-layer

ABSTRACT

A recent report described a very simple and rapid method to prepare colloidal crystal monolayers by rubbing spherical particles between two rubber plates [Park et al., *Advanced Materials*, 26 (2014) 4633]. Here we describe a commensurately simple extension of Park's procedure to prepare films that are much more robust, yet retain the overall structure of the colloidal crystal monolayer. The procedure produces solid necks that connect pairs of particles and also connect particles to the solid. These connections between particles are achieved by first transporting liquid to menisci between the particles and then solidifying those necks by exposure to gas phase reactant and catalyst. We show that the stabilized films are much more resistant to removal of particles during a peel test. We also show that the stabilization method is effective on silica layer-by-layer films.

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1. Introduction

Colloidal crystal monolayers (CCMs) are films consisting of monolayers of organized particles. CCMs have a variety of appli-

cations, including anti-reflective coatings [1,2], surface enhanced Raman scattering films [3], and sensors [4], and are also used as templates for the production of patterned films. Ye and Qi have written a comprehensive review describing the many applications of colloidal crystals [5].

A recent article by Park et al. described an extremely simple method, "the rubbing method", for making CCMs [6]. In brief, spherical micro-particles are simply rubbed onto a rubber material or

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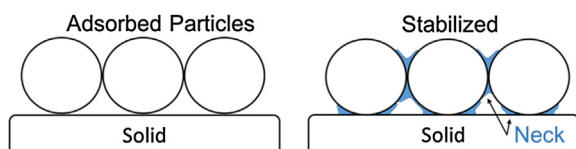


Fig. 1. Our objective is to introduce solid necks between particles and between the particles and the solid.

film. This extremely facile procedure can be used to very quickly coat large areas of objects and may be useful in many applications. Of particular interest to us is that CCMs affect the ability of bacteria to adsorb and colonize surfaces [7,8]. However, for this and some other applications, the particle film must be robust. For example, if the colloidal crystal is used to coat a catheter that is inserted into a human body, then the particles must remain on the catheter during handling, insertion, and subsequent use, both to be effective against bacteria and to avoid unwanted distribution of micro-particles within the body. Unfortunately, our experience is that the particles in CCMs produced by the rubbing method (and also by the convective [1] and surface deposition [9] methods) are very easily removed simply by wiping a tissue or a hand against the solid. This makes them impractical for some applications.

The objective of this work is to develop a simple extension to the rubbing method in which CCMs are made robust (more stable) while maintaining the essential shape and organization of the constituent particles. The increased stability is assessed by a standard peel test. The lack of stability of the particles in colloidal crystals is due to the weak forces that hold the particles together and to the solid support. In the case of the rubbing method, these forces are probably capillary forces and van der Waals forces. Stronger forces and therefore greater stability can be achieved by increasing the work of adhesion or the contact area between the spheres (the formation of necks) as shown in Fig. 1. Several prior methods have been explored for increasing the stability of particles in the film. The most obvious method is to heat the film above the softening point such that molecular mobility is increased. This facilitates deformation of the particles and migration of molecules to form necks between particles, and between particles and the underlying substrate. Necks can be developed between polymer particles with low chain melting temperatures (T_g), simply by heating above T_g [8] as is done for latex paints [10], but for a shorter time such that the particle shape is not lost. For high-melting-point inorganic materials, such as SiO_2 , sintering requires a high temperature ($>1000^\circ\text{C}$) which may damage other components and introduce stresses that cause cracking [11].

Other methods for stabilizing colloidal crystals are hydrothermal treatment [12] and vapor deposition – either chemical vapor deposition (CVD) [13] or atomic layer deposition (ALD) [14]. Both CVD and ALD are very effective at stabilization and offer good control of thickness, but require strictly anhydrous conditions [12] and may be time consuming to produce strong and therefore thick connections.

Here we describe a method of stabilization (see Fig. 2) that is based on the widely-implemented sol-gel process [15]. This method is similar to that used previously by Vossen et al. to control the pore size in colloidal masks for creating metallic nanoparticle arrays [16]. After the particle array is formed, we clean the sample with O_2 plasma, which also creates hydroxyl groups that are the reaction sites for the sol-gel process. A small droplet of liquid tetraethylorthosilicate (TEOS) solution is infused into the surface film to produce capillaries between particles, and then the film is exposed to a vapor consisting of NH_4OH , H_2O , and ethanol to form a sol-gel, and then finally heat treated to form solid necks. Sepa-

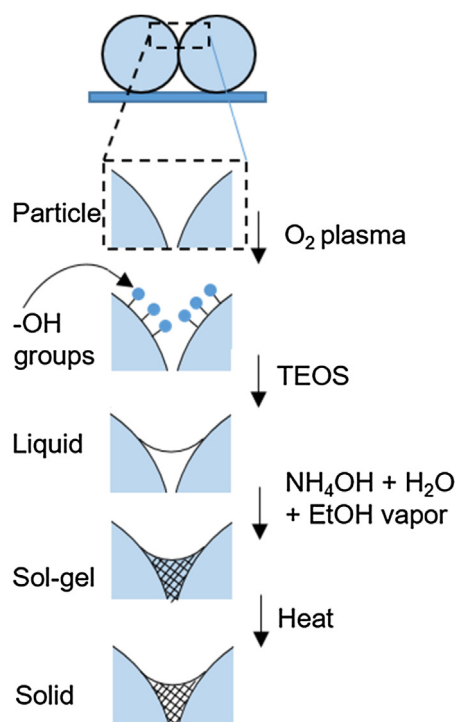


Fig. 2. Schematic of the TEOS method.

rate delivery of liquid and gas components allows us to first create the desired structure of necks by capillary forces in the liquid phase and then to maintain the neck structure by reaction gas-phase reactants only. This procedure is very simple and rapid and has only one liquid-phase step. We find that it dramatically increases the stability of particles within the colloidal crystal monolayer.

We also applied our method to silica layer-by-layer (LbL) films. LbL deposition has found application in pressure sensors [17], catalysis [18], biosensors [19–21], electrochromism [22,23], second harmonic generation [24,25], photovoltaics [26,27], and narrow [28,29] and broadband [30] anti-reflection coatings. But in common with colloidal crystal monolayers, there is a significant challenge in making robust particle films via LbL deposition. While films of alternating polycation and polyanion layers are quite stable due to significant interleaving of the oppositely charged flexible polymer chains [31], films made of alternating polyelectrolyte and colloid layers can be removed with gentle abrasion [12]. This may be a consequence of reduced electrostatic interaction between the polyanion and the rigid colloid [32].

2. Material and methods

2.1. TEOS treatment

A schematic of the TEOS treatment is shown in Fig. 2. Samples were O_2 plasma treated (SPI Supplies, PA) at 100 W for 1 min to form reactive hydroxyl groups on silica surfaces. TEOS (Sigma Aldrich, MO) was diluted in ethanol as a carrier solvent. One concentration (5% (v/v)) was used for colloidal crystal samples and two concentrations (5% and 20% (v/v)) were used for silica LbL samples. Twenty microliters of this solution per 1 cm^2 area were pipetted onto the sample. The solution wetted the sample surface and then the ethanol was allowed to evaporate at room temperature. The TEOS should form necks between particles and between the particle and substrate as the ethanol evaporates. Samples were then placed in a sealed chamber with two separate solutions, 7M ammonium

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