Oscillatory barrier assisted Langmuir-Blodgett deposition of large scale quantum dot monolayers

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ABSTRACT

Depositing continuous, large scale quantum dot films with low pinhole density is an inevitable but nontrivial step for studying their properties for applications in catalysis, electronic devices, and optoelectronics. This rising interest in high quality quantum dot films has provided research impetus to improve the deposition technique. We show that by incorporating oscillatory barriers in the commonly used Langmuir-Blodgett method, large scale monolayers of quantum dots with full coverage up to several millimeters have been achieved. With assistance of perturbation provided by the oscillatory barriers, the film has been shown to relax towards thermal equilibrium, and this physical process has been supported by molecular dynamics simulation. In

addition, time evolution of dilatational moduli has been shown to give a clear indication of the film morphology and its stability.

KEYWORDS

Langmuir-Blodgett, Oscillatory Barriers, Molecular Dynamics, Quantum dot monolayer

1. INTRODUCTION

Functional nanoparticle (NP) films have burgeoning applications in the fields of computation, sensing, energy, and biology[1–4]. Fabrication of large scale NP monolayers is critical for expanding potential device structures and applications. Making use of inter-particle interactions, two-dimensional films can be assembled by methods including drop casting[5], spin casting[6,7], inkjet printing[8], electrostatic adsorption[9], solvent evaporation at the air/water interface[10–12], and Langmuir Blodgett deposition[13–15]. The latter two methods are widely applied for depositing monolayers. After dispersion of NPs on the air/water interface, both processes exert compression on NP assemblies, where one exploits evaporation of a non-miscible liquid and the other additionally employs mechanical barriers. The evaporation method drives monolayer formation depending on the monodispersity of the NPs, while Langmuir Blodgett (LB) technique uses a mechanical barrier to further regulate NP density, where dense films comprised of polydispersed NPs can be formed[16,17]. LB technique demands greater technical involvement, but offers precise control over the compression process and can provide abundant information on the mechanical properties of monolayers. Moreover, the LB method has the potential to deposit NPs on non-flat substrates[18], form controllable striped patterns[19], and deposit multilayers in a layer by layer fashion, making it promising for device manufacturing.

In this technique, compact and continuous films can be deposited at appropriate particle densities[20], typically identified by surface pressure-area isotherms (π -A curves). There are clear signs of phase transitions[21,22], determined by changes in the slope of π -A curves. However, surface pressure is rather unstable, especially for self-assembling NPs. Compression with a finite barrier speed is a non-equilibrium process[23], and the pressure changes over time. Moreover, surface pressure does not correlate well to the local density of NP assemblies due to the inherent morphological inhomogeneity of the constituting NPs. This is especially true for NPs with strong attractive interactions, which are very common among colloidal quantum dots (QDs). Large grains of NP assemblies can readily form without changing the surface tension near the Wilhelmy plate[24–26]. For these two reasons, a parameter other than surface pressure needs to be investigated and tuned in order to enhance the quality of the film being deposited. Given that phase transitions involve changes in the derivative of π -A curves, the dilatational modulus[27–29], which is proportional to the relative change of surface pressure with the change in trough area is a suitable candidate.

Deposition at non-equilibrium conditions usually result in voids[30,31] and fragmented domains[32] in the films. A rise in the surface pressure is not necessarily a result of an increase in the particle density, but rather compression among assembled NP grains and dislocations; likely resulting in a misinterpretation of the π -A curves. To address this issue in the past, successive compression cycles[23,25] have been applied showing improvement in film homogeneity and long range order. However, in these reports, the choice of starting/ending area is unclear and the selected range of area may extend to several different phases whose relaxation dynamics may vary significantly. On the other hand, the oscillatory barrier process that is used for measuring dilatational modulus is also a cyclic compression process, fixed around the target

area, allowing minimal variation in area. Compared to the method of successive compression, the relaxation occurring via the oscillatory barrier process corresponds to both; a well-defined particle density and phase.

In this work, we present the use of dilatational modulus for determining morphology of a film comprised of oleic acid capped lead sulfide (PbS) quantum dots (QDs) less than 5 nm in size and demonstrate a large area coverage of the QD films. The physics of such a process is further corroborated by molecular dynamic simulations.

2. EXPERIMENTAL

2.1 QD synthesis:

PbS QDs were synthesized using the hot-injection method[33]. In a typical synthesis, 0.758 g of lead acetate ($\text{Pb}(\text{Ac})_2$), 5 ml of oleic acid (OA) and 10 ml of 1-octadecene (ODE) were dissolved and degassed for 10 mins at room temperature and then an additional 10 mins at 60 °C. The solution was then heated to 135 °C under constant N_2 flow. Heating under N_2 or vacuum did not appear to have any noticeable change on the outcome of the synthesis. A solution of 0.2 ml of bis(trimethylsilyl)-sulfide (TMS) in 4 ml ODE was prepared in a glove box with a molar ratio of 2:1 Pb/S and was injected into the vigorously stirring solution at 120 °C. The solution was annealed at that temperature for 3 mins and then the temperature was lowered to 100 °C for another 15 mins. Post synthesis, acetone was used as the non-solvent for the purification step. The precipitated nanocrystals were then collected by centrifugation. These precipitated nanocrystals were re-dissolved in acetone and the aforementioned steps were repeated twice to remove all the unreacted reactants. After filtering via 1.0 μm PTFE membrane filters, these purified nanocrystals were then dispersed in toluene for further characterization. UV-vis

measurements were used to estimate the concentration of the QD solution at 1.9 g/L, where the corresponding molar concentration is 9.7×10^{-12} mol/ μ L or 5.8×10^{12} QD/ μ L. The concentration was calibrated to the reference sample (MKNano, MKN-PbS-T1500) with a known concentration using the Beer Lambert's law, where the extinction coefficient was assumed to be the same across several dilutions of QD samples at the lower wavelengths.

2.2 Langmuir Blodgett process:

LB deposition was conducted on a KSV NIMA trough, model KN2001, with a maximum trough area of 77.5 cm². Prior to each experiment, the trough was cleaned with toluene and ethanol, and the cleanness was verified by the bare compression of the subphase that was comprised of Millipore water (18.2 M Ω ·cm). The solution was injected on the subphase evenly. This is important to prevent local aggregation of these NPs. Compression was started 20 mins after injection of the solution at room temperature. Unless specified, the compression speed was 2 mm/min. The barriers were programmed to oscillate sinusoidally around the trough areas of interest. There is a proper range for the choice of oscillation amplitude. Low amplitude may not provide enough perturbation for film relaxation, while high amplitude will prevent retaining a specific phase of the film. The strain was set to 3 %, which is in the linear region from the strain sweep curve (Fig. S1 in Supplementary Material) and is also where no major barrier drift occurs. The frequency was set to 0.1 Hz (details discussed in the later sections). Time evolution of surface pressure and trough area were recorded. Sine waves were used for data fitting after performing moving average corrections. The moving average window corresponds to 10 s, which is the oscillation period. Various window spans were used to determine the time evolution of the dilatational moduli.

2.3 Molecular Dynamics simulation:

Each NP is modeled as a sphere comprised of a NP core and a shell (organic ligand), both of which are rigid. The interactions among the particles are modeled using a combination of van der Waals attraction[34] and Lennard-Jones form repulsion[35]. Attraction is the major contributor to particle self-assembly, while repulsion is introduced to prevent particles from colliding. A potential well perpendicular to the water/air interface is added as described in Ref[36] for investigating multilayer formation and allowing an extra degree of relaxation. The details of potential functions are included in the Supplementary Material. A periodic boundary condition is used on a square simulation box which contains 195 particles. Since the inter-particle spacing is critical to the pair potentials, all ensembles are relaxed as NPT ensembles coupled to a Nose-Hoover thermostat[37] and a Berendsen barostat[38]. The temperature is set to 300 K, with a fluctuation of 10 K. The size of the simulation box is changed with an amplitude of 3 % as the simulation progresses to simulate a faster pace of film compression and relaxation. The time step is 2 ps, and the simulation time is 15 ns for one cycle of compression and expansion.

3. RESULTS AND DISCUSSION

Fig. 1 presents π -A curves of the compression processes with oscillatory barriers applied. Along the process of finite speed barrier compressions, barriers were programmed to oscillate sinusoidally at the areas of interest. Examples of time evolution of surface pressure with oscillatory barrier can be found in Fig. 2. For each compression route, 15 minutes of barrier oscillation were applied after reaching the target area. In a typical curve, for example the one with 40 μ L QD solution, oscillations and drops in surface pressure during the barrier oscillation

processes can be clearly observed. In the low density regions, which correspond to large areas, the magnitude of oscillation almost coincides with the differential of the pressure curves, and the pressure drop is not significant compared to that in the high density region. A drop in surface pressure is an indication of film reorganization, probably due to nonequilibrium states formed during the finite-speed compression. The large drop in surface pressure at the high density region can possibly be attributed to a larger defect density or a higher probability of collapsing. With respect to the converging surface pressures with barrier oscillation (Fig. 2), a collapse is unlikely in the system of study, especially given the morphologies of deposited film. It is more probable that the oscillation serves as a perturbation that relaxes the film, promoting it from meta-stable states towards an equilibrium state. This approach towards equilibrium acts to increase the viscoelastic behavior of the film. As mentioned in the introduction, surface pressure can be unstable, especially at areas with high particle density. Without applying barrier oscillation, by directly compressing the film to a target area, a pressure drop can also occur. If one relies on the spontaneous pressure drop for film relaxation, a practical question will be posed on the required wait time before film deposition. Moreover, a set of morphological characterizations will be required to relate the stabilized surface pressure to film phase and deposition quality. Another advantage of using oscillatory barrier is that one can extract the dilatational modulus, which can be directly related to the phase of the film.

By analyzing surface pressure oscillating curves, the real and imaginary parts of the dilatational moduli can be evaluated. The average of the elastic moduli (real part) is plotted as a function of the trough area as shown in Fig. 1b. The elastic modulus dropped twice during the compression, once during the phase change from gas to liquid expanded (LE), and another from LE to liquid condensed (LC). To better investigate this process, different volumes of the same

QD solution were used for comparison and to test the robustness of our result. With different total number of QDs, the areas corresponding to the same average particle density varies, and therefore the onsets of surface pressure and the position of elastic moduli dips change. Both parameters are proportional to the volume of QD solutions, which confirms that the surface process is not primarily governed by trough area but by the density of the QDs. In the later part of the discussion, we use average inter-particle distances that are converted from the trough area and the number of QDs to compare results across experiments. To be noted, the average inter-particle distance is a measurement of overall density. It can only present local inter-particle distances when the film is close to the LC phase.

Fig. 3 shows dilatational moduli as a function of average inter-particle distance. Experiments with different volumes of QDs peaked at similar average inter-particle distances. All curves show that moduli decline with time. There are minor changes in the dilatational moduli as a function of time when average particle distances are large; whereas the time evolution of dilatational moduli is more significant as the inter-particle distance decreases. Since the dissolution of the QD film has been deemed unlikely, instead it appears that certain irreversible features may be forming, which may result from it equilibrating to the liquid compressed phase[39]. The convergence of the dilatational modulus indicates the film is approaching thermal equilibrium. As surface pressure relates to the first derivative of particle energy E as a function of distance (Equation 1), the elastic modulus relates to its secondary derivative (Equation 2), where A is trough area, π is surface pressure, ϵ is elastic modulus, u is energy of individual particle, and N is the number of particles in the trough.

$$dE = -\pi dA = d\left(Nu\left(\frac{A}{N}\right)\right) = u'\left(\frac{A}{N}\right)dA \Rightarrow u'\left(\frac{A}{N}\right) = -\pi \quad (1)$$

$$\varepsilon = \frac{d\pi}{dA} A = u'' \left(\frac{A}{N} \right) \frac{A}{N} \quad (2)$$

If the particle is insoluble and distributes homogeneously within the trough, the product of elastic modulus and particle density shall be related to the energy-distance function and is primarily a function of particle density. Also, only with this homogeneous distribution assumption, the chemical potential of water near the Wilhelmy plate can be representative, and its evaluation of surface pressure is valid. Examining experimental data in Fig. 3d, this assumption holds well for injection volumes over 40 μL at our set concentration (5.8×10^{12} QD/ μL), but diverges greatly when the number of QDs in the trough is lower. Nevertheless, when the film is in the gas or early LE phases (corresponding to large average inter-particle distances), this divergence is less noticeable. In this regard, inhomogeneity in the morphology of these QDs at the air-water interface starts to become severe in the later part of the LE phase and into the LC phase. Given the size of the QDs, appropriate compression should be conducted at the area corresponding to an inter-particle distance of around 6 nm (4.1 ± 1.1 nm QD diameter and 2.0 ± 0.8 nm edge-to-edge distance due to ligand). It is also shown in Fig. 3 that the dilatational modulus is greatest around 6.9 nm followed by a decline at 6.3 nm, which probably corresponds to the end of LC phase and the beginning of the solid phase.

Given the phase transition processes revealed by the dilatational moduli, in order to achieve a full monolayer, we first compressed the film to 20 cm^2 (for 40 μL of QD solution with set concentration), followed by 15 minutes of an oscillatory barrier process to allow relaxation to occur. For deposition, the substrate was first immersed, then 15 minutes of oscillatory barrier with 1 % strain (decrease in strain because final state had been reached) was applied to accommodate the area change as a result of substrate penetration, and finally pulled up to complete the transfer process. Large scale film morphology can be examined by Scanning

Electron Microcopy (SEM). Almost full coverage of the film is shown with scales of 1 mm and 50 μm , respectively in Fig. 4a and 4b. In comparison to deposition following direct compression to a target surface pressure (Supplementary Material Fig. S2), the substrate coverage and continuity is shown to be significantly improved. Higher resolution SEM image (Fig. 4c) shows a polycrystalline QD arrangement. Similar sized QDs are locally arranged in hexagonal patterns with grain sizes up to 100 nm. A small fraction of the lighter area is probably residual ligands (confirmed by Atomic Force Microscopy shown in Fig. S3 and S4). Since the barrier can geometrically confine the NPs at the air-water interface, our result affirms that LB is one of the few techniques to form large continuous films from NPs with large size dispersions (size dispersion 26.8 % as shown in Supporting Fig. S5). The use of this technique improves the film deposition quality in two ways. First, the dilatational moduli provided by oscillatory barrier studies have revealed the appropriate particle density for long range film formation. Second, the convergence of dilational moduli has served as an indicator for telling the degree of film relaxation which offers better control on time required to reach equilibrium before the deposition.

To further demonstrate potential relaxation processes after conventional direct compression, we applied the Langmuir-Schaefer technique to promptly transfer films to Transmission Electron Microscopy (TEM) grids with a silicon dioxide support film. This was done to directly compare deposition on TEM grids to that on a silicon substrate covered with native oxide. Since compression speed was higher in this particular compression, significant non-equilibrium was expected. As shown by the TEM image in Fig. 4d, parts of the film had voids and other parts were covered by double layers. Another direct compression run was followed by the oscillatory barrier process. Time evolution of the surface pressure and dilatational moduli convergence are

presented in Fig. 5. The decrease in both surface pressure and dilatational moduli suggest these defects were annealed, leading to full monolayer coverage, demonstrated in Fig. 4e.

Molecular dynamics simulation was conducted to explore the microscopic dynamics during the oscillatory barrier process. Ligand capped NPs were first dispersed in a simulation box, whose size was then changed uniaxially. During this simulated compression process, the surface pressure of the system increased (Animation 1 in Supplementary Material). Although the changing rate of the box size in the simulation is much larger than that of the real process due to limitation on the total number of simulation steps, this fast compression process can lead to states further away from equilibrium, which makes it an ideal system to study the formation and relaxation of nonequilibrium states. Relaxation can be facilitated by perturbation. As suggested by the previous experiments, one method is to perturb the local density of the NP film via changing the trough area. Therefore, we provide changes at areas corresponding to proper NP density in the simulation, but used a linear form of perturbation instead of the sinusoidal form in order to speed up the calculation. Fig. 6a and 6b plots the surface pressure and potential energy of the first 10^6 steps. As a result of perturbation, both variables oscillate. It is noticeable that the amplitude of pressure oscillation decreases as the process proceeds and so does the dilatational moduli. In this particular process, there are roughly three stages: from 0 to 0.2 μs , from 0.2 μs to 1.1 μs , and from 1.1 μs on, manifested by the drop of average surface pressure. The potential energy also decreases with time, indicative of an approach towards equilibrium. The time of the most significant energy drops coincide with the drops in surface pressure and dilatational moduli. Morphological information is recorded in Animation 2 in Supplementary Material. Shortly after the compression of the film, there are a number of defects in the film. With relaxation, the defects adjust locally. After further drop in surface pressure, the defect starts to propagate as the

film approaches equilibrium. Given the simplified potential energy function, simulation time scale, and limited number of particles, there are finite discrepancies between the modeled surface pressure and that of the experiment. The decrease in both surface pressure and dilatational moduli with time are in agreement with the experimental results. It is shown that film relaxation can occur when a real perturbation is applied. The results of a control simulation without areal changes are plotted in the same set of Fig.S6. In this simulation, the film was first compressed to the area equal to the average area in the simulation where oscillatory barrier had been applied, but no areal change was provided afterwards. The pressure and potential energy also dropped. This is in agreement with the experimental observation that film relaxation can occur spontaneously. However, compared to the case where oscillatory barrier is applied, the drop in pressure is slower and less significant, and this implies the perturbation provided by oscillatory barrier may provide energy that helps facilitate the relaxation process. With respect to amount of perturbation energy, there is an expected optimal range. For a frequency that is too large, significant energy is supplied to the system but the cycle time may be lower than the time constant of the relaxation process. As a result, the relaxation process cannot occur (Supplementary Material Fig. S6). When given a frequency that is too low, the energy supplied may not be enough for the defect to overcome traps in the energy landscape. Moreover, too low of a frequency will prolong the barrier oscillation process, which will lower the accuracy of the surface pressure reading due to subphase evaporation and QD dissolution/degradation. Due to limited computation resources, only frequencies that are orders of magnitude higher than the experimental ones are examined in the molecular dynamics simulation that suggests a lower frequency for relaxation to occur. In the practical experiment, the frequency is chosen to be high

enough to collect a reasonable number of cycles to obtain the time evolution of dilatational moduli, and yet low enough for relaxation to occur and to avoid barrier drifts.

4. CONCLUSION

In summary, we present the benefits of incorporating oscillatory barriers in direct compression when applying the Langmuir-Blodgett method for NP film deposition. First, dilatational moduli are shown to provide phase information as an alternative to surface pressure. By examining dilatational moduli as a function of average particle density, one can obtain an appropriate density and proper timing for depositing desired films. This can be especially helpful for self-assembly systems with unstable surface pressure when finite speed compression is applied. Second, the convergence of dilatational moduli can suggest the degree of film relaxation, which is important for forming continuous and large scale monolayers. Relaxation can occur during barrier oscillations as shown by both experiments and simulations. Although film relaxation can occur spontaneously to a certain degree, barrier oscillation can provide the perturbation that facilitates this process and the information provided by the dilatational moduli can indicate the degree of relaxation, which can help deposition of high quality NP monolayers.

Fig. 1. (a) π - A compression isotherm using oscillatory barrier with three different injection volumes of a set concentration (1.9 g/L), (b) elastic moduli extracted from (a) as a function of trough area. The ellipses shown in the inset (a) represent the pressure oscillation and drop as a result of barrier oscillations.

Fig. 2. Surface pressure dynamics with oscillatory barrier at different trough areas. The barrier oscillation experiment was done with a frequency of 0.1 Hz and an amplitude of 3 %. The curves correspond to a spreading volume of 40 μ L of 1.9 g/L QD solution in Fig. 1.

Fig. 3. (a-c) Dilatational moduli as a function of average inter-particle distance (core to core). A decrease and convergence of dilatational moduli with time of applied oscillatory barrier is shown pointed by the arrows. (d) Evaluation of the secondary derivative of energy-inter-particle distance function with oscillatory barrier measurement on different volumes of solution at set concentration (1.9 mg/mL) injected on the subphase.

Fig. 4. (a-c) SEM images of QD film deposited on substrate at different magnifications. TEM images of film deposited on silicon dioxide grid (d) at 25 mN/m with direct compression at 10 mm/min, and (e) after 15 mins oscillatory barrier after conditions in (d).

Fig. 5. Relaxation of surface pressure (a) and dilatational modulus (b) after a direct compression to 20 cm² with a barrier speed of 10 mm/min followed by an oscillatory relaxation.

Fig. 6. (a) Time evolution of surface pressure during the simulated compression process with oscillatory barrier. The surface pressure is smoothed as a moving averages every 200 steps (4 ns). (b) Time evolution of potential energy of the system, corresponding to a moving average

every 200 steps. Dashed lines in both panels are moving average of every 15000 steps (2 oscillation cycles). Blue dashed lines in both panels are moving average of every 2 oscillation cycles of a control simulation where no oscillatory barrier is applied.

Supplementary Material available: It contains data on surface pressure dynamics with oscillatory barriers and more comparisons of deposition results of this technique to that of direct compression by Scanning Electron Microscopy, Atomic Force Microscopy and Auger Electron Spectroscopy.

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