Highly Controlled Nanoparticle Deposition using the Langmuir-Blodgett Method

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[Progress Together]

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Coatings and thin films made from nanoparticles (NPs) are gaining recognition and use in various products and applications including displays, sensors, medical devices, energy storage devices and energy harvesting. Synthesis methods for nanoparticles [1] are already relatively well known, but to be able to utilize them in the applications mentioned above, NPs need to be transferred from the solution phase to a substrate's surface – often as strict monolayer or defined thickness multilayer. For this, controlled deposition methods are required. This white paper reviews the methods for forming nanoparticle monolayers at the air-liquid interface and their subsequent transfer onto solid substrates using the Langmuir-Blodgett and Langmuir-Schaefer methods. These methods can form high-density (poly-crystalline) monolayers on a wide variety of solid substrates, including conventionally challenging non-flat surfaces.

Methods for Nanoparticle Deposition

Common methods to fabricate nanoparticle thin films include Langmuir-Blodgett (LB) and Langmuir–Schaefer (LS) depositions [2], self-assembly during solvent evaporation, dip coating and spin coating. These methods are summarized in **Table 1**. As this white paper discusses only deposition of nanoparticles from suspension, the chemical vapor deposition methods commonly utilized with e.g. nanotubes and -wires, are not included in the comparison.

Most technologies that employ self-assembled nanoparticle monolayers require dense packing arrangements and, in many cases, that the particles are organized in regular arrays. Therefore, it is vital for a successful fabrication method to demonstrate the precise control over the particulate assembly kinetics.

The simplest method for nanoparticle deposition is the solvent evaporation technique. In this method the colloidal nanoparticle solution is first spread on the substrate. The solvent is then evaporated and the nanoparticles are thus stabilized on the substrate and held in place by a Van der Waals attraction. Marangoni flow during the evaporation of the solvent liquid leads to the so-called coffee ring effect, whereby more nanoparticles are deposited at the meniscus pinning line, often leading therefore to multilayered regions at the droplet edge.

Another relatively simple method is known as the Doctor blade method. With this technique, a nanoparticle solution is dispensed on the surface and a blade is used to spread the solution. The speed at which the blade tracks across the surface defines a drying front and influences the way in which the nanoparticles convectively assemble. This technique is also prone to multilayered assembly and non-flat substrate topologies can pose a problem.

The spin and dip coating methods are easy to perform and can avoid the occurrence of multilayer formation. However, strict environmental control is necessary and high density monolayers can prove elusive. By nature, the volume of nanoparticle suspension required for both spin coating and dip coating can render the technique unattractive when using rare or expensive materials, as a large portion of the suspension goes to waste.

The LB and LS deposition methods offer the possibility for excellent control over packing density; readily achieving close-packed monolayers whose crystallinity can extend over millimeters and centimeters. Lower volumes of colloidal solution are required and deposits can be made on conventionally challenging substrates (curved or hierarchical).
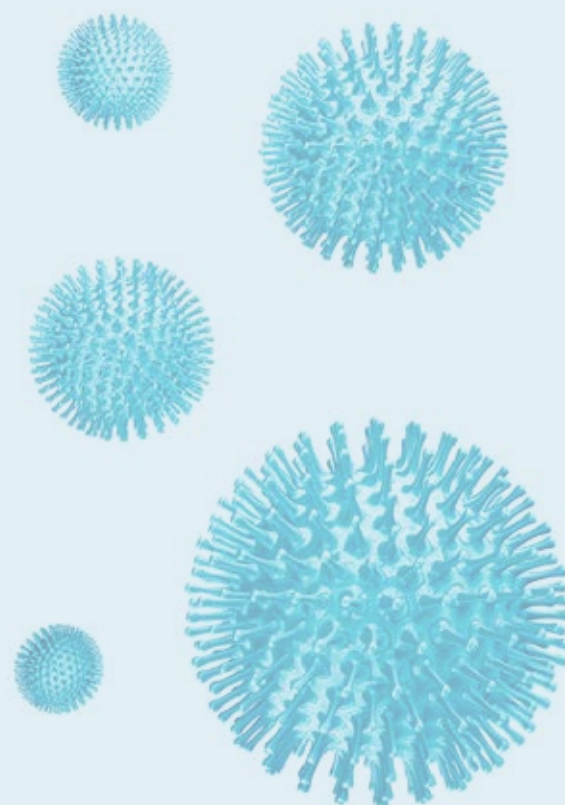
As a summary, with LB and LS methods, it is possible to:

• Precisely control the monolayer (thin film) thickness and packing density

• Achieve homogenous deposition over large areas

• Intentionally form multilayer assemblies with specific layer compositions

• Deposit to any kind of rigid, or even semi-rigid, substrate

• Efficiently use the available nanoparticle suspension

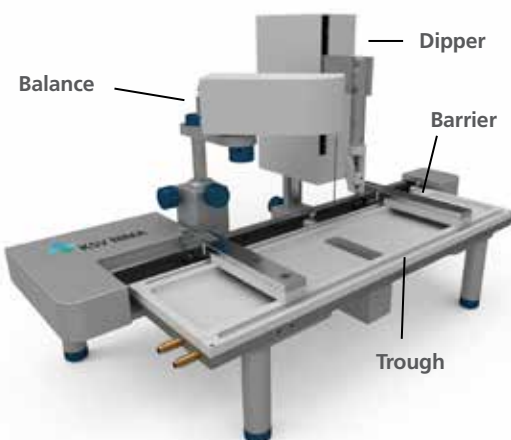The key principles of LB and LS deposition methods are discussed in more detail in the next section.

Method	Control of packing
Langmuir-Blodgett/Langmuir-Schaefer	High
Solvent evaporation	Low
Dip coating	Low
Spin coating	Intermediate
Doctor blade	Low

[Table 1] *Common methods to fabricate nanoparticle thin films and their control of packing.*

[Figure 1] *Langmuir-Blodgett instrument.*

Principles of Langmuir-Blodgett and Langmuir-Schaefer Techniques

The Langmuir-Blodgett (LB) technique is recognized as an elegant method to deposit well-defined monolayers and multilayers on a solid substrate [3]. Systems used nowadays are sophisticated, computer-controlled instruments enabling precise deposition. A typical Langmuir-Blodgett instrument is illustrated in **Figure 1**. The main part of the system is a Teflon trough that holds the subphase, on top of which the monolayer is spread. Hydrophilic Delrin barriers are used to compress the monolayer whilst a highly sensitive Wilhelmy balance is used to monitor the surface pressure and therefore the monolayer state. An electronic dipper is attached to the trough frame to enable the transferral of the monolayer from the air-water interface and onto a substrate.

Subphase and spreading solvents

Langmuir-Blodgett deposition starts with the selection of the subphase. Water has traditionally been used due to its high surface tension making it able to support monolayers of materials that have much higher density than water itself. Molecules possessing hydrophobic (water-hating) and hydrophilic (water-loving) parts naturally orientate themselves and become trapped at the air-water interface. In a typical Langmuir experiment, the molecules are well dispersed in a compatible volatile spreading solvent (e.g. chloroform or hexane) that is immiscible with the subphase. This solution is then spread on the water surface and the spreading solvent is left to evaporate. This facilitates the trapping of the molecules at the air-water interface.

Compression and deposition

Once a monolayer has been formed on the subphase surface, the surface pressure is measured as a function of the area available to each molecule/particle. An isotherm is recorded by compressing the film (reducing the subphase surface area with barriers) whilst continuously monitoring the surface pressure. An example isotherm is seen in **Figure 2**, where the surface pressure is presented as a function of the molecular area. A number of distinct regions, called phases, are apparent on examining the isotherms. First, the monolayers exist in the gaseous state (G) and on compression undergo a phase transition to the liquid (L) and solid state (S). If the monolayer is further compressed after reaching the S state, the monolayer will collapse – changing from a densely packed two-dimensional monolayer to form a disordered three-dimensional structure.
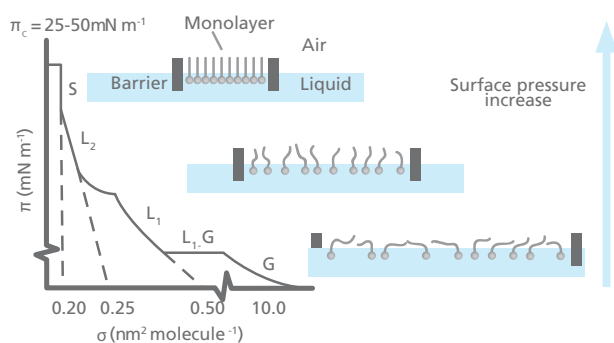
[Figure 2] *Langmuir Isotherm.*

In an LB deposition process (**Figure 3a**), a molecule or nanoparticle is first trapped at the air-water interface and compressed to the desired surface pressure or molecular density. Subsequently, the resulting film is transferred onto a solid substrate by dipping the substrate vertically through the molecular or nanoparticulate layer. A horizontal variation of the deposition method was developed by Langmuir and Vincent Schaefer, and is referred to as a Langmuir-Schaefer (LS) deposition (**Figure 3b**). Using either mode of deposition, the process can be repeated to fabricate multiple or alternating layer structures.
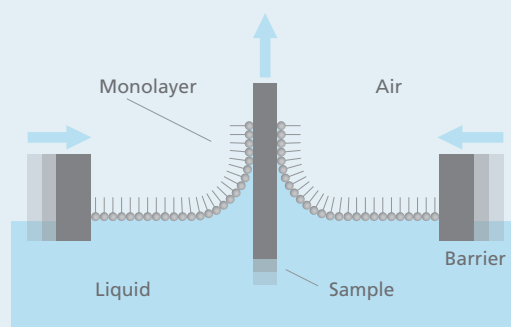
Formation of Langmuir Monolayer of Nanoparticles

In addition to being an excellent method for amphiphilic molecule assembly, the value of the LB technique for nanoparticle deposition has become apparent. The challenge of trapping non-amphiphilic particles, or those that are soluble in aqueous solution, at the air-water interface can be overcome by careful attention to the spreading method.

Spreading solvent plays a major role in nanoparticle deposition. The traditional method applied to form nanoparticle monolayers at the air-water interface has been droplet casting with an subphase-immiscible spreading solvent. However, some of the most commonly used spreading immiscible solvents such as chloroform or hexane can dissolve polymeric nanoparticles or their ligand shells and must therefore be avoided. In situations where a nanoparticle-compatible and a subphase-immiscible solvent is not available, low surface tension subphase-miscible solvents can be used, such as ethanol or methanol.

When subphase-miscible spreading solvents are used, extra care must be taken whilst adding the nanoparticle solution to the subphase surface in order to avoid sedimentation of the nanoparticles into the subphase bulk. One such approach with miscible spreading solvents is to use a flume addition method (as shown in **Figure 4**) [4, 5]. The use of a hydrophilic flume for subphase-miscible spreading solvents promotes the formation of a surface monolayer over sedimentation into the bulk, as vertical momentum of the colloidal solution is minimized and the three-phase contact line maximized. When a low surface tension nanoparticle solution meets a high surface tension subphase, Gibbs-Marangoni mass transfer at the interface leads to the formation of a two-dimensional monolayer. Over a short period of time the miscible components of the nanoparticle solution diffuse into the bulk subphase leaving behind the immiscible nanoparticle components trapped at the interface.

One drawback of the flume method is a loss of monolayer coverage, as the flume is withdrawn prior to compression. Nonetheless, by using this method with water-immiscible spreading solvents, the monolayer yield can remain high and well-ordered nanoparticle layers are formed. Variations of the methods described above include the use of syringe pumps or electrospraying to introduce an ethanolic nanoparticle solution to the subphase interface [6, 7]. Subphase composition also plays a role. As with traditional Langmuir experiments, water is the most popular subphase liquid. In some cases, however, the aqueous subphase can be an issue, as nanoparticles tend to agglomerate and later sink due to their comparatively high density. To reduce agglomeration, other polar subphases such as ethylene glycol and diethylene glycol have proven to be successful [8, 9].
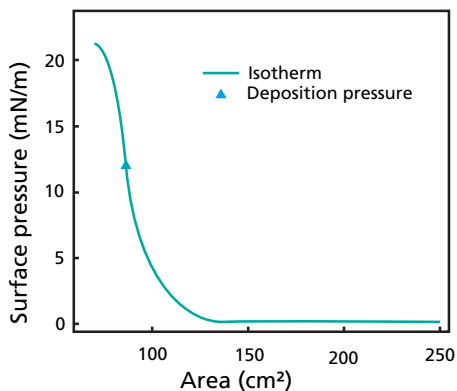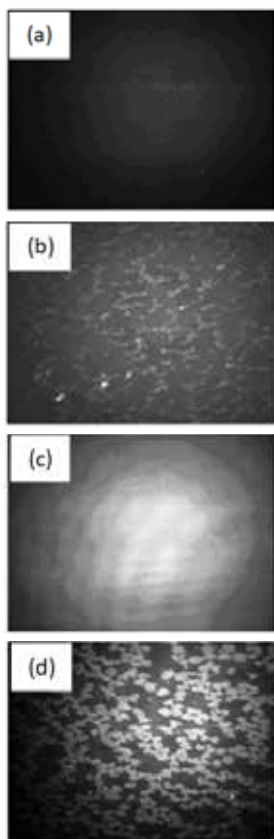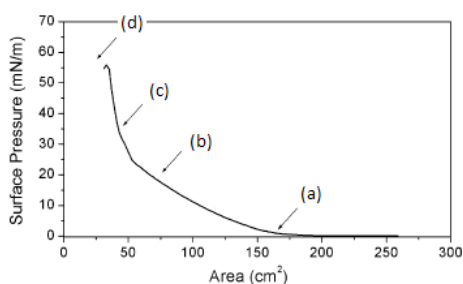

[Figure 3a] *Langmuir-Blodgett deposition.*
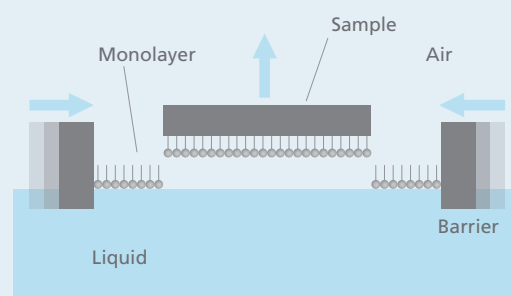
[Figure 3b] *Langmuir-Schaefer deposition.*
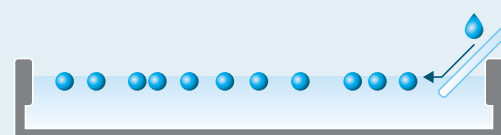
[Figure 4] *Floating nanoparticle monolayer formation with the help of a glass slide.*

[Figure 5] *Nanoparticle isotherm.*

[Figure 6] *Brewster microscopy images of Fe_3O_4 nanoparticles at (a) 2 mN/m (b) 20 mN/m (c) 35 mN/m and (d) after collapse. "Adapted from [10]. Copyright (2007) Americal Chemical Society".*

Compression of nanoparticle monolayer

After nanoparticle assembly at the interface, barrier compression can be started. A typical surface pressure vs surface area isotherm obtained during compression is shown in **Figure 5**. At the beginning, the compression does not cause a rapid increase in surface pressure, as particles are still relatively distant from each other. As the compression is continued further, a steep increase in surface pressure is observed indicating a close-packed monolayer. At a certain pressure the monolayer collapses. If the nanoparticles are at a wavelength scale this can also be visually observed. Deposition of the monolayer is performed at surface pressures approaching those of a close-packed monolayer but still below the collapse pressure. Compression of a nanoparticulate monolayer can be performed at a wide range of speeds. Performing rapid barrier compression prior to deposition can be helpful in order to avoid the nucleation issues described above. However, the cost of doing so is a loss of sensitivity to features in the surface pressure isotherm that indicate subtle monolayer phase changes. In practice, compression speeds of 10-20 mm/min are often sufficient.

One of the key advantages of the Langmuir techniques is that, when trapped at the air-liquid interface, a nanoparticle's mobility in two-dimensions can be very high, thereby facilitating high-quality self-assembly.

Another advantage is the possibility to visualize at an earlier stage the floating monolayer, making it possible to detect possible problems in the monolayer formation prior to deposition [9]. It is also possible to determine the suitable deposition pressure by simply looking at the monolayer formation kinetics. Brewster angle microscope has been utilized to visualize the iron oxide magnetic nanoparticles at air-water interface [10]. In **Figure 6**, the image of the monolayer is shown at different surface pressures. The optimal surface pressure point for deposition can easily be determined at 35 mN/m.

Nanoparticle monolayer deposition

When the monolayer is compressed to a desired surface pressure, it can be transferred onto a solid substrate. Traditional methods are the previously discussed Langmuir-Blodgett and Langmuir-Schaefer depositions. If hydrophilic substrates such as glass or silicon are used, the substrate is immersed into the dipping well prior to the spreading of the monolayer. For hydrophobic substrates, the dipping can be started with the substrate above the interface. A dipping speed of 1mm/min is recommended but, if surface pressure measurements remain stable, then higher speeds are possible. Counterintuitively, higher dipping speeds of up to 20 mm/min can yield good quality films. The barriers are programmed to move freely during deposition to maintain the target surface pressure over the course of the deposition. This is one of the advantages of the LB technique, as it ensures a uniform packing density over the entire deposition area. **Figure 7** shows nanoparticle arrays deposited with LB technique.
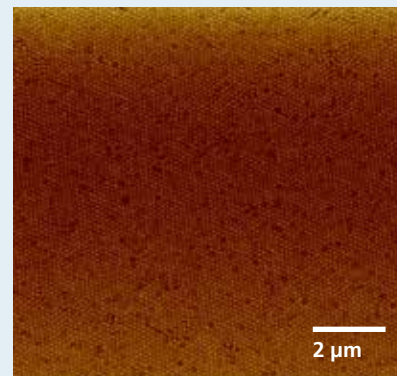
[Figure 7] *AFM image of a monolayer of 200nm-diameter polystyrene nanospheres deposited on a quartz substrate using the automated Langmuir-Blodgett technique. Copyright Dr. Alaric Taylor.*

Conclusions

The Langmuir-Blodgett and Langmuir-Schaefer deposition methods are widely used to fabricate controlled monolayers and multilayers of nanoparticulate materials. Unlike any other deposition method, LB and LS methods offer the possibility to control the packing density of the monolayers prior to their deposition. For this reason alone, the LB technique has a critical role in current advanced material science and nanotechnology. In addition, LB can be utilized with a vast selection of different types of nanoparticles on practically any solid substrate including non-flat ones. Due to its long history, the method is relatively well established and thousands of high quality academic publications have been written on it. However, as the Langmuir-Blodgett technique is still relatively new in the field of advanced material science and nanotechnology, there is plenty of room for new innovate research in this field.

[References and further reading]

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