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Langmuir-Blodgett Assembly to order Nanoparticles and Colloidal Objects

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ABSTRACT: *Bottom-up assembly of nanoparticles and colloidal objects pose a formidable challenge when processing devices. Speed, compatibility with various materials, defect tolerance and cost effectiveness are among the desired properties of a suitable nanoscale assembly process. In this regard, the Langmuir-Blodgett (LB) technique is a highly sought-after candidate which aids in arranging a large number of nanostructures on solid surfaces. This mini-review aims to provide a concise account on the LB technique and four distinct ways of how it allows to assemble systems made of nanoparticles and colloidal objects: namely, close-packed nanoparticle superlattices by compression, micrometer scale nanoparticle fingering patterns by dip coating, single nanoparticle lines by stick-slip deposition and one-step patterning of aligned nanowire arrays.*

KEYWORDS: Langmuir; Blodgett; Nanoparticles; Colloidal Objects; Self-assembly; Dip coating; Stick slip deposition; One-step patterning

INTRODUCTION

Irving Langmuir extensively studied fatty acid monolayers in the early 1900s and reported the correlation between pressure-induced force and phase transitions of long-chain surfactant monolayers. His study includes surface tension, molecular orientation, free energy, steric hindrance, and molecular rearrangement [1]. A *Langmuir thin film* comprised of a molecular monolayer (water-supported) can be obtained when amphiphilic molecules (dissolved in immiscible and volatile solvent) are spread on to a water surface. This monolayer's molecular density can be changed using compression or expansion of the film using a barrier; this film can then be transferred onto a substrate. Finally, solid-state thin film will be resulted after evaporating the water layer lying underneath.

Katherine Blodgett has extensively studied Langmuir's research and thus the Langmuir-Blodgett (LB) technique was born. In this technique either monolayer or multilayer deposition can be obtained by passing a solid barrier vertically through the air/water interface [2]. Films of organic compounds such as aromatic compounds, dyes, long-chain aliphatic compounds, porphyrins, and even large biological molecules were traditionally produced using the LB assembly and deposition techniques [3]. Similarly, nanoparticles and colloidal objects of different compositions, sizes, and morphology such as 2D monolayers of nanomaterials [4], nanorods[5], nanowires[6], and carbon nanotubes[7] and colloidal objects [8] have been produced using the LB techniques.

Macroscopic properties such as surface pressure can be tuned to control nanoscale assembly by controlling isothermal compression of fluid- supported nanoparticles and nanowires. Particle density, particle arrangement and spacing between particles can be controlled under optimized conditions. One of the distinct advantages is that patterning can be achieved without a predefined template ranging in size from a micrometer to 10s of nanometers. This renders LB compression technique ideal to form high density assemblies of nanocrystals as well as nanowires. Below are some ways how the Langmuir-Blodgett technique allows to order nanoparticles and colloidal objects and examples of how systems are assembled.

Close-Packed Nanoparticle Superlattices by Compression

Volatile solvents like chloroform or hexane are used to disperse the nanoparticles. A water surface is used to spread this solution dropwise to form an equilibrium surface pressure; this then evaporates resulting in a film of particles. A water filled trough comprising of a pressure sensor and a mobile barrier is used for this assembly process. Nanostructures with dense material composition can be supported due to the high surface tension property of water. The monolayer is laterally compressed at a controlled speed using the mobile barrier. Colloidal nanostructures can be condensed to form a solid, cohesive film via ordered arrays at high surface pressure.

Temperature gradient and intentional interface agitation can be used to control convective flow at low surface pressures. Metal nanoparticles with size dependent dispersion forces make use of this process giving rise to self-segregation of 2D nanoparticle superlattices[9] which are transferred using dip-coating on to solid substrate. Particle shape, particle size, and ligands are important factors which determine nanoparticle arrays. Close-packed superstructures can be formed using spherical nanoparticles. To obtain 2D lattices with alternative symmetries, faceted particles can be used [10].

Ag octahedral nanocrystals can be used to form LB films of interlocked architectures. Liquid crystals- like oriented films can be obtained using anisotropic structures like rods and wires. In nanorods, when the aspect ratio increases, the film adopts nematic like order since order is lost in one dimension [6]. Very high-density nanowire arrays which can accommodate flexible substrates can be obtained via versatile processing method which uses nanowire films deposited on to arbitrary substrates [6,11]. The interparticle distance of the nanoparticle film is changed by moving the barrier thus tuning the monolayer area. Transition between coupled and uncoupled arrays can be easily observed due to the reduction in interparticle spacing [10].

This proves that LB technique is a remarkable choice to construct large scale bottom-up materials. By controlling organization at nanoscale level, their collective properties can be easily programmed. They also have distinct applications such as Surface Enhanced Raman Spectroscopy (SERS), exhibiting large electromagnetic field enhancement and assembling high density electromagnetic hotspots for analyte adsorption [6,12-14].

Micrometer-Scale Nanoparticle Fingering Patterns by Dip Coating

Deposition process can be controlled to produce nanostructures with regular patterns by utilizing LB films. The free space between particles in low-density monolayers allows higher degree of motion during evaporation thus giving interesting de-wetting process properties. Facile dip coating process can be used to fabricate well aligned stripe patterns whose thickness, orientation and periodicity can be tuned at micrometer scale [15]. The meniscus formed between the monolayer and moving substrate can determine the resulting stripe pattern since nanoparticles will be loosely arranged. Thus, macroscopic patterning of nanoparticle arrays can vastly benefit from this process since it doesn't involve special templates. Precisely arranged nanoparticles stripes can be used to overlay microfluidic channels which can be used for quantitative chemical analysis. In this process, speed of the moving substrate controls evaporation rate and nanoparticles will be dried onto the substrate once they are carried off the surface film after segregation [16-19]. Chemical and physical nature of the monolayer is highly influenced by viscoelasticity, surface tension and fluid height.

Brush polymer monolayers inhibit conformation changes and hydrodynamic instabilities [20]. Lipid molecule Langmuir films inhibit unique patterns based on monolayer density [21]. The resulting stripe patterns can be changed for nanowires and nanoparticles during LB film transfer. E.g. Particle density on water surface which is controlled by the changes in surface pressure at the air/water interface influences stripe width. The stripes can be made thicker by compressing the film. The periodicity of stripe patterns is inversely proportional to the pulling speed of the substrates. Stripe patterns can also be regulated by tuning viscosity of the underlying liquid [22].

Single-Nanoparticle Lines by Stick-Slip Deposition

By transferring LB film onto a substrate where contact line is not favorable, control over nanowire and nanoparticle placement can be obtained. A completely wettable substrate is where water contact angle is <10°. When such a substrate is vertically pulled, perpendicular deposition of ordered micrometer scale strips can be obtained [15].

If water-contact angle is >20° where the substrate is hydrophobic, dip-coating can produce patterns of single particle lines which are parallelly directed to the meniscus. The meniscus will be formed between the partially wettable substrate and particle monolayer; contact line pinning takes place at this meniscus. Raising the substrate can drag this pinned meniscus and stretch it during the dip-coating process. Later, it breaks and reaches a new pinning site. Spatially resolved 1D arrays of nanoparticles are deposited due to this "stick-slip" motion. In other words, the "stick" event leads to nanoparticle line deposition and the "slip" event of the meniscus leads to the spacing between the lines.

Even if lithographic processing is absent, the size, shape and composition can be controlled in 1D array of nanoparticles due to this. Lines with particle diameters ranging from a few nanometers to micrometers can be produced over large areas. Particle density within the patterned lines can be tailored by changing nanoparticle density within the monolayer. This monolayer can undergo compression or expansion using an LB through which it helps to change particle concentration. Different surface pressures give rise to small groups of nanoparticle oligomers; high pressures yield 1D arrays. Branched and buckled lines can be produced using high compression. This allows hierarchical device structures to be designed. E.g.: 1D Au nanoparticles have been used to catalyze Si nanowire (vertical) array growth [23].

One-Step Patterning of Aligned Nanowire Arrays

When nanowires are in the micrometer range of lengths, controlled stick-slip deposition can be used to obtain aligned single-nanowire arrays from isotropic colloidal dispersion as well as 2D monolayers. Deposition along the contact line is influenced by capillary flow toward the meniscus when solvent meniscus is pinned on a substrate[24]. Nanowires can be directed along the flow direction by this capillary flow for an evaporating nanowire dispersion. In this unique situation, aligned arrays will be selectively deposited at the meniscus. A mechanical dipper can be used to program nanowire density and line spacing by regulating the sticking time and slipping distance respectively. The advantages of this method are, scalability, low cost, selective positioning of nanowires, minimal material consumption and direct production from a nanowire dispersion [22].

CONCLUSION

Using a tunable macroscopic property (e.g.: surface pressure) to precisely control nanoscale assembly of fluid-supported nanoparticles and colloidal objects, is the key feature of the LB technique. The isothermal, uniaxial compression of these monolayers (supported in fluid media) leads these nanostructures to assemble over a large area which can then be transferred to a solid surface. This low-cost technique helps to achieve controlled organization over assembly of nanostructures by allowing continuous variation in the spacing between particles, particle arrangement, and particle density when conditions such as substrate hydrophobicity, surface pressure and pulling speed are optimized. This technique is also highly practical since it enables the formation of highly dense assemblies of nanoparticles and colloidal objects even over unique surfaces. Patterning can also be achieved within micrometers to tens of nanometers range due to the dewetting properties of LB monolayers.

Conflict of interest

The author declares no conflict of interest.

Reference

[1] Langmuir, I.; Blodgett, K. B. A New Method of Investigating Unimolecular Films. Kolloid-Z. 1935, 73, 258–263.
[2] Blodgett, K. Films Built by Deposting Successive Monomolecular Layers on a Solid Surface. J. Am. Chem. Soc. 1935, 57, 1007–1022.
[3] Petty, M. C. Langmuir-Blodgett Films: An Introduction; Cambridge University Press: Cambridge, U.K., 1996.
[4] Song, H.; Kim, F.; Connor, S.; Somorjai, G. A.; Yang, P. Pt Nanocrystals: Shape Control and Langmuir-Blodgett Monolayer Formation. J. Phys. Chem. B 2005, 109, 188–193.
[5] Yang, P.; Kim, F. Langmuir-Blodgett Assembly of One-Dimensional Nanostructure. ChemPhysChem 2002, 3, 503–506.
[6] Tao, A.; Kim, F.; Hess, C.; Goldberger, J.; He, R. R.; Sun, Y. G.; Xia, Y. N.; Yang, P. D. Langmuir-Blodgett Silver Nanowire Monolayers for Molecular Sensing Using Surface-Enhanced Raman Spectroscopy. Nano Lett. 2003, 3, 1229–1233.
[7] Li, X.; Zhang, L.; Wang, X.; Shimoyama, I.; Sun, X.; Seo, W. S.; Dai, H. LangmuirBlodgett Assembly of Densely Aligned Single-Walled Carbon Nanotubes from Bulk Materials. J. Am. Chem. Soc. 2007, 129, 4890–4891.
[8] Vogel, N.; de Viguerie, L.; Jonas, U.; Weiss, C.K.; Landfester, K. Wafer-Scale Fabrication of Ordered Binary Colloidal Monolayers with Adjustable Stoichiometries. Adv. Funct. Mater. 2011, 21, 3064–3073
[9] Ohara, P. C.; Leff, D. V.; Heath, J. R.; Gelbart, W. M. Crystallization of Opals from

Polydisperse Nanoparticles. Phys. Rev. Lett. 1995, 75, 3466–3469.
[10] Tao, A.; Sinsermsuksakul, P.; Yang, P. Tunable Plasmonic Lattices of Silver Nanocrystals. Nat. Nano 2007, 2, 435–440.
[11] Whang, D.; Jin, S.; Wu, Y.; Lieber, C. M. Large-Scale Hierarchical Organization of Nanowire Arrays for Integrated Nanosystems. Nano Lett. 2003, 3, 1255–1259.
[12] Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. Self-Assembled Metal Colloid Monolayers: An Approach to SERS Substrates. Science 1995, 267, 1629–1631.
[13] Haynes, C. L.; Yonzon, C. R.; Zhang, X.; Duyne, R. P. V. Surface-Enhanced Raman Sensors: Early History and the Development of Sensors for Quantitative Biowarfare Agent and Glucose Detection. J. Raman Spectrosc. 2005, 36, 471–484.
[14] Jeong, D. H.; Zhang, Y. X.; Moskovits, M. Polarized Surface Enhanced Raman Scattering from Aligned Silver Nanowire Rafts. J. Phys. Chem. B 2004, 108, 12724–12728.
[15] Huang, J.; Kim, F.; Tao, A. R.; Connor, S.; Yang, P. Spontaneous Formation of Nanoparticle Stripe Patterns through Dewetting. Nat. Mater. 2005, 4, 896–900.
[16] Fitzgerald, S. D.; Woods, A. W. The instability of a Vaporization Front in Hot Porous Rock. Nature 1994, 367, 450–453.
[17] Cazabat, A. M.; Heslot, F.; Troian, S. M.; Carles, P. Fingering Instability of Thin Spreading Films Driven by Temperature Gradients. Nature 1990, 346, 824–826.
[18] Karthaus, O.; Grasjo, L.; Maruyama, N.; Shimomura, M. Formation of Ordered Mesoscopic Polymer Arrays by Dewetting. Chaos 1999, 9, 308–314.
[19] Chen, X.; Lenhert, S.; Hirtz, M.; Lu, N.; Fuchs, H.; Chi, L. Langmuir-Blodgett Patterning: A Bottom-Up Way To Build Mesostructures over Large Areas. Acc. Chem. Res. 2007, 40, 393–401.
[20] Xu, H.; Shirvanyants, D.; Beers, K. L.; Matyjaszewski, K.; Dobrynin, A. V.; Rubinstein, M.; Sheiko, S. S. Molecular Visualization of Conformation-Triggered Flow Instability. Phys. Rev. Lett. 2005, 94, 237801.
[21]LeGrange, J. D. Observation of Directional Pattern Formation near the Three-Phase Contact Line in a Langmuir-Blodgett Transfer Configuration. Phys. Rev. Lett. 1991, 66, 37–40.
[22] Tao, A.R.; Huang, J.; Yang, P. Langmuir-Blodgettry of Nanocrystals and Nanowires. Acc. Chem. Res. 2008, 41, 1662-1673
[23] Huang, J. X.; Tao, A. R.; Connor, S.; He, R. R.; Yang, P. D. A General Method for Assembling Single Colloidal Particle Lines. Nano Lett. 2006, 6, 524–529.
[24] Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. Capillary Flow As the Cause of Ring Stains from Dried Liquid Drops. Nature 1997, 389, 827–829.