High-Yield Spreading of Water-Miscible Solvents on Water for Langmuir−Blodgett Assembly

Hua-Li Nie,[†,‡] Xuan Dou,[‡] Zhihong Tang,[‡,§] Hee Dong Jang,[∥] and Jiaxing Huang[*,‡]

[†]College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China
[‡]Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States
[§]School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China
[∥]Rare Metals Research Center, Korea Institute of Geoscience & Mineral Resources, Deajeon, 305-350, Korea

S *Supporting Information*

ABSTRACT: Langmuir−Blodgett (LB) assembly is a classical molecular thin-film processing technique, in which the material is spread onto water surface from a volatile, water-immiscible solvent to create floating monolayers that can be later transferred to solid substrates. LB has also been applied to prepare colloidal thin films with an unparalleled level of microstructural control and thickness, which has enabled the discovery of many exciting collective properties of nanoparticles and the construction of bulk nanostructured materials. To maximize the benefits of LB assembly, the nanoparticles should be well dispersed in both the spreading solvent and on water. This is quite challenging since colloids usually need contrasting surface properties in order to be stable in the water-hating organic solvents and on water surface. In addition, many organic and polymeric nanostructures dissolve in those organic solvents and cannot be processed directly. Using water-liking spreading solvents can avoid this dilemma. However, spreading of water-miscible solvents on water surface is fundamentally challenging due to extensive mixing, which results in significant material loss. Here we report a conceptually simple strategy and a general technique that allows nearly exclusive spreading of such solvents on water surface using electrospray. Since the volume of these aerosolized droplets is reduced by many orders of magnitude, they are readily depleted during the initial spreading step before any significant mixing could occur. The new strategy drastically reduces the burden of material processing prior to assembly and broadens the scope of LB assembly to previously hard-to-process materials. It also avoids the use of toxic volatile organic spreading solvents, improves the reproducibility, and can be readily automated, making LB assembly a more robust tool for colloidal assembly and thin-film fabrication.
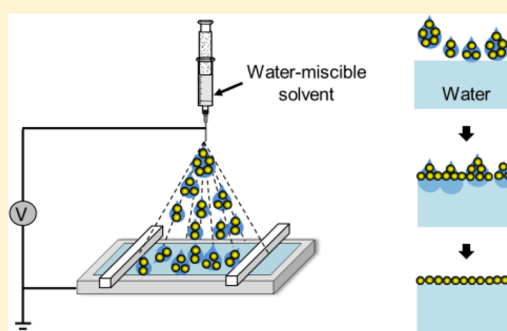
INTRODUCTION

Langmuir−Blodgett (LB) assembly is a nearly century-old but increasingly popular material processing technique that was initially developed to create molecular monolayers.[1−5] In a typical process, the molecules are first dissolved in a volatile, water-immiscible organic solvent and then spread onto water surface. A water-supported molecular monolayer is formed after the spreading solvent evaporates, which can be further compressed by barriers to obtain densely-packed molecular thin films and transferred onto solid substrates.[6] Analogous to molecular LB assembly, monolayers of colloidal materials of diverse shapes and material compositions have been demonstrated.[7−9] When optimized, LB assembly allows continuous tuning of particle density, spacing, and even their relative orientations in a monolayer as well as the number of layers in a thin film. In addition, spontaneous alignment and patterning of nanoparticles can be achieved without using any template, by tailoring the dewetting instability of the wet monolayer upon transferring to a solid substrate.[10,11] Due to such unparalleled capabilities of microstructural control, LB assembly has enabled

the discovery of many exciting collective properties of nanoparticles[12−14] and has been employed to construct nanostructured thin films for device and coating applications.[15−20]

To maximize the benefit of LB assembly, the nanoparticles should be well dispersed in both the water-hating organic spreading solvent and on water. This is quite a dilemma since colloids typically need to have contrasting surface properties to disperse in organic solvents and water. If the starting stock solution is in a different solvent than the one for spreading, the challenges become even greater since the colloids need to be simultaneously stable, or refunctionalized several times to remain stable in three different solvents. Some surface functionalization agents do allow nanoparticles to disperse in both water and organic solvents, at least temporarily. For example, one of the best demonstrated examples of LB colloidal assembly is metal nanoparticles coated with polyvinylpyrroli-

done (PVP).[8,10,11,16,21,22] Such nanoparticles, many of which have become commercially available, are typically synthesized in polyol solvents with PVP as the surface capping agent.[23] They disperse well in alcohol solvents after purification and are usually stored and processed in methanol or ethanol. Since these alcohol solvents are completely miscible with water, usually water-immiscible solvents such as chloroform have to be added to make them more spreadable on water surface. Higher chloroform content improves spreading but unfortunately makes the colloids much less stable as shown in Figure 1.
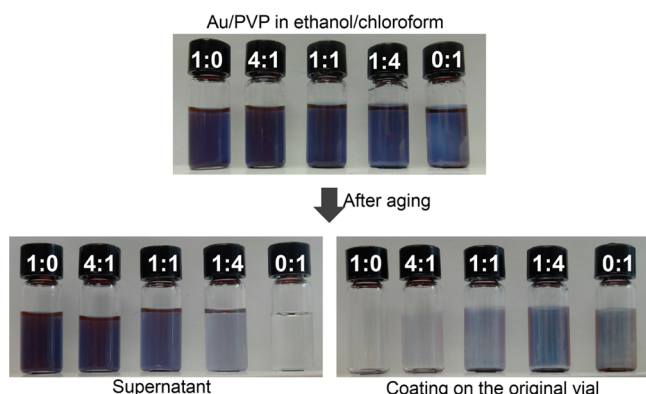

Figure 1. An example illustrating the colloidal stability challenge and dilemma during LB assembly. Au/PVP nanoparticles are stable in ethanol, which is water miscible and unsuitable for spreading. Typically, a volatile, water-immiscible solvent such as chloroform is added to the dispersions to make them spreadable. However, this results in significantly decreased colloidal stability. The photos of the dispersions before and after aging for a day clearly show that the colloids become increasingly unstable (and more likely to deposit on the wall of the vials) as the fraction of chloroform increases.

The Au/PVP particles are only temporarily dispersed in ethanol/chloroform mixtures, and they aggregate and deposit on the vial during storage. Uncontrolled particle aggregation disables the fine-tuning capabilities of LB technique on the microstructures of the final monolayer. Therefore, one would have to prepare the spreading solution on-demand and spread it immediately to avoid particle aggregation, which makes the process hard to standardize and scale up. In addition to the above-mentioned colloidal stability challenge, the use of organic spreading solvents also prevents the LB assembly of organic and polymeric nanostructures that can dissolve in those solvents. For example, polystyrene beads, a model system that has been routinely employed for colloidal assembly, can dissolve in common spreading solvents such as chloroform, methylene chloride, and toluene and therefore are very difficult to process by conventional LB technique.

The need for water-immiscible spreading solvent not only significantly increases the burden of preassembly material processing but also strongly limits the capability and scope of LB assembly. There are additional concerns about their toxicity. All these problems can be solved if more benign, water-miscible solvents, such as alcohols are used for spreading. Due to surface tension mismatch with water, alcohol droplets will partially spread on water surface before mixing. Indeed, they have been used to replace common spreading solvents for LB assembly of polymer colloids[24−27] and graphene oxide (GO) sheets[19,28] that would otherwise dissolve or aggregate. However, the obvious disadvantage of alcohol solvents is their intermixing with water, which tends to lose the majority of the spreading materials to

the water subphase.[24] In addition, the mixing behaviors of alcohol and water are quite complex and strongly dependent on the local alcohol concentration beneath the spreading droplets,[29] which is also dynamically changing. Therefore, spreading with alcohol solvents is not only a compromise between maintaining colloidal dispersity and suffering very low yield of surface deposition but also difficult to standardize.

If the intermixing problem of water-miscible solvents can be solved, LB assembly will become significantly easier, more standardizable, more scalable, and greener. Taking ethanol for example, when a droplet is dispensed onto water surface under gravity, it can mix with water in two ways. If the droplet is bombarding the water surface (Figure 2a), a large portion of its
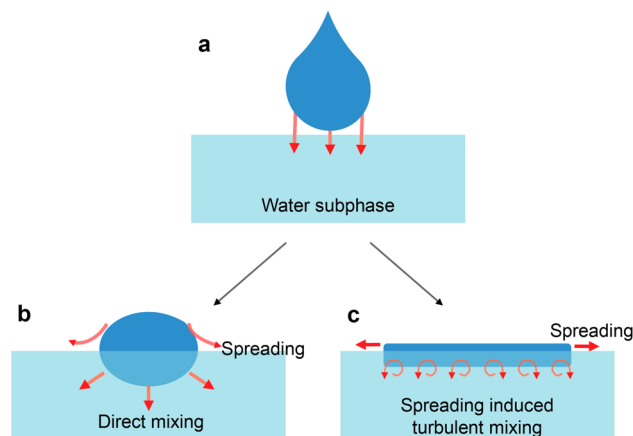

Figure 2. (a) Spreading water-miscible solvent on water is inefficient due to extensive degree of mixing. (b) Direct mixing occurs when a dispersed droplet is partially or fully submerged in the water subphase. (c) Careful dispersing can reduce the degree of direct mixing and allow more spreading. However, spreading itself induces and escalates turbulent mixing as the solvent spreads.

volume will submerge and directly mix with water (Figure 2b). This type of mixing can be significantly reduced by some skillful dispensing methods, such as gently releasing the droplets by dragging on water surface.[19] Since the density of ethanol is lower than water, careful dispensing will increase the retention time of the freshly dispensed ethanol near water surface, thus increasing the degree of spreading. However, such techniques cannot mitigate spreading-induced turbulent mixing (Figure 2c). The initial spreading step induces turbulent flows right beneath the water surface, which then escalates the mixing of the remaining ethanol with water.[29] From the above analysis, it becomes clear that even careful dispensing cannot solve the problem of intermixing. Therefore, although LB assembly with water-miscible spreading solvents is possible, it tends to waste most of the materials and has been hard to standardize.

Here we report a conceptually simple and effective strategy to solve the problem of intermixing: Reduce the size of the spreading droplets. If the size of the droplets is reduced to micron-scale, they will not be significantly affected by gravity, and they will be completely depleted during the initial spreading step, thus avoiding both types of intermixing shown Figure 2 altogether. In other words, mixing can be minimized when there is not much left to mix. In this work, electrospray is chosen over other aerosol generation techniques based on ultrasound or compressed air to nebulize the spreading solution, because it does not involve air flows that can disturb the water surface and its electrical field helps to

direct and confine the aerosol droplets in the targeted area on the LB trough. While the diameter of droplets dispensed by pipettes or syringes is typically of a few millimeters, the diameter of electrosprayed droplets is in the micron to submicron scale,[30,31] which can be reduced further due to evaporation before arrival at the water surface. Thus, electrospray can readily reduce the volume of spreading droplets by over 6 orders of magnitude. In the sections below, using three model colloids, we demonstrate that electrospray can effectively spread colloidal materials on water surface from their dispersions in ethanol, ethanol/water mixture, and even water itself.

EXPERIMENTAL SECTION

Materials. All chemicals, except for graphite powders (Bay Carbon, SP-1) were purchased from Sigma-Aldrich and used as received. All the water used in this work was deionized. Three model colloids were chosen in this work. Au/PVP nanoparticles were synthesized by a polyol route in ethylene glycol using PVP as the capping agent, purified by multiple centrifugation steps, and stored in ethanol.[32] Polystyrene colloids were synthesized by a surfactant-free route as reported previously and stored in water.[33] Graphene oxide sheets were synthesized based on a modified Hummers method,[34] purified by a two-step washing procedure,[35−37] and stored in water.

LB Assembly. All the isothermal surface pressure/area plots were recorded on a NIMA 116 LB trough (10 × 25 cm) equipped with a tensiometer and a dip coater. Some experiments were performed on a homemade mini LB trough (2.5 × 13 cm) as shown in Figures 3 and 4. Conventional drop spreading was done with a glass syringe. For electrospray spreading, the syringe was connected to a syringe pump
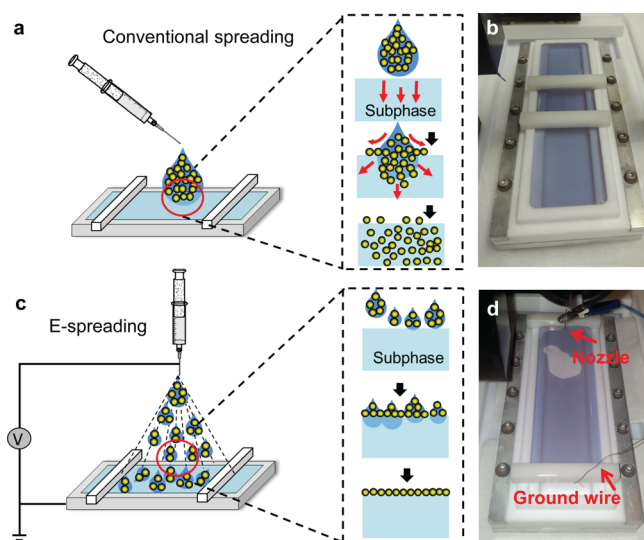
to control the flow rate. The metal needle was connected to a power supply (Series EH, Glassman High Voltage, Inc.) set at 10 kV and positioned at about 2.5 cm above the water surface. A copper grounding wire is submerged in the water subphase from the area outside the two barriers (see Figure 3d). The typical spray time is about 10−40 min. A feed rate of 2.0 mL/h was used to electrospray ethanol or ethanol/water mixtures for Au/PVP nanoparticles and polystyrene beads. For spreading GO sheets from their aqueous dispersion on water (Figure 6), the flow rate was reduced to 0.5 mL/h.

Characterization. All monolayers were transferred to Si wafers for scanning electron microscopy (SEM, Hitachi S4800) or optical microscopy (Nikon E600) observations by dip coating (pulling speed 2 mm/min).

RESULTS AND DISCUSSION

Conventional Drop Spreading vs Electrospray Spreading (E-Spreading). To compare the efficacy of conventional drop spreading and E-spreading, Au/PVP particles dispersed in ethanol were chosen as the model system.[8,32] These particles are around 50 nm in diameter and are strongly colored, so they can serve as markers for visual distinction between spreading and mixing. Conventional spreading was done by dispensing the particles with a glass syringe, which produced droplets of around 3−5 mm in diameter. As illustrated by Figure 3a, droplets were dispensed in the area between the two moving barriers, which can be closed or opened to tune the particle packing density on the surface. If water outside the area defined by barriers becomes colored, it suggests that significant mixing has occurred. When such large droplets are placed on water surface, intermixing becomes the dominating process, which brings most of the nanoparticles down to the water subphase. Indeed, as shown in the photo in Figure 3b, even after the two barriers were closed to densify the surface materials, the color of water outside or inside the barriers was still indistinguishable, which confirmed that only a negligible amount of Au/PVP particles were on the surface. In contrast, when electrospray was employed for spreading the ethanol dispersion, the Au/PVP nanoparticles were exclusively deposited on water surface. As mentioned earlier, electrospray reduces the volume of ethanol droplets by many orders of magnitude. Their volume can be depleted during initial spreading, thus leaving all the nanoparticles on the water surface (Figure 3c). The photo in Figure 3d captured a moment during E-spreading. The formation of a water-supported Au/PVP film is evident. The area of water outside the two barriers was clear, suggesting that no obvious intermixing. An alternative explanation is that the ethanol aerosol droplets may have completely evaporated before they reach water surface, and the Au/PVP particles are already dried when they land on water and trapped by surface tension. However, Figure 3d shows that there was a large opening in the monolayer right underneath the spraying nozzle. This is due to the spreading of the ethanol aerosol droplets, which pushes the Au/PVP particles away (also see Video S1). Therefore, we can conclude that in our experiments, the ethanol aerosol droplets were still wet when they arrived at water surface, which confirms the earlier hypothesis of the effect of ethanol droplet size on spreading.

Model System 1: Unstable Colloids. Electrospray-assisted LB assembly can avoid the use of water-immiscible spreading solvents, in which many colloids are unstable. Figure 4 shows the LB assembly of Au/PVP after E-spreading. The isothermal surface pressure−area plot (Figure 4a) confirms the efficacy of E-spreading. For conventional drop spreading, even

Figure 3. E-spray enabled high-yield spreading of ethanol on water surface, which is visualized using Au/PVP nanoparticles. (a) Conventional spreading results in extensive mixing with the subphase and very little material left on water surface. The photo in (b) shows that water in the entire trough is uniformly colored by the Au/PVP nanoparticle. (c) This problem can be solved by electrospray spreading. The small volume of the microdroplets can be readily depleted during spreading, leaving no extra solvent for mixing. The photo in (d) shows that electrospray can selectively deposit Au/PVP nanoparticles on water surface with no visible color in the subphase (also see the area outside the two barriers). The opening in the Au/PVP monolayer, located right beneath the spraying nozzle, was caused by the dynamic spreading of ethanol aerosol droplets (also see Video S1). As more materials are deposited, the surface pressure builds up, and the opening will gradually shrink and eventually close.
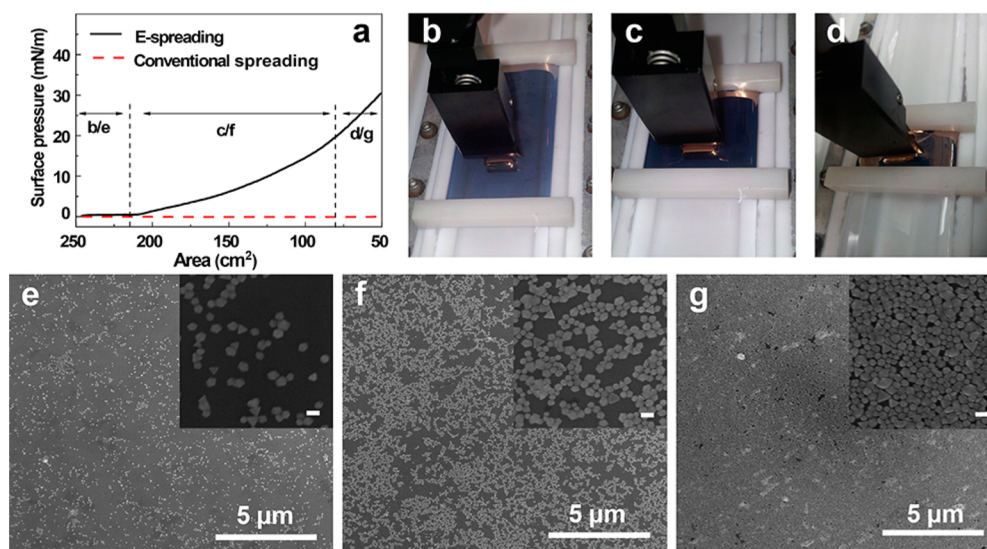
Figure 4. Au/PVP nanoparticle LB monolayer prepared by E-spray spreading using ethanol. Here it is challenging to use common spreading solvents such as chloroform and toluene due to poor colloidal stability of Au/PVP in these solvents. (a) Isothermal surface pressure/area curve (solid black line) shows that E-spray spreading indeed produced a surface monolayer, while conventional drop spreading (dashed red line) of equal volume of dispersion did not leave detectable amounts of material on the surface. The surface pressure remains near zero even after the two barriers are closed. (b−d) Photos of the Au LB monolayer at increased surface pressures, as marked in (a). The transparent blue monolayer eventually turned into a highly reflective golden film, indicating close packing of Au nanoparticles. (e−g) SEM images of the Au monolayer, corresponding to the photos (b−d), after being transferred to Si wafer by dip coating. The scale bars in the insets represent 100 nm.

after the barriers are fully closed, no observable increase in surface pressure can be noted (red dashed line) because there was very little material on water surface. When the E-spread monolayer was compressed by the two barriers, its blue color continuously intensified (Figure 4b,c). Eventually the monolayer turned into a highly reflective golden film, suggesting close packing of the gold nanoparticles (Figure 4d). The monolayer was transferred to Si wafers at the moments shown in Figure 4b−d by dip coating, and the corresponding scanning electron microscopy (SEM) images in Figure 4e−g confirm that the E-spread particles indeed formed a monolayer, which was gradually densified to reach the final close-packed state. The Au/PVP model system represents a large group of colloidal materials that are usually stored and processed in water-miscible solvents such as alcohols and some polar aprotic solvents including tetrahydrofuran, dimethyl sulfoxide, dimethylformamide, and N-methyl-pyrrolidone. They usually becomes unstable in common water-immiscible spreading solvents, making their LB assembly difficult. Electrospray now allows them to be spread directly from their stock solution without the need for extra surface modification or solvent exchange.

Model System 2: Soluble Polymer or Organic Colloids. E-spreading now enables LB assembly of particles that would be dissolved in conventional spreading solvents. The need for volatile water-immiscible spreading solvents makes it very challenging to LB assemble many organic and polymer colloids that are soluble or extensively reconfigured in those solvents. Latex beads, a model system in colloidal assembly, is one of such examples. These polystyrene (PS) nanospheres can disperse in water and alcohol-based solvents but dissolve in common spreading solvents. LB assembly would be a very good tool to create their close-packed monolayers over large areas, which can be very useful for photonics[38] and lithography applications.[39−41] However, LB assembly of such polymer colloids has been limited. Conventional drop spreading from

alcohol solvents[24−26] suffers from great material loss.[24] There have been a number of strategies to mitigate material loss. For example, using long chain alcohols that are less soluble in water can reduce the degree of intermixing. But these solvents tends to compromise colloidal stability and are much less volatile or soluble in water. One could also significantly increase the particle concentration in the spreading solvents, so that eventually a sufficient quantity of materials can be accumulated on water surface to produce a monolayer, even if the material loss is high. Alternatively, a carefully formulated cocktail of water, alcohol, and another common spreading solvent is needed to improve spreading, suppress mixing, while maintaining colloidal stability.[24] E-spreading avoids all these dilemmas. Figure 5 shows monolayers of polystyrene beads with diameter of around 300 nm obtained by E-spreading assisted LB assembly. The spreading solution was prepared by simply adding an equal volume of ethanol to their stock solution in water. Again surface pressure readings confirmed highly selective surface deposition on water surface by E-spreading, while conventional drop spreading was far less effective. The photos in Figure 5a−d show the collected monolayer on a Si wafer at different viewing angles. The film exhibited angle-dependent colors, which is characteristic for close-packed colloidal crystals. The optical (Figure 5f) and SEM images (Figure 5e, 5g) confirmed that the colloidal film was indeed a high-density monolayer extended over the entire deposited area, with line defects separating single crystalline domains that are typically made of hundreds to thousands of particles.

Model System 3: E-Spreading of Water on Water. The extraordinary capability of electrospray for spreading materials on water surface can be demonstrated by using water itself as the spreading solvent. One of such examples is GO sheets, which disperse best in water, but can stay at the air/water interface when spread onto water surface. Since GO sheets do not disperse well in the common weakly polar spreading
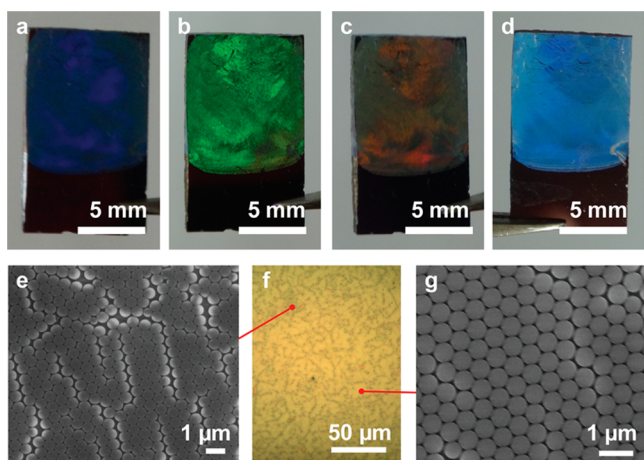
Figure 5. E-spray-assisted LB assembly of PS colloids using ethanol as the spreading solvent. Here common spreading solvents cannot be used because they will dissolved these polymer colloids. (a−d) Photos showing a monolayer of close-packed PS colloids on Si wafer viewed at different angles. SEM (e, g) and optical microscopy (f) images confirm the monolayer nature of the PS film.

solvents, LB assembly of GO sheets has relied on the use of water/alcohol mixture as the spreading solvent, which has resulted in very low yield.[19,28] As expected, using electrospray can drastically reduce the volume of spreading solution for LB assembly. However, here we noted that even water itself can act as spreading solvent. As illustrated in Figure 6a, GO sheets could accumulate at the surface of water droplets due to their amphiphilic nature.[42,43] When these GO wrapped droplets mix with water, the sheets on surface could readily spread. Common droplets dispensed by pipet or syringe have very small surface area and, therefore, cannot produce a discernible amount of GO on the surface (Figure 6b, red dashed line). With orders of magnitude enhanced surface area, the aerosolize droplets become much effective in producing a GO monolayer on water (Figure 6b, black solid line). Figure 6c−e is SEM

images of GO monolayer collected at increasing surface pressure zones as marked in Figure 6b. A transition from dilute, well isolated flat sheets to density titled, partially overlapped sheets is observed, similar to the results produced in previous LB experiments that needed to spread excessive volume of GO dispersion in water/alcohol mixture.[19]

The experiment shown in Figure 6 is a proof-of-concept that electrospray can indeed spread aqueous colloidal dispersions on water surface. In practice, many such aqueous colloids can remain stable when a small fraction of alcohol is added, so E-spreading can be more rapidly completed in such solvent mixtures. However, some amphiphilic macromolecular or biological colloids, such as proteins and cells, may experience configurational change or lose their functionalities upon exposure to alcohol solutions. Therefore, direct spreading from water may become necessary to create highly uniform films without altering thin-film properties.

■ CONCLUSION

LB assembly has been routinely used in research laboratories for nearly a century for preparing molecular and colloidal monolayers, yet it has not quite become a scalable manufacturing tool for nanomaterials. Volatile, water-immiscible solvents are convenient for spreading, but they also greatly limit the versatility of the assembly technique and bring environmental and safety concerns in scaled up applications. The use of water-miscible spreading solvents has not been effective or reproducible and tends to lose most materials to water subphase due to intermixing. Electrospray spreading solves the intermixing problems by depleting the volume of the droplets during the initial spreading step, thus leaving little solvent for mixing. As we have demonstrated here, electrospray allows high-yield, high-throughput spreading of colloidal materials on water surface using environmentally benign, water-miscible solvents, which liberates this century-old technique from many constrains related to material processing and significantly expands its scope. Essentially any colloidal
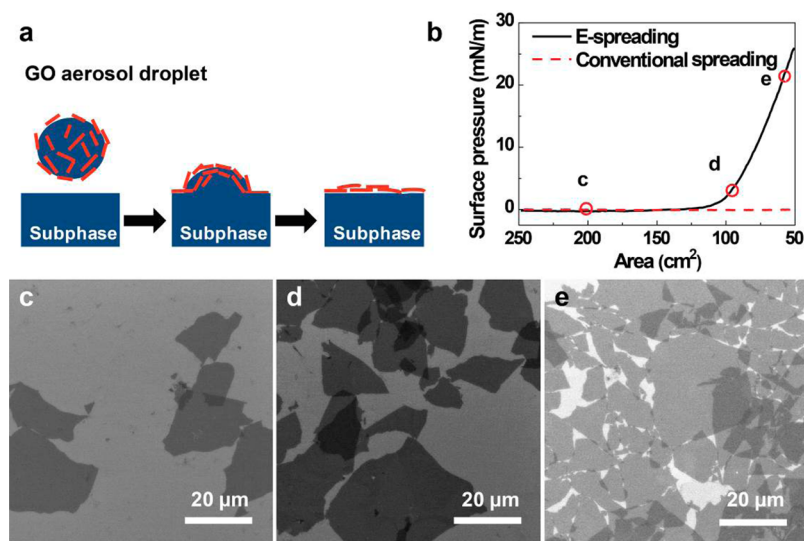

Figure 6. Spreading water-dispersed colloids directly on water by E-spray using GO as an example. (a) GO sheets could migrate to the surface of water droplets due to their amphiphilic nature, which can then spread when the droplets impinge the water surface. Aerosolized droplets have a much higher surface area, thus resulting in much higher spreading yield. (b) Isothermal surface pressure/area curves confirm that E-spray spreading is very effective in placing GO on water surface (solid black line), while conventional drop spreading failed (red dashed line). (c−e) SEM images of GO monolayers collected on Si wafer at increasing surface pressures as marked in (b).

material that can float on water surface, even temporarily, can now be processed by LB assembly. In addition, electrospray apparatus can be readily automated and fully integrated with existing LB systems, which will help to standardize and scale up this technique for manufacturing bulk nanostructured thin films.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06052.

Video showing electrospray spreading of ethanol on water surface without intermixing. Ethanol solvent was colored by Au/PVP nanoparticles (AVI)

■ AUTHOR INFORMATION

Corresponding Author
*Jiaxing-huang@northwestern.edu

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Pockels, A. Nature 1891, 43, 437−439.
(2) Blodgett, K. B. J. Am. Chem. Soc. 1934, 56, 495−495.
(3) Langmuir, I.; Blodgett, K. Colloid Polym. Sci. 1935, 73, 257−263.
(4) Collier, C. P.; Wong, E. W.; Belohradsky, M.; Raymo, F. M.; Stoddart, J. F.; Kuekes, P. J.; Williams, R. S.; Heath, J. R. Science 1999, 285, 391−394.
(5) Gleiche, M.; Chi, L. F.; Fuchs, H. Nature 2000, 403, 173−175.
(6) Roberts, G. G. Langmuir-Blodgett films; Plenum Press: New York, 1990.
(7) Yang, P. D. Nature 2003, 425, 243−244.
(8) Tao, A. R.; Huang, J. X.; Yang, P. D. Acc. Chem. Res. 2008, 41, 1662−1673.
(9) Ariga, K.; Yamauchi, Y.; Mori, T.; Hill, J. P. Adv. Mater. 2013, 25, 6477−6512.
(10) Huang, J. X.; Tao, A. R.; Connor, S.; He, R. R.; Yang, P. D. Nano Lett. 2006, 6, 524−529.
(11) Huang, J. X.; Kim, F.; Tao, A. R.; Connor, S.; Yang, P. D. Nat. Mater. 2005, 4, 896−900.
(12) Collier, C. P.; Saykally, R. J.; Shiang, J. J.; Henrichs, S. E.; Heath, J. R. Science 1997, 277, 1978−1981.
(13) Kim, F.; Kwan, S.; Akana, J.; Yang, P. D. J. Am. Chem. Soc. 2001, 123, 4360−4361.
(14) Tao, A.; Sinsermsuksakul, P.; Yang, P. Nat. Nanotechnol. 2007, 2, 435−440.
(15) Lu, Y.; Yang, Y.; Sellinger, A.; Lu, M.; Huang, J.; Fan, H.; Haddad, R.; Lopez, G.; Burns, A. R.; Sasaki, D. Y.; Shelnutt, J.; Brinker, C. J. Nature 2001, 410, 913−917.
(16) Tao, A.; Kim, F.; Hess, C.; Goldberger, J.; He, R. R.; Sun, Y. G.; Xia, Y. N.; Yang, P. D. Nano Lett. 2003, 3, 1229−1233.
(17) Jin, S.; Whang, D. M.; McAlpine, M. C.; Friedman, R. S.; Wu, Y.; Lieber, C. M. Nano Lett. 2004, 4, 915−919.
(18) Li, X. L.; Zhang, G. Y.; Bai, X. D.; Sun, X. M.; Wang, X. R.; Wang, E.; Dai, H. J. Nat. Nanotechnol. 2008, 3, 538−542.
(19) Cote, L. J.; Kim, F.; Huang, J. J. Am. Chem. Soc. 2009, 131, 1043−1049.
(20) Cao, Q.; Han, S. J.; Tulevski, G. S.; Zhu, Y.; Lu, D. D.; Haensch, W. Nat. Nanotechnol. 2013, 8, 180−186.
(21) Zhang, Y. W.; Grass, M. E.; Habas, S. E.; Tao, F.; Zhang, T. F.; Yang, P. D.; Somorjai, G. A. J. Phys. Chem. C 2007, 111, 12243−12253.
(22) Mahmoud, M. A.; Tabor, C. E.; El-Sayed, M. A. J. Phys. Chem. C 2009, 113, 5493−5501.
(23) Xia, Y. N.; Xiong, Y. J.; Lim, B.; Skrabalak, S. E. Angew. Chem., Int. Ed. 2009, 48, 60−103.
(24) Sheppard, E.; Tcheurek, N. Colloid Polym. Sci. 1968, 225, 162−163.
(25) Fulda, K. U.; Tieke, B. Adv. Mater. 1994, 6, 288−290.
(26) Fulda, K. U.; Tieke, B. Supramol. Sci. 1997, 4, 265−273.
(27) Tosheva, L.; Gospodinova, N.; Vidal, L.; Mihai, I.; Defaux, M.; Ivanov, D. A.; Doyle, A. M. Thin Solid Films 2009, 517, 5459−5463.
(28) Cote, L. J.; Kim, J.; Zhang, Z.; Sun, C.; Huang, J. X. Soft Matter 2010, 6, 6096−6101.
(29) Walters, D. A. Langmuir 1990, 6, 991−994.
(30) Chen, D. R.; Pui, D. Y. H. Aerosol Sci. Technol. 1997, 27, 367−380.
(31) Basak, S.; Chen, D. R.; Biswas, P. Chem. Eng. Sci. 2007, 62, 1263−1268.
(32) Kim, F.; Connor, S.; Song, H.; Kuykendall, T.; Yang, P. D. Angew. Chem., Int. Ed. 2004, 43, 3673−3677.
(33) Zou, D.; Derlich, V.; Gandhi, K.; Park, M.; Sun, L.; Kriz, D.; Lee, Y. D.; Kim, G.; Aklonis, J. J.; Salovey, R. J. Polym. Sci., Part A: Polym. Chem. 1990, 28, 1909−1921.
(34) Hummers, W. S.; Offeman, R. E. J. Am. Chem. Soc. 1958, 80, 1339.
(35) Luo, J. Y.; Kim, J.; Huang, J. X. Acc. Chem. Res. 2013, 46, 2225−2234.
(36) Krishnan, D.; Kim, F.; Luo, J.; Cruz-Silva, R.; Cote, L. J.; Jang, H. D.; Huang, J. Nano Today 2012, 7, 137−152.
(37) Kim, F.; Luo, J.; Cruz-Silva, R.; Cote, L. J.; Sohn, K.; Huang, J. Adv. Funct. Mater. 2010, 20, 2867−2873.
(38) Kurokawa, Y.; Miyazaki, H.; Jimba, Y. Phys. Rev. B: Condens. Matter Mater. Phys. 2004, 69, 155117.
(39) Fischer, U. C.; Zingsheim, H. P. J. Vac. Sci. Technol. 1981, 19, 881−885.
(40) Zhang, X. Y.; Yonzon, C. R.; Van Duyne, R. P. J. Mater. Res. 2006, 21, 1083−1092.
(41) Vogel, N.; Weiss, C. K.; Landfester, K. Soft Matter 2012, 8, 4044−4061.
(42) Kim, J.; Cote, L. J.; Kim, F.; Yuan, W.; Shull, K. R.; Huang, J. X. J. Am. Chem. Soc. 2010, 132, 8180−8186.
(43) Kim, J.; Cote, L. J.; Huang, J. X. Acc. Chem. Res. 2012, 45, 1356−1364.