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Forming Nanoparticle Monolayers at Liquid–Air Interfaces by Using Miscible Liquids

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Supporting Information

ABSTRACT: One standard way of forming monolayers (MLs) of nanoparticles (NPs) is to drop-cast a NP dispersion made using one solvent onto a second, immiscible solvent; after this upper solvent evaporates, the NP ML can be transferred to a solid substrate by liftoff. We show that this previously universal use of only immiscible solvent pairs can be relaxed and close-packed, hexagonally ordered NP monolayers can self-assemble at liquid—air interfaces when some miscible solvent pairs are used instead. We demonstrate this by drop-casting an iron oxide NP dispersion in toluene on a dimethyl sulfoxide (DMSO) liquid substrate. The NPs are energetically stable at the DMSO surface and remain there even with solvent mixing. Excess NPs coagulate and precipitate in the



DMSO, and this limits NPs at the surface to approximately 1 ML. The ML domains at the surface nucleate independently, which is in contrast to ML growth at the receding edge of the drying drop, as is common in immiscible solvent pair systems and seen here for the toluene/diethylene glycol immiscible solvent pair system. This new use of miscible solvent pairs can enable the formation of MLs for a wider range of NPs.

■ INTRODUCTION

Close-packed, highly ordered monolayers (MLs) of nanoparticles (NPs) have recently attracted interest because of their flexibility, large surface/volume ratio, and the zero-dimensional properties of the ligand-capped NPs. They can be used as a building block in vertical heterostructures^{1,2} consisting of NP MLs and van der Waals MLs.³ NP MLs can be prepared by drop-casting them directly on a solid surface 4^{-10} or on a liquid surface, followed by transferring them onto a solid substrate using a liftoff technique.^{1,2,11–13} The former technique requires wettability of the NP carrier solvent on the targeted substrate. The latter technique is more flexible in that it can be adapted to almost any solid substrate, but has been limited in the choice of the immiscible liquids for NP dispersion (upper solvent) and as the substrate for drop-casting (lower solvent). We overcome this potential limitation by showing that a close-packed NP ML can indeed form at the lower solvent/air interface even when the solvents are miscible, and even as many NPs concomitantly precipitate; this ML can then be transferred to a solid substrate.

The conventional criteria for selecting the two solvents for ML formation at a liquid surface are as follows: (1) The NPs must disperse well in the upper, but not in the lower solvent, so they remain in it as it dries. For NPs capped by ligands with nonpolar ends, this means that the upper solvent needs to be more nonpolar and the lower one more polar. (2) The solvents must be immiscible, so they do not mix. (3) The upper solvent must be less dense, so it does not displace the lower solvent. (4) The upper solvent must have a higher vapor pressure than

the lower solvent so it evaporates faster and the NPs can remain at the lower solvent/air interface and, better yet, have a high vapor pressure (low bp) so it evaporates quickly. When the solvents do not satisfy criterion (2) and are miscible, it is usually thought that all of the NPs will precipitate in the lower solvent. Miscible solvents are used in the standard NP size selection/washing procedure, where NPs in a nonpolar solvent (e.g., hexane) precipitate when large amounts of polar solvent, an antisolvent, (e.g., ethanol) are added.^{14,15}

We relax criterion (2) by dispersing iron oxide particles in the toluene (density = 0.867 g/mL, bp = $111 \degree \text{C}$) upper solvent and drop-casting this dispersion on the dimethyl sulfoxide (DMSO) (density = 1.101 g/mL, bp = $189 \degree \text{C}$) lower solvent.¹⁶ The NPs do not disperse in the DMSO, an antisolvent. Though this miscible solvent pair satisfies only criteria (1), (3), and (4), we still can form a NP ML by using it. To contrast the assembly mechanisms when using miscible and immiscible solvent pairs, we compare NP assembly using this miscible solvent pair and the conventional, immiscible pair, with toluene as the upper solvent and diethylene glycol (DEG) (density = 1.120 g/mL, bp = $246 \degree \text{C}$) as the lower solvent.¹³ The NPs do not disperse in the DEG, an antisolvent.

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EXPERIMENTAL SECTION

Synthesis and Drop-Casting. Iron oxide (magnetite) NP cores with 13.2 nm diameter capped by oleates (from oleic acid (OA)) were synthesized using previously published methods by injecting iron pentacarbonyl into an octadecene and oleic acid solution at 300 °C.^{14,15} The mixture was held at this temperature for 1 h before the product was washed twice in ethanol and dispersed in toluene for drop-casting on the lower solvent, DMSO or DEG. A volume of 20 μ L of the toluene NP dispersion was drop-cast on ~2.5 mL of the lower solvent in an ~2.9 cm diameter glass Petri dish (except for the in situ small-angle X-ray scattering experiments, as noted below).

Real-Time Optical Microscopy. The events after drop-casting the toluene NP dispersion were monitored by using real-time optical microscopy in a dry glovebox filled with N_2 (<10 ppm of H_2O); an Amscope SFZJ-2TR long working distance microscope was placed above the top surface, pointing toward it, with white LED light illuminating the sample from underneath the Petri dish.

Small Angle X-ray Scattering (SAXS). In situ small-angle X-ray scattering in grazing incidence configuration¹⁷ at beamline X9A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL) was used to probe the lower solvent-air interface after drop-casting a 10 μ L drop of toluene NP dispersion on the ~1 mL DMSO lower phase within a Teflon transmission cell (7 mm beam path, with two 2 cm diameter kapton windows sealed by Aflas Orings); these measurements used a 0.918 Å X-ray beam, with $\sim 100 \,\mu m$ spot size and 0° tilt angle, and were in the ambient. Only NPs that remain on at the DMSO-air interface after the rapid toluene evaporation and mixing with the subphase could be probed in principle. However, because the transmission length DMSO is very short (~1.01 mm)¹⁸ at this X-ray wavelength, the detected signal would be too small if the beam were aligned at the bottom of the DMSO top surface, as is common practice;¹⁷ consequently, the stage was lowered by ~400 μ m so the beam traveled above the liquid except at the menisci formed of the DMSO subphase at the kapton windows, so only the NP layer there was probed.

Ex situ grazing incidence SAXS (GISAXS) was used to probe the NP ML on either the DMSO or DEG surface after drop-casting the dispersion and transfer of the surface layer to a SiO_2/Si substrate by using the liftoff method.^{1,2,11-13} This occurred in a Bruker Nanostar U at the BNL Center for Nanofunctional Materials (CFN).

Transmission Electron Microscopy (TEM). TEM (JEOL 100CX) was used to image the NP layer transferred to a carbon-coated Cu TEM grid; transfer occurred 5 min after drop-casting for the miscible solvent pair with the grid inserted for liftoff just below the surface to avoid collecting sinking clusters of NPs.

RESULTS AND DISCUSSION

Real-time optical microscopy showed that the NP droplet spread fast (<1 s) on the DMSO surface, forming regions that were darker than the baseline solvent/air interface. Figure 1a-f follows this evolution when imaging the top surface from 5 s to 3 h after drop-casting by using relatively low magnification. Given the depth of field, regions near the top of the liquid remain in focus even as the toluene evaporates and some regions below it are also seen, but are somewhat out of focus under low magnification. There appear to be two overlapping patterns on the optical images, regions on the surface that are slightly darker than the liquid/air interface and even darker, more extended regions, in the DMSO bulk. The darker regions in the bulk DMSO are coagulated regions of NPs that form and later are no longer seen under these conditions. Viewing this progression from the side of a beaker confirms the formation of coagulated regions that move down and laterally and precipitate to the bottom in several hours (not shown). Figure 1g and h shows the view from above at \sim 120 h, at higher magnification, focused on either the top DMSO/air interface in (g) or the bottom of the Petri dish in (h). Precipitated clumps of NPs are



Figure 1. Time-resolved optical microscopy of iron oxide NP monolayer formation monitored from above. Panels (a)–(h) are from one run using the toluene/DMSO miscible solvent pair, with (a)–(f) taken from 5 s to 3 h (5, 96, 263, 659, 1960, and 10 486 s), and (g) and (h) at 120 h. Panels (i)–(k) (13, 20, and 30 s) and (l)–(n) (70, 213, and 313 s) are time sequences of the very center of the drying droplet near the end of two runs using the toluene/DEG immiscible solvent pair, in which 0.8 and 1.2 ML equivalents were drop-cast, respectively. The lower solvent/air interface was imaged in each case (for (g) after tapping it with the pipet tip on the top-left corner), except for (h) where the bottom of the Petri dish was imaged. The scale bars in (a)–(f) and (i)–(n) are 2 mm wide. Images (g) and (h) are taken at higher magnification.

seen in (h), which are also seen out of focus in (g). The top surface showed no sharp features until it was tapped with the pipet tip. Cracks are then seen, as shown in Figure 1g, which indicates that there is a film on the top surface, even after the observed NP coagulation and precipitation.

Figure 1i-k and l-n shows the evolution at the surface after the drop-casting the toluene NP dispersion on the immiscible DEG with relatively smaller and larger quantities of NPs.^{17,19-21} (This is explained below as being due to dropcasting 0.8 and 1.2 ML equivalents of NPs, respectively.) In both, in the very center of the surfaces, the drop of the toluene NP dispersion is becoming smaller, respectively from (i) to (j) and (1) to (m), as toluene evaporates and NPs are being deposited in the receding drop edge; evaporation is complete in (k) and (n). The intermediate gray regions at the peripheries are from 1 ML of NPs; these regions extend out of the range of the images to most of the surface. The lighter regions in the center of (k) are due to sub-ML coverage (0.8 ML equivalents), sometimes with no NPs. The much darker regions in the center of (n) are from multi-ML coverage (1.2 ML equivalents), due to the excess of particles in the drying drop, as shown in (1) and (m).^{19,20} This shows the difficulty of forming exactly 1 ML NPs

Such optical micrographs after toluene evaporation with immiscible solvent pairs were used to dilute the stock solution to form a single ML on the entire surface (ignoring small corrections for the meniscus); this 1 ML equivalent corresponded to an ~20 μ L drop of ~1.5 × 10¹⁴ NPs/mL on this \sim 6.6 cm² area surface; this same calibration was used to determine the number of NPs that are drop-cast, in terms of (immiscible pair) ML equivalents for miscible and immiscible solvent pair experiments. Drop-casting 1 ML equivalent using the miscible solvent pair case produced a NP layer over the entire surface, but the image was not as dark as for a full ML, suggesting less than full monolayer coverage; the image darkness also varied across the surface. Drop-casting roughly 2 ML equivalents using the miscible pair case produced a NP ML all over the surface, as determined by the optical microscopy and the below TEM studies.

Figure 2 gives the results of the in situ SAXS analysis (BNL NSLS) after drop-casting the toluene NP dispersion onto the



Figure 2. (a) Schematic showing the in situ SAXS setup. The beam is aligned with the meniscus of DMSO and vertical kapton window. (b) Collected scattering pattern after drop-casting the toluene NP dispersion on a DMSO lower phase (miscible solvent pair), with the dashes showing the calculations for (10), (11), and (20) (red, green, and white, from the innermost to outermost fits). Only the lower half of these symmetric fits are shown. The average scattering intensity vs scattering wave vector is plotted in Figure S1 in the Supporting Information, and shows these three peaks.

surface of the DMSO lower phase (corresponding to ~8 ML equivalents). The elliptical scattering pattern in Figure 2b is that expected for a very thin close-packed NP film (1 ML or a few monolayers) on a tilted planar surface, with an ellipse aspect ratio of sin α , where α is the tilt angle.^{4,5} This pattern differs from a typical 3D superlattice pattern, which is a circle instead of an ellipse due to the absence of a dominating

orientation, and also differs from a typical 2D superlattice pattern on a parallel surface along the X-ray direction, which is a straight line due to the absence of the projection of the momentum transfer component q_y . The fit of Figure 2b using ref 4 is consistent with a 2D close-packed film of 13.2 nm iron oxide NPs on a tilted surface, with tilt angle of 51.4° and corecore distance of 15.8 nm. (For comparison, this method was also used to examine a toluene/DEG immiscible solvent pair run, though it was not needed because of adequate X-ray transmission through DEG; the SAXS pattern was also elliptical, indicating a thin film on the meniscus.)

The ex situ GISAXS streak patterns (in the Bruker Nanostar) in Figure 3 were seen after drop-casting \sim 1 ML equivalent and



Figure 3. GISAXS pattern of transferred iron oxide NP monolayer on SiO_2/Si substrates, prepared using (a) miscible solvent pairs (300 s signal collection) and (b) immiscible solvent pairs (600 s).

subsequent transfer to a SiO₂/Si substrate by liftoff. They suggest an ordered 2D NP structure.^{22,23} The features are broader when using the toluene/DMSO miscible solvent pair procedure (Figure 3a) than when using the toluene/DEG immiscible pair (Figure 3b), so the ordered regions are smaller when using the miscible solvent pair. They were found to have an effective domain size of ~100 nm, relative to ~200 nm for the immiscible solvent pair, by using the analysis in ref 5. (See Figure S2 in the Supporting Information.)

Figure 4 shows TEM images of the NP layer after dropcasting ~ 2 ML equivalents using miscible solvent pairs and ~ 1 ML equivalent using immiscible solvent pairs, and subsequent transfer. The domains consist of hexagonally ordered NPs and were generally smaller using miscible solvent pairs (but the



Figure 4. TEM image of the 13.2 nm iron oxide NP monolayer prepared by using (a) miscible solvent pairs and (b) immiscible solvent pairs, showing domains and cracks.

layer is more continuous macroscopically and easier to control than those formed using immiscible solvent pairs). Such domains generally have similarly shaped boundaries that do not appear to be cracks and neighboring domains typically have different lattice orientations. This suggests that for miscible solvent pairs each domain nucleates at approximately the same time at random points and then they grow laterally until they meet. Most regions have 1 ML NPs, but a second ML is sometimes seen over up to $\sim 10\%$ of the surface. Figure 4a and Figure S4 in the Supporting Information demonstrate that the NP film at the surface self-limits to \sim 1 ML when using miscible solvent pairs, due to the transport of excess NPs from the surface. In contrast, to achieve 1 ML coverage over the entire surface using immiscible solvent pairs and when drop-casting directly on solid substrates, the drop volume and NP concentration must be prepared with very tight tolerances. Figure S4 also shows the TEMs of samples collected across the surface 24 h after drop-casting, which demonstrate good uniformity across the surface when using miscible solvent pairs.

Using immiscible solvent pairs, ML domains can be as large as several micrometers. They sometimes have cracks within a single domain, with the lattice orientations that usually match on either side of the crack, as across the wide crack in Figure 4b. (These cracks may be caused by surface tension after the final stages of drying and ML formation, in agreement with the mechanism from the above real-time optical microscopy studies and previous work,^{17,21} or by the transfer process itself. Grain rotation and nonalignment are not expected for either case.) Less often, lattice orientations do not match at boundaries, which is likely due to defects during crystallization. As suggested in Figure 1i–n and previous work,^{17,21} NPs from this drop combine with the existing NP ML, perpendicular to the shrinking direction of the droplet inner boundary, so the domain size can be very large.

It is not surprising that miscible solvents could be used to form such NP MLs in some cases, because NPs may be energetically stable at the lower solvent surface. The binding energy of individual NPs at the lower solvent/air interface relative to that in the bulk of the lower solvent can be estimated by using Pieranski's model:²⁴

$$\Delta E = \pi R^2 \gamma_{\rm s} \left(1 - \frac{\gamma_{\rm p} - \gamma_{\rm p/s}}{\gamma_{\rm s}} \right)^2 \quad \text{when} \quad \frac{\gamma_{\rm p} - \gamma_{\rm p/s}}{\gamma_{\rm s}} < 1 \tag{1}$$

where *R* is the NP radius, $\gamma_{s'} \gamma_{p'}$ and $\gamma_{p/s}$ are the surface tension coefficients of the lower solvent, NPs, and NPs/lower solvent interface. If $\frac{\gamma_p - \gamma_{p/s}}{\gamma_s} \ge 1$, NP binding at the interface is not expected in this model. The NP surface tension coefficient is estimated by using that of the surface ligands, here using that of oleic acid for the oleate ligands. The binding energy of iron oxide NPs at the DMSO/air interface is $\sim 79k_BT_{room}$, using $\gamma_p = \gamma_{OA} = 32.79 \text{ mN/m}^{25} \gamma_s = \gamma_{DMSO} = 42.92 \text{ mN/m}^{16}$ and $\gamma_{p/s} = \gamma_{OA/DMSO} = 0 \text{ mN/m}$ (which is a consequence of OA and DMSO being miscible),²⁶ so binding of NPs at the upper surface is energetically favorable by $\gg k_B T_{room}$, as it is for the immiscible solvent pair comparison system with DEG ($\sim 453k_B T_{room}$).¹⁷ (See Figure S5 in the Supporting Information.) NP film stability can also be affected by turbulence during miscible solvent mixing, which could cause NP transport from the surface. Still, enough NPs clearly remain at the surface

to form an NP ML using the toluene/DMSO miscible pair solvent system.

For the immiscible solvent pair case, the toluene evaporates in ~ 1 min. As the drop evaporates, NPs deposit at the receding edge, leaving behind a NP ML. If there are too few NPs to fill the entire region, there will be a submonolayer NP film in the center or no NPs at all (and gaps will form due to fracture arising from surface tension, Figure 1k), and if there are too many, there will be multilayers in the center (Figure 1n), so it can be difficult to have a 1 ML everywhere. For miscible solvent pairs, after drop-casting 2 ML equivalents or more, the toluene rapidly spreads on the DMSO surface, followed by rapid toluene evaporation and mixing with DMSO; this includes the entrainment of the NPs that do not remain in the NP ML on the surface into the bulk DMSO, and these excess NPs then coagulate in the DMSO and precipitate to the bottom.

The mixing of miscible solvents depends on the details of the mixing procedure and is not completely understood.²⁷ Because the DMSO volume is $\sim 125 \times$ that of the toluene, toluene leaves the surface much faster than it does for the toluene/DEG solvent pair due to this mixing. (The actual evaporation rate of toluene after it mixes with DMSO for the miscible solvent pair or after it remains on DEG for the immiscible solvent pair are approximately the same.²⁸) The consequences of this mixing are illustrated in the abstract figure, which depicts the transport of many NPs into the lower solvent for the miscible solvent pair, with ~ 1 ML only of NPs remaining at the top surface, forming smaller independent NP ML domains. This is in contrast to the loss of toluene with the immiscible solvent pair with NPs appearing at the DEG/air interface at the receding edge of the evaporating toluene drop, forming a big NP ML domain that later cracks.

This approach should be extendable to other miscible solvent pairs when energetically favorable and solvent mixing is not severe, and this was seen in survey experiments. These 13.2 nm iron oxide NPs also form a monolayer on the surface when using the benzene/DMSO and fluorobenzene/DMSO miscible pairs, as is seen Figure S6 in the Supporting Information. Clear evidence of NP film formation at the lower solvent/air interface was not seen in brief survey experiments with several other pairs of upper/lower miscible solvents: toluene (0.867 g/mL)/ N,N-dimethylformamide (DMF, 0.945 g/mL), hexane (0.661 g/mL)/ethanol (0.789 g/mL) and hexane/acetone (0.786 g/ mL), for which the lower solvent is also denser, though the density difference is smaller than for toluene/DMSO (1.101 g/ mL),¹⁶ and toluene/ethanol and toluene/acetone, for which the upper solvent is denser. Solvent mixing might be faster and more turbulent in each case. Moreover, the binding energy of iron oxide/oleate NPs to the DMF/air interface is small $\sim 8.0 k_{\rm B} T_{\rm room}^{16}$ (with surface tension coefficient 35.74 mN/m,¹⁶ assuming that DMF and oleic acid are miscible) and binding is not expected for acetone and ethanol lower phases due to their small surface tension coefficients, 22.72 and 21.97 mN/m, respectively.¹⁶ (See Figure S5 in the Supporting Information.)

Also, this approach is extendable to other NPs. Figure S7 in the Supporting Information shows that a monolayer is formed using smaller particles, 5 nm iron oxide NPs capped by oleates (using the benzene/DMSO miscible solvent pair), and other types of particles, 4 nm CdSe quantum dots capped by oleates (using the toluene/DMSO miscible solvent pair); for these smaller NPs, there is a second layer over a larger fraction of the surface.

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CONCLUSIONS

We have shown that solvent miscibility is not necessarily a barrier in forming NP MLs at liquid surfaces. Using the toluene/DMSO miscible solvent pair, a large-scale, continuous, hexagonally ordered ML of iron NPs forms at the DMSO/air surface. Excess NPs coagulate and precipitate, which can be recycled for future use. Many nucleation centers grow simultaneously with the miscible pair until they touch each other across the entire surface; in contrast, a single domain forms using the toluene/DEG immiscible solvent pair, which can later fracture. Due to the differences in formation mechanisms, it may be easier to form large 1 ML regions when using miscible solvent pairs than when using immiscible solvent pairs due to the self-limiting nature of 1 ML NP formation. Forming a NP ML on a liquid surface using miscible solvent pairs and transferring it to a solid surface has potential advantages compared to direct drop casting on the solid,^{6,7} including this self-limiting feature and the lack of residual solids that sometimes form in the latter method.⁷ The use of miscible solvent pairs can make the method of preparing NP layers at liquid surfaces more flexible, and possible for wider ranges of nanoparticles, quantum dots, and molecular clusters.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.lang-muir.6b00828.

Intensity vs *q* dependence of the in situ SAXS pattern, ex situ SAXS peak fit using the KTHNY model, test of NP monolayer uniformity by TEM analysis, energy diagram of OA-capped NPs at the liquid—air interface, and extension to other miscible pairs and nanoparticles (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

ML, monolayer; NP, nanoparticle; DMSO, dimethyl sulfoxide; DEG, diethylene glycol; OA, oleic acid; SAXS, small-angle Xray scattering; NSLS, National Synchrotron Light Source; BNL, Brookhaven National Laboratory; GISAXS, grazing incidence small-angle X-ray scattering; CFN, Center for Nanofunctional Materials; TEM, transmission electron microscopy; DMF, *N*,*N*dimethylformamide

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