Video Article

A Technique to Functionalize and Self-assemble Macroscopic Nanoparticle-ligand Monolayer Films onto Template-free Substrates

Jake Fontana[1], Christopher Spillmann[1], Jawad Naciri[1], Banahalli R. Ratna[1]

[1]Naval Research Laboratory

Correspondence to: Jake Fontana at jake.fontana.ctr@nrl.navy.mil

URL: http://www.jove.com/video/51282
DOI: doi:10.3791/51282

Keywords: Chemistry, Issue 87, phase transfer, nanoparticle, self-assembly, bottom-up, fabrication, low-cost, monolayer, thin film, nanostructure, array, metamaterial

Date Published: 5/9/2014

Citation: Fontana, J., Spillmann, C., Naciri, J., Ratna, B.R. A Technique to Functionalize and Self-assemble Macroscopic Nanoparticle-ligand Monolayer Films onto Template-free Substrates. *J. Vis. Exp.* (87), e51282, doi:10.3791/51282 (2014).

Abstract

This protocol describes a self-assembly technique to create macroscopic monolayer films composed of ligand-coated nanoparticles[1,2]. The simple, robust and scalable technique efficiently functionalizes metallic nanoparticles with thiol-ligands in a miscible water/organic solvent mixture allowing for rapid grafting of thiol groups onto the gold nanoparticle surface. The hydrophobic ligands on the nanoparticles then quickly phase separate the nanoparticles from the aqueous based suspension and confine them to the air-fluid interface. This drives the ligand-capped nanoparticles to form monolayer domains at the air-fluid interface. The use of water-miscible organic solvents is important as it enables the transport of the nanoparticles from the interface onto template-free substrates. The flow is mediated by a surface tension gradient[3,4] and creates macroscopic, high-density, monolayer nanoparticle-ligand films. This self-assembly technique may be generalized to include the use of particles of different compositions, size, and shape and may lead to an efficient assembly method to produce low-cost, macroscopic, high-density, monolayer nanoparticle films for wide-spread applications.

Video Link

The video component of this article can be found at http://www.jove.com/video/51282/

Introduction

The self-assembly of macroscopic nanoparticle films has attracted great attention for their unique properties determined from the geometry and composition of the elements[5] and may lead to of a wide range of optical, electronic and chemical applications[6-14]. To self-assemble such films metallic nanoparticles capped with ligands must be packed into high density, monolayers. However several assembly issues need to be addressed to advance the development of such materials.

First, surfactant stabilized metallic nanoparticles are typically synthesized by wet-chemistry methods in dilute suspensions[15]. To prevent aggregation and to control the interparticle spacing of the nanoparticles in the films, the nanoparticles need to be capped with ligand shells. After the nanoparticles have been functionalized with ligands the nanoparticles typically remain in relatively dilute suspensions. A technique is then needed to self-assemble the nanoparticles into macroscopic, high-density, monolayer films[16,17].

Cheng *et al.*[18] phase transferred gold nanorods using thiolated polystyrene in a water-tetrahydrofuran suspension. The nanorods where then re-suspended in chloroform and a drop was placed at an air-water interface and evaporated slowly, forming monolayer films. Bigioni *et al.*[17] created macroscopic monolayers of dodecanethiol capped gold nanospheres using excess ligand and rapid solvent evaporation, but the nanospheres needed to be phase transferred prior to self-assembling.

Once the monolayer films are formed they typically need to be transported onto a substrate. Mayya *et al.*[3] confined nanospheres at a water-toluene interface and transferred them onto template-free substrates using surface tension gradients. Similarly, Johnson *et al.*[4] suspended silver nanospheres in excess ligand and then translated the nanoparticles up the walls of the vial using surface tension gradients from two immiscible fluids. While assembly techniques exist to address each of these issues the need for more efficient techniques is needed to aid in the development of large-scale nanoparticle film production.

Here we demonstrate a straightforward and robust technique that combines the three self-assembly issues described above in to a single 'one-pot' technique, shown in **Figure 1**. A water miscible organic solvent (*e.g.* tetrahydrofuran, dimeythl sulfoxide), is used to first quickly and efficiently functionalize thiol-ligands (*e.g.* thiol-alkane, thiol-ene, thiol-phenol) onto the nanoparticles (*e.g.* gold nanospheres, nanorods, etc.). The mixture then drives self-assembly of the nanoparticles into macroscopic, high-density, monolayer films at the air-fluid interface using phase separation. Finally, monolayer films of nanoparticles form onto template-free substrates using surface tension gradients from the water/organic solvent mixture, **Figure 2** and **Figure 3**.

Protocol

1. Self-assembled Ligand-nanoparticle Monolayers

As an illustrative example of the self-assembly technique, macroscopic, thiol-alkane capped gold nanosphere monolayer films are produced as follows:

1. Concentrate 15 nm gold nanospheres (commercially available at a number density: 10^{12} particles/ml) to ~10^{13} particles/ml in water.
    1. Place 15 ml of the dilute nanosphere water suspension into an ultra centrifugal filter (100 K nominal molecular weight limit).
    2. Centrifuge the filter/vial at 4,500 x g for 2 min or until only a few ml remain in the filter chamber.

2. Resuspend the nanosphere in approximately 1 ml of deionized (DI) water such that the nanoparticle concentration is 10^{13} particles/ml. The suspension is stable for several hours once resuspended in DI water.
    1. Verify the number density and confirm the nanoparticles have not aggregated. Dilute the concentrated nanoparticle suspension by a factor of 1:10 back to the original concentration by placing 0.150 ml of the suspension into a cuvette (1 cm path length), and to this add 1.35 ml of DI water.
    2. Place the cuvette into a spectrometer and measure the absorbance spectrum of the suspension and the original suspension. Compare the peak position and full width at half maximum to ensure aggregation has not occurred. The magnitude of the absorbance peaks for both samples should be approximately the same, thus ensuring the concentrated sample is denser by a factor of 10.

3. In a separate clean 20 ml borosilicate glass vial add 1 ml of tetrahydrofuran (THF).
4. Add the thiol-alkane ligands (*e.g.* 5 ml of 1,6-hexanedithiol and 5 ml of 1-dodecanethiol) to the THF and shake the solution to mix uniformly. Enough ligand should be added to cover at least the entire surface area of the suspended nanoparticles. Excess ligand increases the speed and efficiency of the reaction.
5. In a fume hood, pour the contents of the vial containing the gold nanospheres into the vial of THF-ligands.
6. Quickly screw on the lid and shake the vial vigorously for 15 sec.
7. Remove the lid and set the vial down in the fume hood, **Figure 1(a)**. Depending on the ligands used, domains of gold nanoparticle films quickly form at the air-liquid interface, **Figure 1(c)**. The films will then begin to translate up the sides of the vial, **Figure 1(d)**. Nearly all the nanoparticles are capped with thiol-ligand, removed from the suspension, and transported to the sides of the vial within 1 hr, **Figure 1(e)**.

2. Transferring the Monolayers onto Removable Substrates

1. To transfer the films onto removable glass and silicon wafer substrates: cut the substrates into an area of 12.5 mm x 25.4 mm using a scribing pen/wheel.
    1. Glass Substrates: clean using an acetone rinse, followed by an isopropyl alcohol rinse, and finally a DI water rinse. Allow the substrates to dry, proceed to section 2.2.
    2. Silicon Wafer Substrates: in a fume hood prepare Piranha solution (3 parts concentrated sulfuric acid to 1 part 30% hydrogen peroxide, **CAUTION:** oxidizer, corrosive). Place 15 ml of sulfuric acid into a 20 ml borosilicate glass vial. To this **slowly** add 5 ml of 30% hydrogen peroxide. **Do not** cap the vial. Use caution; the mixture is highly exothermic. See reference for more safety information[19].
    3. Carefully submerse the silicon wafer substrates into Piranha solution for 30 min, remove, rinse with DI water and dry with nitrogen.
    4. As an optional step, the vial used for the nanoparticle ligand exchange and self-assembly can be salinized to force all the nanoparticles onto the glass substrate or silicon wafer instead of the walls of the glass vial, otherwise proceed to section 2.2.
    5. Fill the glass vial with piranha solution (**CAUTION:** oxidizer, corrosive), refer to section 2.1.2.
    6. Allow the vial to soak for 30 min. After 30 min rinse the vial out with DI water.
    7. Fill vial with 1% v/v of hexamethyldisilazane in acetone and cap.
    8. Allow the sealed vial to soak for 24 hr, then rinse with DI water and dry with nitrogen.

2. Prior to shaking (section 1.6) insert the substrate into the vial. Screw on lid and shake.
3. After shaking remove lid and, using tweezers, position the substrate nearly vertical against the vial wall.
4. Use a pipette to coat the reaction mixture onto the substrate. The reaction stops when all the organic solvent has evaporated or all the nanoparticle have been removed from the suspension.

3. Monolayer Analysis

1. Estimate the packing efficiency of the nanospheres in the monolayer quickly by observing the transmission and reflective properties of the film. Illuminate the monolayer on glass substrates from behind with a white-light source. With a white light source, a uniform colored film should be observed for high-density nanoparticle monolayer films in transmission and a gold-like reflection observed in reflection, **Figure 2**.
2. Use a spectrometer (see section 1.2.2) to quantify the macroscopic absorbance spectrum from the monolayers, **Figure 4**. Normalize the absorbance spectrum with a clean glass slide. Mount the monolayer film, on a glass substrate, into the beam path of the spectrometer and collect the absorbance spectrum.

    Note: The absorbance peak should be significantly red-shifted several hundred nanometers depending on the ligand used. The quality factor of the absorbance peak should be comparable to the dilute suspension value, but only slightly broadened (**Figure 4**). If the absorbance peak is very broad or not well defined then the monolayer films are probably of poor quality, proceed to section 3.3 for further characterization.

3. Examine the nanoscopic organization of the nanospheres using scanning electron microscopy (SEM) of monolayers transferred onto silicon wafer substrates (see section 2.1.2) as shown in **Figure 3**. If the films are on glass substrates connect conductive tape to one corner of the film and ground it to the SEM pedestal to prevent charging and allow imaging.

4. Efficient Phase Transfer Technique for Organic Soluble Nanoparticles

1. To use the technique as an efficient means to functionalize the nanoparticles with thiol-ligands, decant the remaining solution from the bottom of the vial after the reaction is complete, section 1.7, and dry the material in the vial under nitrogen.
2. Add an organic solvent (*e.g.* chloroform, toluene) to re-suspend the nanoparticles with nearly 100% particle phase transfer and recovery.
3. Repeat section 1.2.1 to ensure the nanoparticles have not aggregated upon re-suspension into the organic solvent. If the absorbance peak is board, relative to the original suspension, sonicate the sample for 15 min to help redisperse the nanoparticles, **Figure 4**.

Representative Results

Figure 1(a) shows a suspension of gold nanospheres, thiol-alkane ligands, tetrahydrofuran and water in a glass vial immediately after mixing. A schematic of the three main self-assembly stages, phase transfer, phase separation, and surface tension gradient mediated film transport is shown in **Figure 1(b)** as an expanded view at the air-fluid interface near the side of the vial.

The thiol groups on the ligands rapidly bond to the gold nanospheres after mixing, displacing the ionic surfactant, causing the nanospheres to become hydrophobic and more miscible in THF. The lower density of THF, relative to the water, aids to quickly transport the nanospheres to the air-fluid interface where they become confined by the reduction of free energy, **Figure 1(c)**. Suspending the ligands in a water-miscible organic solvent also increases the available surface area between the thiol-ligands and nanospheres, increasing the rate the nanospheres phase transfer, compared to systems that use two immiscible fluids[3,4].

Macroscopic monolayer domains of nanospheres typically begin to form at the air-fluid interface within several minutes after mixing, but this process is ligand dependent. The shaking of the vial also coats the sides of the vial with a thin film of the suspension. The THF in the thin film on the sides of the vial evaporates faster than the water, creating a surface tension gradient between the thin film and bulk suspension. The fluid then flows from the low to the high surface tension regions carrying the nanospheres domains from the air-fluid interface up the side of the vial, **Figure 1(d)**[3]. After all the organic solvent has evaporated or all the nanosphere have been removed from the suspension the reaction is complete, **Figure 1(e)**.

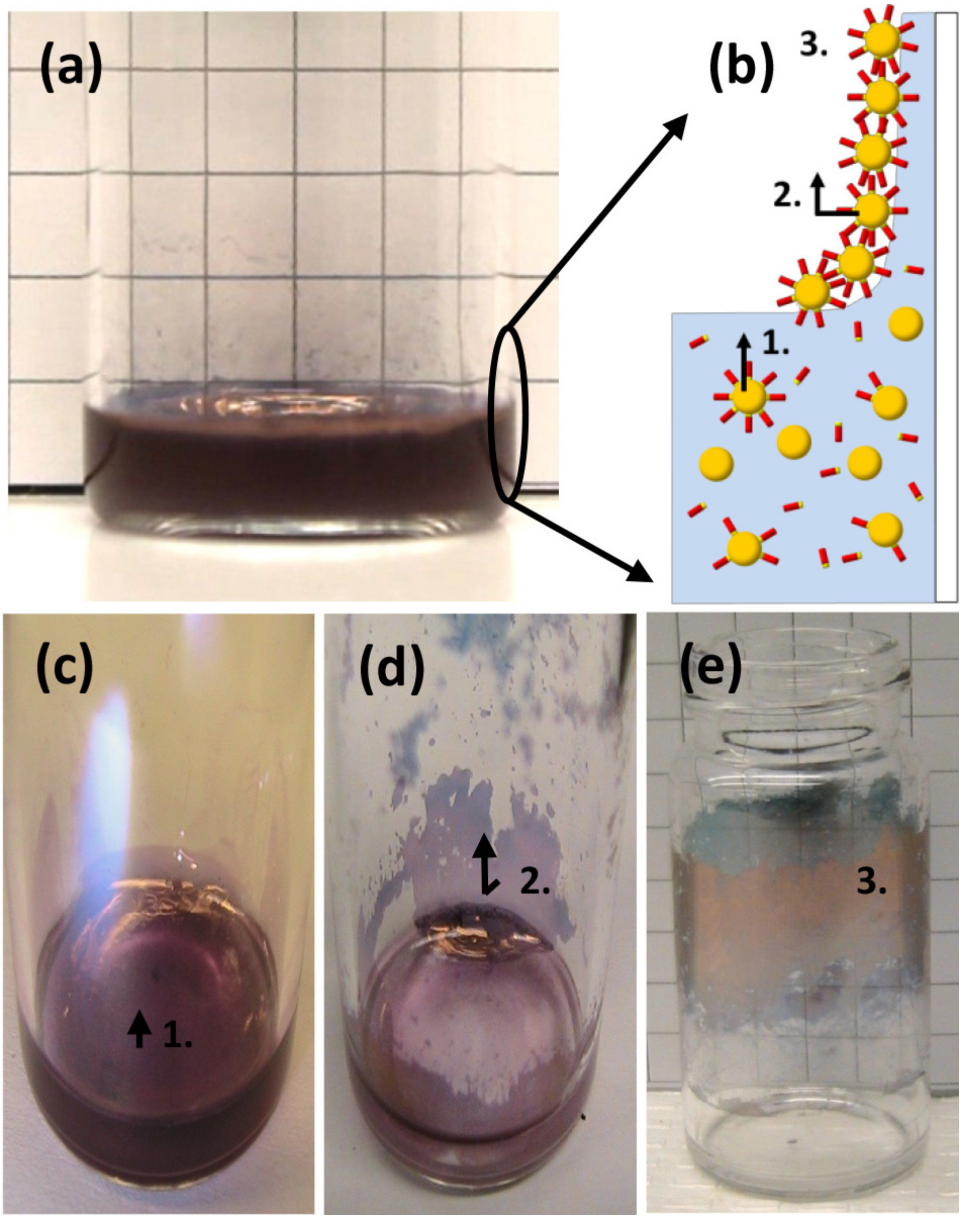

Figure 1. Self-assembly technique. (a) A suspension of 15 nm gold nanospheres, thiol-alkane ligands, tetrahydrofuran and water in a glass vial. **(b)** Schematic of the three main self-assembly stages; phase transfer, phase separation, and film transport. **(c)** Phase transfer and separation of the nanoparticles at the air-fluid interface. **(d)** Surface tension gradient mediated transport of the nanoparticle monolayer domains. **(e)** Completed reaction.

Macroscopic nanoparticle-ligand monolayer films (~cm) are demonstrated using this technique without multilayers or large particle density gradients on a template-free substrate. **Figure 2** is an image of a thiol-alkane capped 15 nm gold nanosphere monolayer film on a glass substrate partially reflecting light (right side), signifying the high volume fraction of nanospheres and transmitting light (left side), demonstrating the preservation of the plasmon resonances, uniformity and optical clarity. If more than one layer is present it can easily be seen with the naked eye[1]. The right edge of the film has excess surfactant present on the top surface giving rise to the slight discoloration in the reflected light. Additional monolayer images can be found in references[1,2].

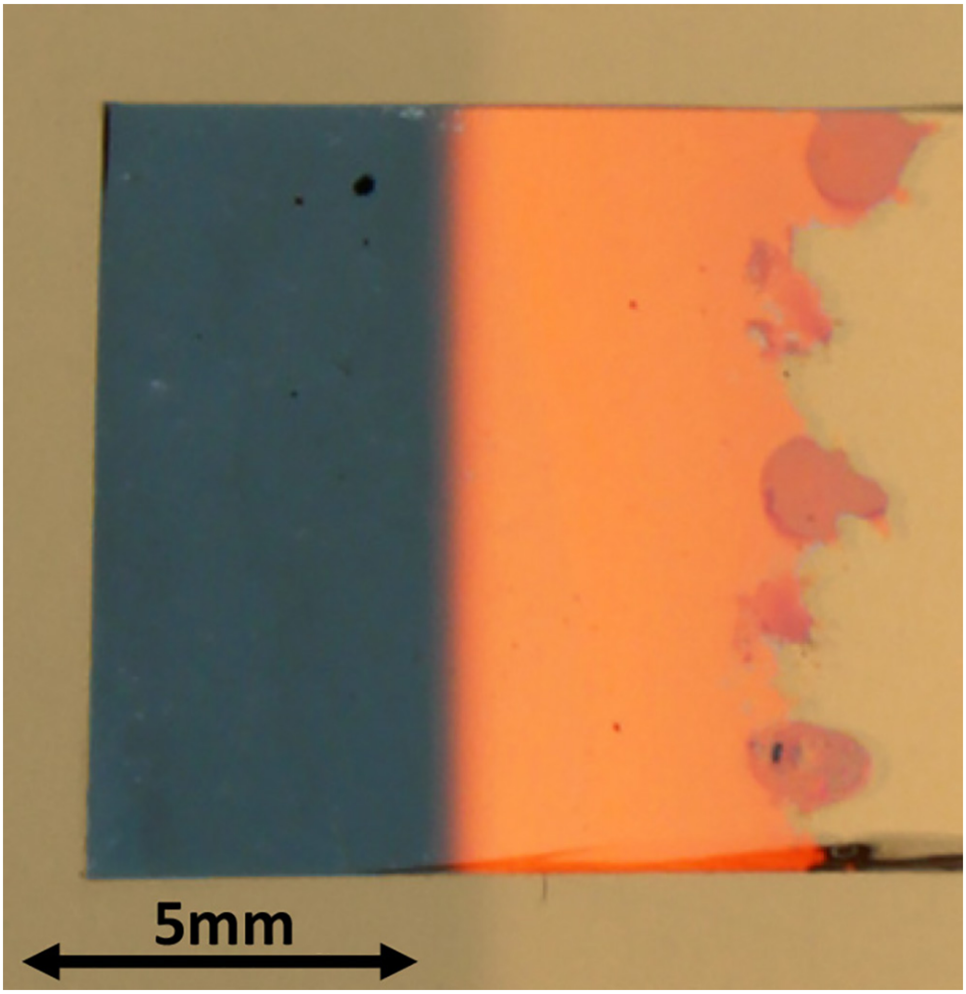

Figure 2. Macroscopic gold nanosphere monolayers. Alkane-thiol capped gold nanosphere monolayer film on a glass substrate is partially transmitting light (left side) and reflecting light (right side).

Figure 3 presents false-colored SEM images of a thiol-alkane capped 15 nm gold nanosphere monolayer film on a silicon wafer substrate. **Figure 3(a)** shows the edge of the film, demonstrating the films are monolayers and the nanospheres pack into amorphous domains at microscopic length scales. At nanoscopic length scales the films contain hexagonally close packed domains as demonstrated by the Fourier transform of the image in **Figure 3(b)** (inset).

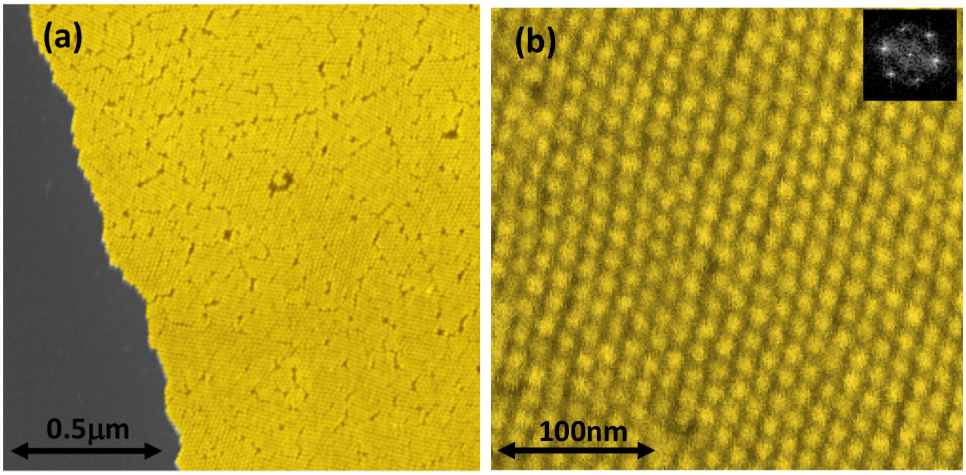

Figure 3. False-colored SEM images. Thiol-alkane capped 15 nm gold nanosphere monolayer films. The inset in upper-right corner of **(b)** is the Fourier transform of the image.

The normalized experimental absorbance from a monolayer film consisting of thiol-alkane capped 15 nm gold nanospheres on a glass substrate (red line), and a suspension of 15 nm gold nanospheres in water (blue line) and phase transferred into chloroform (green line) is shown in **Figure 4**. Although shifted and slightly broadened, relative to the aqueous suspension, due to particle-particle coupling[20] and changes in the host medium, the plasmon resonances are preserved well for the monolayer film given the density of nanospheres.

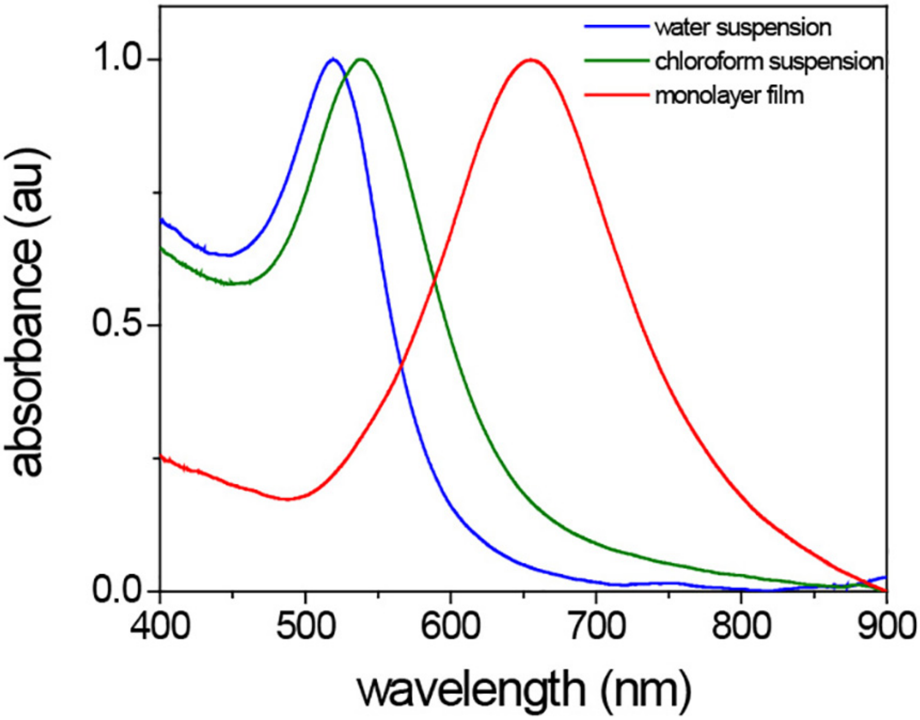

Figure 4. Normalized experimental absorbance spectra. Macroscopic absorbance from 15 nm gold nanospheres in a water suspension (blue line), phase transferred into a chloroform suspension (green line) and as a monolayer film (red line).

Discussion

This protocol describes a single 'one-pot' self-assembly technique to create macroscopic nanoparticle-ligand monolayer films using phase transfer, phase separation and surface tension gradients. The advantage of this technique is that it combines three self-assembly processes into a single, low-cost process; by quickly and efficiently phase transferring the nanoparticles, assembling the particles into monolayers at the air-fluid interface and transporting the monolayer films onto template-free substrates.

The most critical elements for creating high-density monolayers are using freshly synthesized citrate stabilized gold nanoparticles, choosing a suitable substrate/ligand/solvent, controlling the evaporation rate and temperature, and using materials free of contaminates.

The rate of the nanosphere phase transfer was observed to decrease with the age of the nanoparticles, presumably from changes in the nanosphere surface chemistry[21]. Typically the 'life-time' of the gold nanoparticles was less than 3 months from when they were synthesized. If the gold nanoparticles are purchased, the phase transfer rate is also greatly reduced if the manufacturer stabilizes the nanoparticles in excessive amounts of 'unknown' surfactants. The phase transfer rate was difficult to quantify for commercial nanospheres since the age and surfactant were unknowns. For larger nanosphere diameters (>30 nm) the size of the nanospheres hinders large film formation and the film areas are decreased typically to square millimeters. Hydrophobic substrates, such as Teflon, did not form good films since the water-THF could not wet the surface and subsequently transport the film onto the substrate surface.

The amount of ligand used needs to be sufficient to cover the entire surface area of the nanoparticles in suspension to observe film formation at the air-liquid interface and to enable the films to translate up the side of the vial. Adding excess ligands greatly increased the speed and final height the films reached on the substrate[1]. The packing density of the nanoparticle into monolayer films also depends on the specific ligand selected; thiol-alkane/ene/phenol were tested and all worked reasonably well, singularly or in combination. The pH of the reaction mixture is also an important parameter and will be the subject of future studies.

This self-assembly technique, with further refinement, may enable the future development of high-throughput, tunable nanoparticle-ligand structures.

Disclosures

The authors have nothing to disclose.

Acknowledgements

This work was supported with funding provided from the Office of Naval Research. J. Fontana acknowledges the National Research Council for a postdoctoral associateship.

References

1. Fontana, J., Naciri, J., Rendell, R. & Ratna, B. R. Macroscopic self-assembly and optical characterization of nanoparticle–ligand metamaterials. *Advanced Optical Materials* **1**, 100-106, doi:10.1002/adom.201200039 (2013).
2. Fontana, J. *et al.* Large surface-enhanced Raman scattering from self-assembled gold nanosphere monolayers. *Applied Physics Letters* **102**, 201606 (2013).
3. Mayya, K. S. & Sastry, M. A new technique for the spontaneous growth of colloidal nanoparticle superlattices. *Langmuir* **15**, 1902-1904 (1999).
4. Spain, E. M., Johnson, D. D., Kang, B., Vigorita, J. L. & Amram, A. Marangoni flow of Ag nanoparticles from the fluid-fluid interface. *J Phys Chem A* **112**, 9318-9323, doi:10.1021/jp802273j (2008).
5. Sihvola, A. Metamaterials: A Personal View. *Radioengineering* **18**, 90-94 (2009).
6. Valentine, J., Li, J. S., Zentgraf, T., Bartal, G. & Zhang, X. An optical cloak made of dielectrics. *Nature Materials* **8**, 568-571, doi:10.1038/nmat2461 (2009).
7. Seo, E. *et al.* Double hydrophilic block copolymer templated Au nanoparticles with enhanced catalytic activity toward nitroarene reduction. *The Journal of Physical Chemistry C* **117**, doi:10.1021/jp4027139 (2013).
8. Ward, D. R. *et al.* Simultaneous measurements of electronic conduction and Raman response in molecular junctions. *Nano Letters* **8**, 919-924, doi:Doi 10.1021/Nl073346h (2008).
9. Perez-Gonzalez, O. *et al.* Optical Spectroscopy of Conductive Junctions in Plasmonic Cavities. *Nano Letters* **10**, 3090-3095, doi:Doi 10.1021/Nl1017173 (2010).
10. Xiao, S. M., Chettiar, U. K., Kildishev, A. V., Drachev, V. P. & Shalaev, V. M. Yellow-light negative-index metamaterials. *Optics Letters* **34**, 3478-3480 (2009).
11. Fang, N., Lee, H., Sun, C. & Zhang, X. Sub-diffraction-limited optical imaging with a silver superlens. *Science* **308** (2005).
12. Liu, Z. W., Lee, H., Xiong, Y., Sun, C. & Zhang, X. Far-field optical hyperlens magnifying sub-diffraction-limited objects. *Science* **315**, 1686-1686, doi:DOI 10.1126/science.1137368 (2007).
13. Valentine, J. *et al.* Three-dimensional optical metamaterial with a negative refractive index. *Nature* **455**, 376-U332, doi:10.1038/nature07247 (2008).
14. Law, M., Greene, L. E., Johnson, J. C., Saykally, R. & Yang, P. D. Nanowire dye-sensitized solar cells. *Nature Materials* **4**, 455-459, doi:Doi 10.1038/Nmat1387 (2005).
15. Frens, G. Controlled Nucleation for Regulation of Particle-Size in Monodisperse Gold Suspensions. *Nature-Phys Sci* **241**, 20-22 (1973).
16. Ye, X., Chen, J., Diroll, B. T. & Murray, C. B. Tunable Plasmonic Coupling in Self-Assembled Binary Nanocrystal Superlattices Studied by Correlated Optical Microspectrophotometry and Electron Microscopy. *Nano Letters* **13**, 1291-1297, doi:10.1021/nl400052w (2013).
17. Bigioni, T. P. *et al.* Kinetically driven self-assembly of highly ordered nanoparticle monolayers. *Nature Materials* **5** (2006).
18. Ng, K. C. *et al.* Free-Standing Plasmonic-Nanorod Super lattice Sheets. *Acs Nano* **6**, 925-934, doi:Doi 10.1021/Nn204498j (2012).
19. Romero, I., Aizpurua, J., Bryant, G. W. & de Abajo, F. J. G. Plasmons in nearly touching metallic nanoparticles: singular response in the limit of touching dimers. *Optics Express* **14**, 9988-9999 (2006).
20. Caragheorgheopol, A. & Chechik, V. Mechanistic aspects of ligand exchange in Au nanoparticles. *Physical Chemistry Chemical Physics* **10**, 5029-5041, doi:Doi 10.1039/B805551c (2008).