# Self-Assembly of Nanoparticle Arrays for Use as Mirrors, Sensors, and Antennas

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**ABSTRACT** The self-assembly of nanoparticles (NPs) at liquid—liquid interfaces (LLIs) has recently emerged as a promising platform for tunable optical devices, sensors, and catalysis. There are numerous advantages for such platforms when compared to more conventional solid-state counterparts. For example, they do not need engineering, self-assemble if proper conditions are provided, are self-healing, are practically nondegrading, and are easily renewable. Furthermore, they have the added benefit of being able to facilitate the interactions of analytes dissolved in often-inaccessible environments. In this Perspective, we highlight some important recent developments in understanding the mechanisms and applications of self-assembly of NPs at LLIs for use as mirrors and sensors. Finally, we explore future directions in this field, focusing on NP arrays with electrotunable properties assembled at a LLI, which has been one of the driving forces for developing such technologies.
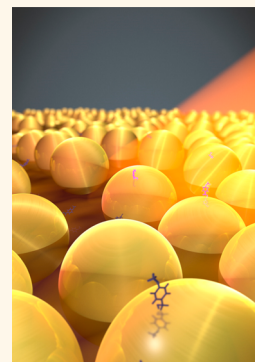
Liquid—liquid interfaces (LLIs) have a long history in the physical sciences.[1] In fact, every curious child is familiar with this fundamental concept in the form of vigorously shaking a bottle containing cooking oil and water with the ultimate goal of trying to achieve some form of mixing. Of course, such attempts are in vain as a LLI is formed between these two immiscible liquids. The polar water and nonpolar oil phase do not "like" each other; that is, the free energy of their contact is high. If you try to mix them, they will rapidly segregate and form a distinct interface that is only a few atomic layers thick. Examples of such interfaces include water—nitrobenzene, water—dichloroethane, and water—toluene; in all cases, phase separation is unambiguous and the boundary is well-defined.

Of late, such interfaces have been the subjects of numerous publications related not only to studying the fundamental properties of such LLIs but also to decorating the LLIs with unique surface-active agents. These advances have resulted in a diverse range of applications from trace analyte (bio)sensing to controlling plasmonic properties and, as we will see, even facilitating molecular purification. The applications to date have been driven by collaborative initiatives

bringing together physical chemists with expertise in materials sciences, nanoplasmonics, physics, and electrochemistry. For example, in the most recent issue of *ACS Nano*, Girault and colleagues report an experimental demonstration of mirror-like properties of self-assembled monolayers of gold nanoparticles (NPs) at the interface of water and dichloroethane.[2] This work is an important milestone in the steps toward the ultimate development of a reversible electrovariable liquid mirror. In this Perspective, we describe the overall progress in this research area, focusing on fundamental principles as well as applications. We note that the intention of this article is not to cite all papers relating to LLIs, but rather to highlight recent, selected developments that we hope will benefit new and seasoned scientists alike.

**Self-Assembly of Nanostructures at Liquid—Liquid Interfaces.** Various types of moieties have been successfully reported to self-assemble at liquid—liquid interfaces. For example, amphiphilic molecules can settle at the interface with their hydrophilic compartments looking into water and their hydrophobic components embedded in oil. The canonical examples of such molecules are surfactants, such as phospholipids, but

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In the most recent issue of *ACS Nano*, Girault and colleagues report on the first experimental demonstration of mirror-like properties of self-assembled monolayers of gold nanoparticles at the interface of water and dichloroethane.

many complex molecules have hydrophilic and hydrophobic terminals. Such molecules will form dense monolayers at interfaces, where their surface density is limited by the repulsive interactions between the molecules. Further, two-dimensional arrays can also be formed by larger objects such as micro- and nanoparticles.[3] Such particles do not necessarily have to be amphipillic, but rather an array may form if the free energies of the contact area of the particle with both water and oil are together smaller than the free energy of the oil/water interface. Individually, each particle will then tend to settle at the interface with the formation of a three-phase boundary. If the system contains more particles than the interface can accommodate, then their density at the interface will be controlled by the repulsive and attractive forces acting between them. As such, strong repulsion will not allow the particles to settle too close to each other.

A classic example of such structures is Pickering emulsions of dielectric particles, which can be as large as 10–100 $\mu$m in size. Achieving self-assembly at the interface therefore requires a fine balance of forces, determined by several factors. These factors must ensure that the particles sufficiently repel each other in order not to aggregate and to sediment in the bulk solution, but not to repel so strongly such that they can still form dense monolayers at the interface (Figure 1A). For example, protection against fusion can be achieved by functionalization of NPs with ligands that are either chemically bonded to the NPs, such as mercaptanes, or alternatively they can be physisorbed (*e.g.*, citrates). Often, the outer terminals of such ligands contain acidic groups. These dissociate in the aqueous phase subject to the solution pH, which, thereby, controls the net charge of the ligand-coated NPs. Furthermore, the strength of particle–particle repulsion may be controlled not only through the average charge of the ligands but also through the screening of Coulombic interactions between them. This control can be achieved by the addition of inorganic electrolytes (Figure 1C), such as NaCl, in the aqueous phase or, alternatively, to a *minor* degree by the addition of organic electrolytes that are dissolvable in the oil phase (the degree of dissociation of ligands' terminal groups on the oil side of the interface is currently an open question, but it must be much less pronounced).

**Liquid–Liquid Interface between Two Immiscible Electrolyte Solutions.** As described above, there are many advantages for adding electrolytes in either or both of the phases. Such platforms are often called "interfaces of two immiscible electrolytic solutions" (ITIES), and they ultimately facilitate assembly or even disassembly of NPs at the interface.[4] Under such conditions, the interface itself becomes polarizable; that is, it can function as a liquid electrode. Namely, applying a voltage across this interface results in back-to-back nanometer-scale electrical double layers being formed on either side of the interface. The net charge in the double layer on the aqueous side will be equal but opposite in sign to the one at the oil side of the interface. This will result in an electric field localized within those two double layers.

These double layers will be discharged if the applied voltage across the interface is larger than the free energy of transfer of ions across the interface. As an example, an ITIES can be formed with the use of hydrophilic ions, such as Li$^+$ and Cl$^-$, which, when given a choice, prefer to be in the aqueous phase, and hydrophobic ions, such as tetrabutylammonium (TBA$^+$) and tetraphenylborate (TPB$^-$), which dissolve better in the oil phase. Each of these ions has a finite free energy of transfer between the corresponding phases (typically on the order of 0.5 eV), a step that the ion must climb to get into the less friendly neighboring liquid. However, applying a substantially larger voltage will eliminate this step and cause ion traffic across the interface. The latter will then stop being an ITIES, at least with respect to the immiscibility of electrolytes. At higher voltages, this may even cause emulsification of the solvents, but at lower voltages, the interface stays locked against penetration and remains statistically impenetrable to ions coming from the opposing phases.

By applying a potential bias across the interface, one can control NP localization at an ITIES. Thus, polarizing the aqueous phase positively relative to the organic phase may help to take the negatively charged NP out of the potential well that traps the particle at the interface in the absence of an applied voltage (eliminate the well), and the particle will be free to leave the surface, diffusing into the bulk. On the contrary, negatively polarizing the aqueous phase may adjust the position of the particle, pressing it deeper into the oil side of the interface. The conceptual study by Flatté et al.[5] shows that applying a voltage of the corresponding sign makes it, in principle, possible to move NPs away from the interface and back.

Ultimately, control over the population of NPs at an ITIES is governed by the interplay of driving forces that determine the potential well for NPs at the interface (or its
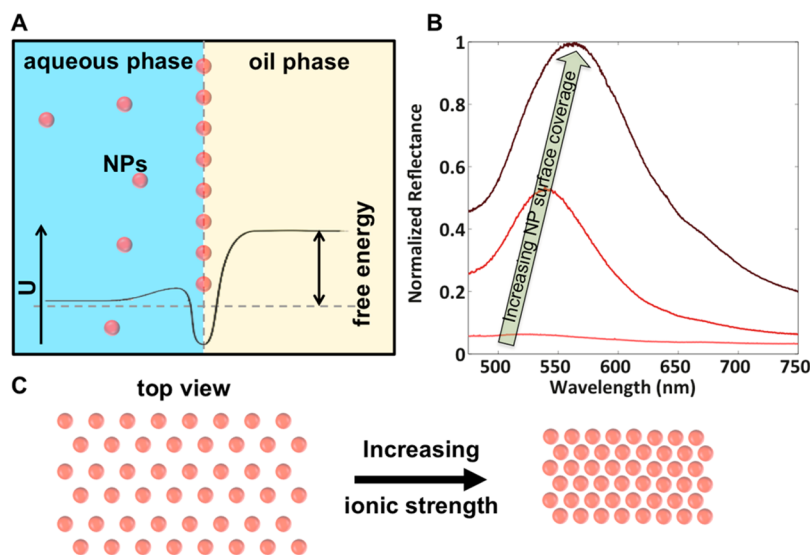
**Figure 1.** (A) Schematic of assembly of nanoparticles (NPs) at a liquid−liquid interface (LLI). Assembly of NPs at the LLI results in a reduction of the system free energy when the NP blocks the energetically unfavorable interface between the aqueous and oil phases. (B) Reflectivity can be controlled by increasing NP surface coverage at the LLI. Increasing surface coverage results in a decrease in the surface-to-surface separation, which can also cause a red shift in the peak maxima. (C) Interparticle spacing of NPs can be controlled by varying the ionic strength of the solution, charge on the NP, or pH. Adapted from ref 12. Copyright 2012 American Chemical Society.

absence). The latter include competitive wetting at the interface, solvation of charged particles, interaction with the electric field, the effect of line tension, and the interface deformability.[5,6] Flatté et al.[5] analyzed this interplay semiquantitatively, based on a number of simplifying assumptions for small NPs; the same team also attempts to show this interplay for larger NPs.[7] For large NPs (>20 nm in radius) without applied voltage, the potential well at the interface can reach thousands of $k_BT$; however, moderate voltages can be used to eliminate the well in order to allow the NPs to leave or to push it away from the interface.[7] In order to achieve this, one needs to find a fine balance between the net charge on the functionalized NPs and the strength and the distribution of the electric field in the double layer. Indeed, for lower electrolyte concentration, the thickness of the double layers will be larger for the same voltage drop across the interface; however, the local values of the electric field will be lower. There will thereby be a trade-off between the absolute value of the electric field and the number of charges upon which it will act.

Recently, reversible control of NPs at a LLI has been achieved for 2 nm particles.[8] However, for larger particles, for which the capillary wells are huge, the electrovariability of the population has not yet been demonstrated. Based on evaluations made by those in refs 5 and 7, the first thought would be to maximize the charge on the NPs by using a more basic pH, as this will (i) promote stronger repulsion between NPs in the layer, diminishing the trapping well, and (ii) maximize the effect of the electric field on each and every NP. However, this approach might simultaneously reduce the density of NPs in the interfacial layer. They will be easier to remove, but they will not necessarily form a sufficiently dense layer at the LLI in the first place, which would reduce the reflectivity of the surface (Figure 1B). Another path would be to add surfactants that will reduce the surface tension at the oil−water interface and thereby decrease the depth of the well, keeping NPs at the interface. However, excessive amounts of surfactant may totally eliminate the propensity for NPs to reside at the interface and may

even destroy the interface in favor of emulsification.

**Nanoplasmonic Platforms at a Liquid−Liquid Interface.** One can potentially envisage a number of applications of self-assembled layers at LLIs, but it would perhaps be fair to say that the driving force in characterizing and validating NP self-assembly at either a LLI or ITIES has been toward the development of reversible nanoplasmonic liquid-like mirrors and for (bio)sensing applications using surface plasmon-enhanced Raman spectroscopy.

*Mirrors.* The first observation of a mirror at a LLI can be attributed to Yogev and Efrima in 1988, who reported on multilayer metal liquid layer films (MELLFs) formed by silver aggregates at an aqueous dichloromethane interface.[9] Although this was a breakthrough achievement, such films are generally not suitable for most nanoplasmonic functions, and furthermore, once aggregated, they exhibit no electrovariability. More recently, mirror properties of unaggregated monolayers of NPs were predicted and explored theoretically at both the LLI and ITIES.[7,10] These works highlight the strong dependence of reflectivity on the

size of NPs and the layer density. Importantly, it was found that reflections as large as 70–80% can be obtained in the main part of the visible spectrum using particles larger than 40 nm in diameter. The high reflectivity was found to be due to the surface-to-surface NP separation, NP size, angle of incidence, and polarization of light.

Experimentally, Girault and colleagues[2] have now measured the reflectivity from such layers, with trends qualitatively agreeing with the theory.[10] The reflectivity of Au NP films, prepared with varying interfacial NP surface coverage and size, was characterized as a function of incident light angle, wavelength, and polarization. They found that the addition of Au NPs to the interface results in a surface-coverage-dependent increase of the reflectance for the incidence angles below the critical angle, $\theta_c$ (the angle of incidence above which total reflection occurs), and a decrease in reflectance for the angles $\theta > \theta_c$. For approximately monolayer coverage, the reflectance for $\theta < \theta_c$ reached a maximum value, with a clearly visible Au NP mirror formed (Figure 1B and Figure 2). With further formation of multilayers, no discernible changes in reflectance were found. The key parameter in this study was the size of the Au NPs. Maximum reflectance was observed with 60 nm Au NPs, while a further increase of the NP size to 100 nm led to a decrease of signal. The observed effects have been ascribed to interplay between Au NP absorption, scattering, and the angular dependence underlying reflectivity of the interface, which have been modeled using three-dimensional finite difference time domain (FDTD) calculations.

What physically happens when we shine light on the layer of NPs, whether it be at a LLI or ITIES or potentially even a solid substrate? The incident light gives its energy to the excitation of the local plasmon modes inside NPs. If these NPs are not too far from each other, these
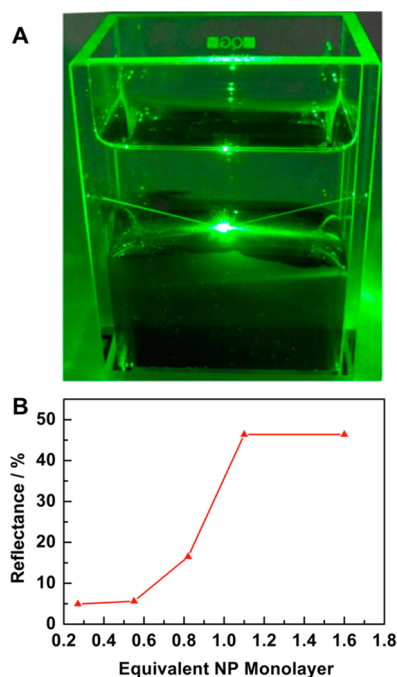


Figure 2. (A) Optical image of a 532 nm laser line reflected on a 60 nm nanoparticle (NP) film at a [heptane + DCE]/water interface. (B) Percent reflectance as a function of NP coverage density for 60 nm particles. Adapted from ref 2. Copyright 2013 American Chemical Society.

modes result in "bonding" and "antibonding" eigenstates,[11] bonding states working as antennas transmitting some part of the light, but also reflecting a large portion of it. However, for a substantial reflection, a sufficient mass of the "plasmonically active" material is needed.

The control of NP surface coverage (i.e., the average distance between the NPs) is crucial for tuning the light reflectance from functionalized interfaces. In the work arising from Girault's group,[2] this has been achieved by direct tuning of the amount of NPs injected onto the interface. Alternatively, in an earlier body of work, Turek et al.[12] characterized the spectral properties of NPs adsorbed to a water–dichloroethane interface at varying surface coverage. The latter was manipulated by controlling the repulsion between the NPs by tuning the pH and electrolyte concentration in water. With this method, it was possible to design a "plasmon ruler" at a LLI whereby the localized surface plasmon resonance maximum could be directly correlated to the surface-to-surface spacing between the NPs.

Exactly as theory predicts, a red shift of the spectra was observed when the NPs approach each other.

*Nanoplasmonic Sensors at a Liquid–Liquid Interface.* Having precise control of the plasmonic properties at a LLI offers significant advantages for using such an interface as a sensor. As discussed above, the reflectance of light of a wavelength much greater than the size of the NPs is determined by spatially averaged properties of the whole layer. However, the same electromagnetic radiation results in the creation of the local resonance fields associated with excitation of localized plasmon modes in NPs. This easily results in 2 orders of magnitude (or higher) enhancement of the electric field component in the gaps between NPs, in the so-called hot spots (Figure 3). This effect can be and is already used in NP-amplified photocatalysis at LLIs.[13] Another application relates to the amplification of Raman scattering from analyte molecules captured by the NPs or trapped between them. A unique property of working with a LLI is that analytes can be
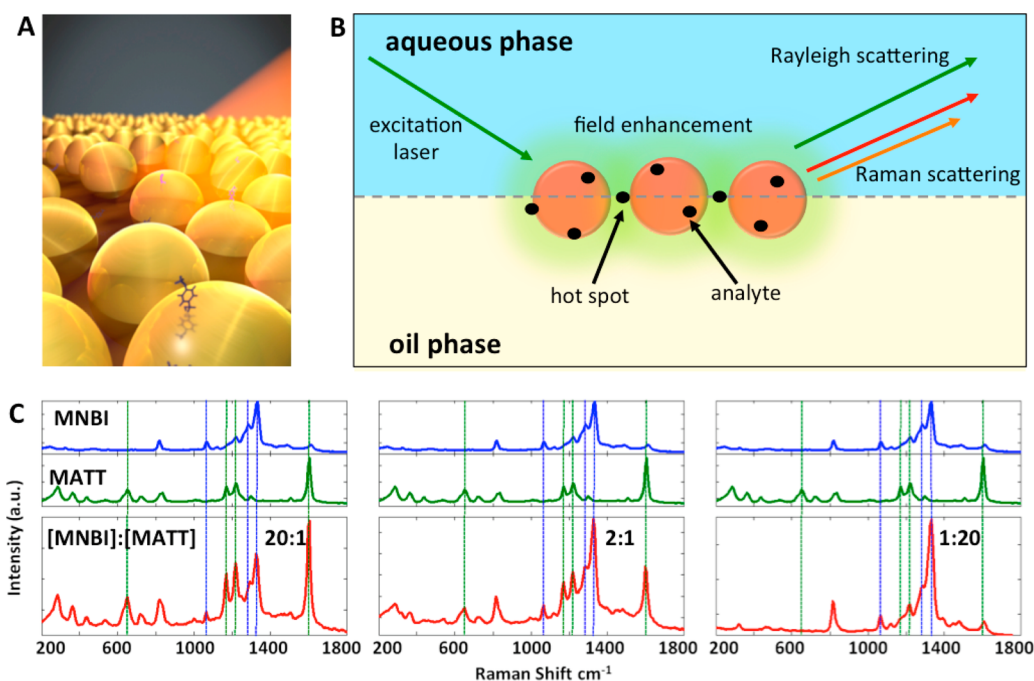
**Figure 3.** (A) Schematic representation of nanoparticles (NPs) adsorbed to a liquid−liquid interface (LLI) with trace analytes bound to 16 nm Au NPs for surface-enhanced Raman spectroscopy (SERS) detection. (B) Schematic representation of the operating principles of a SERS measurement at a LLI. (C) SERS spectra showing multiphase dual analyte detection for MNBI (mercapto-5-nitrobenzimidazole) and MATT (4-methoxy-α-toluenethiol) in ratios of 20:1, 2:1, and 1:20. For reference, pure spectra of MNBI and MATT are also shown. Adapted with permission from ref 14. Copyright 2013 Nature Publishing Group.

captured on the NPs from either the oil or aqueous phases. Furthermore, the NPs can rotate around their axes, which allows analytes to enter the hot spots.

The first successful realization of surface-enhanced Raman spectroscopy (SERS) detection at a LLI was described by Cecchini et al.[14] Trace levels of analytes could be detected from molecules dissolved in either the aqueous or the oil phases. In an extension to this work, it was found that airborne analytes could also be detected at a somewhat modified liquid−air interface. Detection limits down to roughly 1 analyte molecule per 5 NPs, or per $10^{16}$ water molecules, could be achieved in the aqueous phase. For the analytes predominantly dissolving in the organic phase, limits of detection were slightly higher. The reason for this was likely due to the NPs sitting more on the water side of the interface, hence the analyte molecules were less exposed to the hot spots. Trace multianalyte detection has also been demonstrated, including cases when some

molecules were dissolvable in aqueous phase and some in the organic phase (Figure 3C). Altogether, approximately 20 different analytes were tested at different concentrations, showing the impressive capacity of this new SERS platform. Proxy molecules of explosives and nerve gases have also been tested and can potentially enable this inexpensive technology for use in the field for the detection of poisons, chemical weapons, and other illegal substances, as well as the detection of environmental pollutants in

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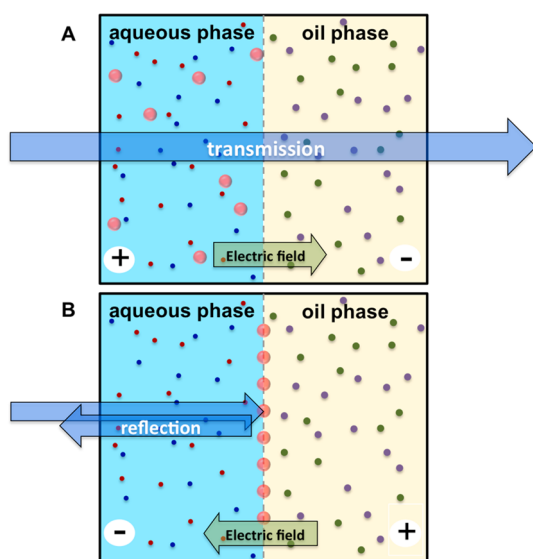
quantities not yet dangerous to life and health.

The trick to obtaining these results was to control the repulsion between the NPs. The repulsion should be sufficient to prevent fusion of NPs and sedimentation, but it must still allow NPs to come close to each other at the surface to warrant the hot spots between them. It is well-known that such spots are the hottest when NPs are about 1 nm away from each other, in terms of surface-to-surface separations. At shorter distances, about 0.5 nm, a "plasmonic short cut" takes place[11] and the hot spots get quenched. When NPs are covered by chemically bonded functional ligands, such close proximity will be unlikely, but if they are covered only by physisorbed citrate, short cuts may result. Thus a fine-tuning of the solution pH, the concentration of electrolyte, and the choice of the ligands is key to success.

## FUTURE CHALLENGES

Returning to the reflective properties of NP arrays, ultimately,

**Figure 4. Schematic representation of an electrovariable mirror in transmission mode (A) and reflectance mode (B).**

interest lies in the system being electrovariable (Figure 4). If achieved, a switching voltage less than 1 V could convert a mirror to a transparent window and back. In order for such a platform to be successful, a suitable concentration of NPs is required that produces a monolayer or more and is highly reflective when the NPs are localized at an interface but remains optically invisible when dispersed in the bulk of the liquid. This area of research has the possibility to contribute to energy-saving technologies in tall glass buildings, where the amount of energy spent on air conditioning in summer exceeds the energy spent on heating in winter. Because the reflection coefficients depend on frequency and the density of NPs, one can tune the optics of reflection, that is, the color of the mirrors, for artistic design or any other purpose. The creation of vertical ITIESs on an industrial scale is a challenge, but one may use a similar principle, replacing one of the liquid phases with a transparent indium tin oxide (ITO) glass electrode. The negatively charged NPs can be driven to the surface with a positive voltage and repelled from it with negative voltage. Interestingly, the energy spent on all these operations would only occur when switching the voltage; the rest of the time

no electrical current would run through the system, incurring no losses. This is in contrast with the windows based on liquid-crystal structures, the orientation and transparency of which is altered by passing current.

Alternatively, NP arrays can be formed on deformable surfaces, such as ITIES-based electrowetting systems (in the so-called "ultralow voltage" regime).[15] Here, a droplet of organic phase with organic electrolyte in it, lying at the solid electrode embedded in a solution of inorganic aqueous electrolyte, changes its shape when voltage is applied between that electrode and the counter electrode located outside the droplet. These are used in variable focus lenses and display technologies. However, when a dense monolayer of sufficiently large metallic (gold or silver) NPs, which warrants the reflection of light, is irreversibly adsorbed at the ITIES, the system can be used to build a mirror that can change its curvature. Such gadgets could be employed in different optical devices that use variable-focus mirrors, including pico-projectors or switchable radar. This principle was mentioned by Girault[16] in his News and Views note on the theory of low voltage electrowetting with ITIES,[17]

but now that the mirror effect has been demonstrated by his group, this dream may soon become a reality, as well as many other ideas concerning the use of mirror properties of functionalized liquid interfaces.

Last but not least, as mentioned, there are numerous other applications that could benefit from NPs adsorbed at a LLI. Among them is the ultraconcentration of NPs, purification, and separation based on size.[18] Nanoparticles initially dissolved in water, and possibly not yet even settled at the interface, are pushed by centrifugation to move to the interface; continued centrifugation moves them even further into hydrated oil, so that they end up at the bottom of the oil phase but encapsulated inside an aqueous droplet. Not only are highly concentrated NPs created using this technique, but they are also cleaned on the way. Alternatively, this droplet can be dissolved in water again. This was shown to be an effective option for cleaning NPs from surfactants and adsorbed molecules.

The use of hot spots, provided by the NP arrays at a LLI, for amplification of chemical reactions in the spirit of applications described by Kleinman et al.[19] is also highly interesting. Practical applications in this area are limited by the very small surface areas, as real photocatalysis or electrocatalysis require volume-filling surfaces to amplify the yield, unless one generates oil—water emulsions. Nevertheless, from a fundamental point of view, such systems may be highly relevant.

All in all, the design and properties of liquid—liquid nanoplasmonic platforms is an exciting, emerging area of research. It awaits the full utilization of many achievements of modern "solid state" nanoplasmonics,[11] such as experimentation with complex aggregates of composite nanoparticles of different architectures, but it can offer some unique new opportunities that solid-state devices cannot, related to adjustability and electrovariability. On the other hand, the

theory of localization of functionalized nanoparticles at liquid interfaces is still in its infancy; this interdisciplinary area will be a melting pot for electrostatic theory, capillarity, statistical mechanics, and cutting-edge molecular dynamic simulations.

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