

# Mixed monolayer coverage on gold nanoparticles for interfacial stabilization of immiscible fluids

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**Gold nanoparticles covered with a mixed monolayer of *n*-dodecanethiol and 11-mercapto-1-undecanol were prepared and found to mediate the oil–water interface, providing access to stable water droplets in oil.**

The synthesis of well-defined materials and structures from nanoscopic components, using simple approaches and readily available starting materials, is essential for the use of these new materials in technological applications. Nanoparticles are of key importance in this regard for the properties they impart when integrated effectively into polymer materials,<sup>1</sup> fluids,<sup>2</sup> or biological systems.<sup>3</sup> The self-assembly of particles at the fluid–fluid interface<sup>4</sup> can be applied to nanoparticles as a simple method to achieve microscale assemblies, capsules, and ultra-thin sheets. Such assemblies retain the characteristic properties of both the nanoparticles (*i.e.*, conductivity, fluorescence, magnetism, *etc.*) and the ligands attached to the nanoparticles, and are uniquely suited as functional materials for encapsulation and controlled release.

We recently reported the interfacial assembly of tri-*n*-octylphosphine oxide (TOPO)-covered cadmium selenide (CdSe) nanocrystals, or quantum dots.<sup>5</sup> These nanocrystals were synthesized by high-temperature methods from CdO and Se(0) precursors,<sup>6</sup> precipitated to remove excess surfactant, and found to assemble at the oil–water interface to encapsulate water droplets in a continuous oil phase, or oil droplets in a continuous water phase. The interfacial activity observed for the CdSe nanoparticles reduces interfacial tension. While quantum dots (*i.e.*, the CdSe core nanocrystalline material) impart electronic and photophysical properties to these assemblies, the ligands define the solubility of the nanoparticles, and their interactions with the oil and water phases. In this sense, the oil–water interfacial assembly of TOPO-covered CdSe nanocrystals could be extendable to other ligand-stabilized nanoparticles, such as *n*-alkanethiol-covered gold nanoparticles.

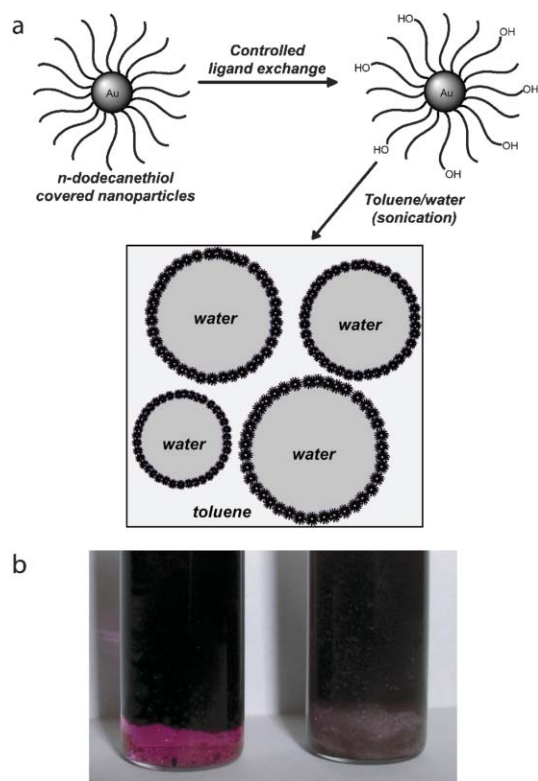
Initial efforts to achieve oil–water interfacial assemblies with the commonly prepared *n*-dodecanethiol-covered gold nanoparticles were unsuccessful. These alkane-covered gold nanoparticles, with an average diameter of about 2.5 nm, were prepared according to the methods of Brust, *et al.*<sup>7</sup> When the gold nanoparticles were shaken vigorously in toluene–water mixtures, no interfacial assembly was observed, and the nanoparticles simply dispersed

in the toluene phase. This suggests that the extent of the hydrocarbon ligand coverage on gold nanoparticles is different, and likely denser, than on the CdSe nanocrystalline quantum dots. Thus, studies were performed to tailor the ligand coverage of the gold nanoparticles to enable their use in interfacial assemblies. To this end, gold nanoparticles with a more hydrophilic periphery were prepared by ligand exchange chemistry, where the *n*-dodecanethiol monolayer on the gold nanoparticle surface was replaced entirely with 11-mercapto-1-undecanol,<sup>8</sup> to give gold nanoparticles with a hydroxyl rich periphery. These hydroxyl-functionalized gold nanoparticles also failed to stabilize the oil–water interface; they did not disperse in either the water or toluene phases, but instead precipitated when shaken in the presence of these two solvents.

Gold nanoparticles are distinct from many other types of nanoparticles in that their coverage with thiol-based ligands provides a robust periphery with strong interactions (near covalent bonding) of the thiol ligands to the gold surface. Yet, the thiol ligands are mobile, and can move laterally along the monolayer surface. Furthermore, gold nanoparticles are amenable to “mixed monolayer” coverages, where different ligands (*i.e.*, alkane thiols with different terminal groups) can be affixed to the particle surface in well-defined ratios.<sup>9</sup> Given our observations with *n*-dodecanethiol and 11-mercapto-1-undecanol coverages, a mixed monolayer of these two ligands was considered as an approach to achieving interfacial assembly. A range of gold nanoparticle samples was thus prepared with different relative ratios of *n*-dodecanethiol and 11-mercapto-1-undecanol ligands in the mixed monolayer surface coverage. These samples were obtained by partial ligand exchange of 11-mercapto-1-undecanol on *n*-dodecanethiol functionalized gold nanoparticles. The mixed monolayer coverage was characterized by <sup>1</sup>H-NMR spectroscopy in CDCl<sub>3</sub>–CD<sub>3</sub>OD solution to determine the relative amounts of the two ligands on the gold surface by integration of the methylene proton resonance of the undecanol ligand (R–CH<sub>2</sub>OH at  $\delta$  3.4 ppm) against the methyl proton resonance of the dodecanethiol (R–CH<sub>3</sub> at  $\delta$  0.70 ppm).

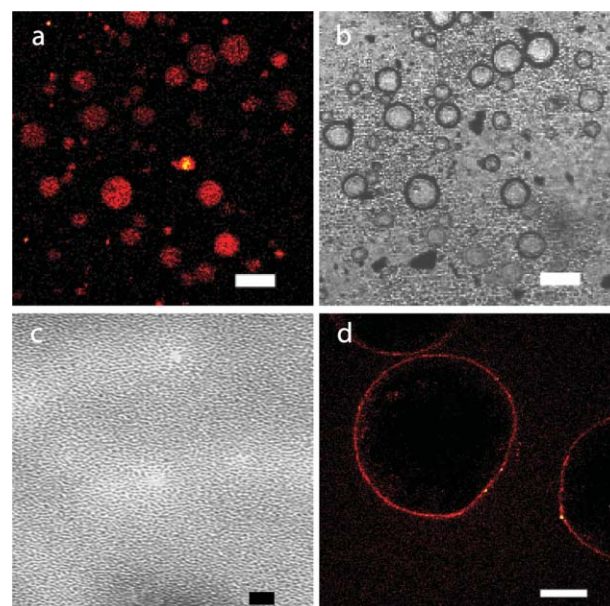
Several gold nanoparticle samples with mixed monolayer coverages were tested for their ability to stabilize the toluene–water interface. These experiments showed that gold nanoparticles with less than 40 mole percent undecanol embedded within the mixed monolayer dispersed in toluene, and those with more than 50 percent undecanol coverage did not disperse in either solvent. However, as shown in Fig. 1, gold nanoparticles with an undecanol-to-dodecane ligand ratio of approximately 1-to-1.1 (determined by <sup>1</sup>H NMR spectroscopy) were found to stabilize the toluene–water interface, and, consequently, water droplets

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**Fig. 1** (a) Schematic of controlled ligand exchange to provide functional gold nanoparticles for interfacial assemblies and the stabilization of water droplets in toluene; (b) left hand side: photograph of dodecanethiol-covered gold nanoparticles in toluene as a dark dispersion resting on top of an aqueous solution of sulforhodamine B, where no droplet stabilization is observed; right-hand side: photograph of water droplets stabilized by the functionalized gold nanoparticles resting on the bottom of the vial below a dispersion of excess nanoparticles.

in a continuous organic phase.<sup>10</sup> When these partially hydroxyl-functionalized gold nanoparticles were sonicated in toluene–water mixtures (MilliQ-purified water), water droplets formed that proved stable against coalescence over considerable time periods (weeks or longer). Performing the same experiment in the presence of the aqueous soluble sulforhodamine B confirmed the aqueous nature of the encapsulated phase. As shown in Fig. 2a, fluorescence confocal microscopy revealed the characteristic dye fluorescence ( $\lambda_{\text{max}} = 554 \text{ nm}$ ) in the encapsulated aqueous region. For this confocal characterization, the droplets were transferred to curved-well glass slides with flat coverslips, and diluted with toluene. The gold nanoparticle-covered droplets were drop-cast onto carbon-coated copper grids and allowed to dry. Transmission electron microscopy (TEM) revealed individual gold nanoparticles (Fig. 2c). The nanoparticle assemblies were stabilized further by the presence of a hydrogel in the capsule interior. An aqueous solution of poly(vinyl alcohol) was added to the mixed monolayer protected gold nanoparticles in toluene, where the nanoparticles were labelled with rhodamine B as part of the ligand structure.<sup>11</sup> Methanol was then used to remove toluene and water from the system, whereupon the assembly was maintained as shown by the presence of the fluorescently labeled particles in the cross-sectional image of Fig. 2d. Droplet size could be controlled roughly by agitation—sonication gave droplets of less than  $50 \mu\text{m}$  diameter,



**Fig. 2** (a) Fluorescence confocal microscope image and (b) optical microscope image of gold nanoparticle-stabilized water droplets with sulforhodamine B in the encapsulated phase (scale bar =  $40 \mu\text{m}$ ). (c) TEM image taken on part of a dried droplet showing individual nanoparticles (scale bar =  $25 \text{ nm}$ ). (d) Fluorescence confocal image of nanoparticle-stabilized water droplets with a poly(vinyl alcohol) interior, and rhodamine B labelled gold nanoparticles after removal of the oil–water interface by washing with methanol (scale bar =  $80 \mu\text{m}$ ).

while vigorous shaking resulted in droplets in the  $100\text{--}200 \mu\text{m}$  range.

The mixed monolayer-covered gold nanoparticles that are found to assemble at the oil–water interface are not amphiphilic in the traditional sense, in that they are not soluble in either water or oil. Nonetheless, the ligand coverage is balanced such that interfacial mediation and droplet stabilization is enabled. The nearly equivalent molar ratio of the dodecane and undecanol ligands used on the particles that gave successful assemblies, combined with the surface mobility of alkane thiols on gold, suggests the possibility that a fluid-induced phase separation of ligands on the gold surface occurred, yielding distinct polar and apolar hemispheres. Related studies using similar ligand coverages on gold nanoparticles have been conducted at the air–water interface.<sup>12</sup> This would give the nanoparticles a surfactant-like structure. Future studies will examine the ligand distribution on the surface of the assembled particles to probe this possibility.

In summary, the ability to generate capsular assemblies of gold nanoparticles at the oil–water interface has been demonstrated through the use of functional ligands and mixed monolayers on the nanoparticle surface. While there have been several recent reports on the mediation of fluid–fluid interfaces by gold nanoparticles<sup>13</sup> these have typically utilized citrate-stabilized gold nanoparticles, co-solvent mediation, or homogenous coverages with specially prepared ligands, containing, for example, bromopropionate groups, that serve to balance the water contact angle of the nanoparticles. The ability to use mixed monolayers to tune interfacial interactions for mediation of the oil–water interface provides a very simple approach to impart precise levels of surface functionality to the monolayer. Our current studies include the use

of chemistries that exploit such surface functionality in post-assembly chemistry with materials in the encapsulated phase, as well as electronic applications that exploit the conductivity of the gold nanoparticles used in the assemblies.

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- 10 Dodecanethiol-capped gold nanoparticles (50 mg, 2.5 nm diameter) were diluted in dichloromethane (5 mL), and 11-mercapto-1-undecanol (5 mg) was added as a solution in dichloromethane (2 mL). The solution was agitated at room temperature, and the mixed monolayer-covered nanoparticles were isolated by precipitation into hexanes. <sup>1</sup>H-NMR spectroscopy revealed the relative percentages of the two ligands on the surface (key resonances:  $-CH_2OH$   $\delta$  3.35 ppm to 3.55 ppm,  $-CH_3$  br centered at  $\delta$  0.70 ppm and  $-CH_2-$  br, spanning  $\delta$  0.90 to 2.00 ppm). Stabilized water droplets were formed by sonication of the mixed monolayer-covered gold nanoparticles in a mixture of toluene (4.5 mL) and MilliQ water (0.5 mL).
- 11 Gold nanoparticles (36 mg) containing 50 mole percent 11-mercapto-1-undecanol and 50 mole percent dodecanethiol were dissolved in a mixture of anhydrous *N,N*-dimethyl formamide (DMF) and dichloromethane. Rhodamine B (74 mg), *N,N'*-diisopropylcarbodiimide (0.2 mL, 160 mg), and 1-hydroxybenzotriazole (160 mg) were combined and transferred as a solution in DMF to the nanoparticle dispersion to a combined volume of 7 mL. The mixture was agitated overnight at room temperature and isolated by precipitation in hexanes and redispersion in dichloromethane until no free rhodamine B remained in the supernatant. UV-Vis spectroscopy of the dye-labelled nanoparticles in reagent alcohol revealed a peak at 555 nm in addition to the broad absorption of the gold nanoparticles across the visible spectrum.
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