Nanoparticles

Directing Self-Assembly of Nanoparticles at Water/Oil Interfaces**

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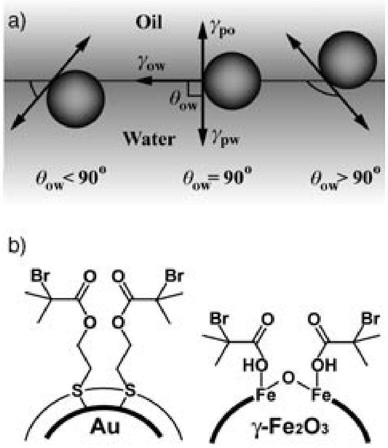
Nanoparticles (NPs) have attracted a great deal of attention because of their promising potential and already realized applications. Their unique electronic, magnetic, and optical properties can be manipulated by simply varying the dimension and geometry.[1] The integration of nanoparticles into one-, two-, or three-dimensional (2D or 3D) structures leads to novel collective properties that can be manipulated by the control of the cooperative interactions between the nanoparticles.[2] While nanoparticles may be chemically assembled by the interaction of ligands capped on nanoparticles, the elaborate design of ligands is a prerequisite.[3] For organic nanoparticles, which are formed directly in organic media or transferred from aqueous media with the aid of surfactants, their 2D or 3D arrays can be simply realized by controlled evaporation of solvents[2b,4] or at the water/air interface by using the Langmuir–Blodgett technique.[2a,5]

Thin films of nanoparticles have been produced in situ at interfaces between immiscible liquids.[6] Most recently, Lin and co-workers directed the assembly of hydrophobic CdSe nanoparticles at the water/toluene interface and they achieved size-dependent interfacial entrapment of CdTe nanoparticles.[7a] Meanwhile, Reincke and co-workers reported that the introduction of ethanol can pull hydrophilic citrate-stabilized Au-NPs into the water/heptane interface, leading to a closely packed monolayer.[7b] These two reports demonstrate a promising way to create a 2D or 3D arrangement of both hydrophobic and hydrophilic nanoparticles at water/oil interfaces. The use of interfaces between water/oil fluids to trap sub- or micrometer-sized particles has been well established.[8] Besides the particle diameter, this interfacial entrapment is mainly determined by the contact angle (θ) of the particle with the water/oil interface—surface wettability.[8] As schematically depicted in Scheme 1 a, when a particle is hydrophilic or hydrophobic it has a contact angle smaller (left) or larger than 90° (right) in a water/oil system and is localized totally within the water or oil phase. When its contact angle is around 90° (Scheme 1 a, center) the particle prefers to reside at the interface. As the particles approach nanometer size, however, the thermal energy becomes comparable to the interfacial energy.[7a] In this case, spatial fluctuations suffice to remove nanoparticles trapped at interfaces into bulk phases. The profile of the calculated partition of 10-nm particles in water/oil two-phase systems shows that only when the contact angle of the nanoparticles is close to 90° may they reside at the interface; when the contact angle slightly deviates from 90°, the nanoparticles prefer to go to the bulk phase, suggesting that the contact angle of 90° should play a pivotal role for the interface entrapment of nanoparticles.[8a] Reincke and co-workers observed that the addition of ethanol renders the contact angle of Au-NPs with the water/hexane interface close to 90°, which is a crucial point for the interfacial entrapment of nanoparticles in their work.[7b]



Scheme 1. a) Schematic representation of the position of a particle at a water/oil interface for a contact angle with the interface less than 90° (left), equal to 90° (center), and larger than 90° (right). b) Schematic illustration of the structures of Au@DTBE (left) and γ-Fe$_2$O$_3$@BMPA nanoparticles (right).

Recent studies on phase transfer of aqueous Au-NPs show that by using single long-chain alkylamines, one may transfer carboxylic acid derivatized Au-NPs onto water/oil interfaces.[9] Wei and co-workers have observed interfacial attachment of the Au nanoparticles capped with a resorcinarene ligand.[5c] These reports suggest that interfacial entrapment and self-assembly of nanoparticles might be realized by appropriate hydrophobic coating. It is well known that substrates with carboxylic ester groups possess contact angles in the range of 80–110°.[10] Herein, we report that the capping with ligands with a terminal 2-bromopropionate group may lead to contact angles for aqueous or organic nanoparticles close to 90°, thus driving nanoparticles to reside and self-assemble at water/oil interfaces. The choice of these ligands was encouraged by the success of living free-radical polymerization on nanoparticles.[11] The significance of our work lies on the fact that it should provide a general protocol for trapping and organizing nanoparticles at water/oil interfaces.

In this work, 5-nm and 12-nm Au nanoparticles were synthesized by citrate reduction of chloroauric acid in the aqueous phase.[12] Owing to their negatively charged surface, these Au-NPs are highly hydrophilic, residing only in the water phase. By means of ligand exchange, these aqueous Au-NPs were capped with 2,2′-dithiobis[1-(2-bromo-2-methyl-

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[**] This work is supported by the Max Planck Society. We thank J. Hartmann and R. Pitschke for assistance with the TEM measurements.

DOI: 10.1002/ange.200460920

propionyloxy)ethane] (DTBE), denoted as Au@DTBE. Scheme 1b (left) schematically represents the structure of Au@DTBE nanoparticles. The optimal density of DTBE capped on Au-NPs, determined by thermogravimetric analysis, is around 3 wt% in our work, corresponding to about 800 DTBE molecules per Au-NP. Addition of toluene to the aqueous dispersions of Au@DTBE nanoparticles led to their spontaneous transfer onto the water/toluene interface, and their self-assembly into thin films. This interfacial entrapment of Au@DTBE nanoparticles may be accelerated by gentle shaking. Figure 1a is a typical photograph of the result of the self-assembly of 12-nm Au@DTBE nanoparticles at the water/toluene interface; one can see a giant water droplet enclosed by a thin film of golden reflectance and blue transmittance. This metallic luster results from the electronic coupling of Au-NPs, suggesting the formation of closely packed nanoparticle thin films.[2a,9,13] The UV/Vis spectra demonstrate that no Au@DTBE nanoparticles exist in water or are transferred into the toluene phase. The films of Au@DTBE nanoparticles formed at the water/toluene interface can be transferred onto solid substrates by using the Langmuir technique, which allows us to determine the contact angle of Au@DTBE nanoparticles with the water/toluene interface. Figure 1b reveals that Au@DTBE nanoparticles have a contact angle of 90° with the water/toluene interface, whereas the contact angle of citrate-stabilized Au-NPs is about 60° (Figure 1c). After optimizing the concentration of Au@DTBE nanoparticles and the area of the water/toluene interface, we obtained the monolayer of Au@DTBE nanoparticles at the interface. Figure 1d shows a typical transmission electron microscopy (TEM) image of a monolayer of 12-nm Au@DTBE nanoparticles. This monolayer does not display long-range order, possibly because of the broad size distribution of nanoparticles used. In such a monolayer, as observed by Reincke and co-workers,[7b] domains of close-packed Au@DTBE nanoparticles coexist with large voids; the latter is difficult to explain. In addition, we also achieved interfacial entrapment and self-assembly of Au@DTBE nanoarticles by addition of chloroform and even triethylamine, that is partially immiscible with water. Besides DTBE, we obtained similar results using 11,11′-dithiobis[1-(2-bromo-2-methylpropionyloxy)undecane] (DTBU) as capping ligands,[11b,d] suggesting that in our system surface wettability of nanoparticles mainly depends on the terminal group of the capping ligand, 2-bromopropionate group, rather than on the length of the alkyl chain. Furthermore, using DTBE and DTBU as capping ligands, we have also attached and organized 5-nm Au-NPs into a closely packed monolayer at the water/oil interface.

As the surface wettability of the nanoparticles is predominant in the process of interfacial entrapment, our procedure has been successfully extended to aqueous Ag-NPs. Following the aforementioned ligand-exchange procedure, aqueous Ag-NPs of 10–40 nm in size, prepared by reduction of silver nitrate by sodium borohydride,[14] were capped with DTBE (Ag@DTBE). The as-made Ag@DTBE nanoparticles display interfacial behavior similar to that of Au@DTBE nanoparticles; they prefer to reside at the water/oil interface, creating a film with metallic reflectance (Figure 2a). Furthermore, the mixture of Au@DTBE and Ag@DTBE naoparticles has been attached at water/toluene interfaces, leading to nanoalloy films (Figure 2b). Their TEM images reveal random close-packing arrays, in which, however, one has difficulty in identifying the chemical identity of the nanoparticles based on the contrast level in the bright field

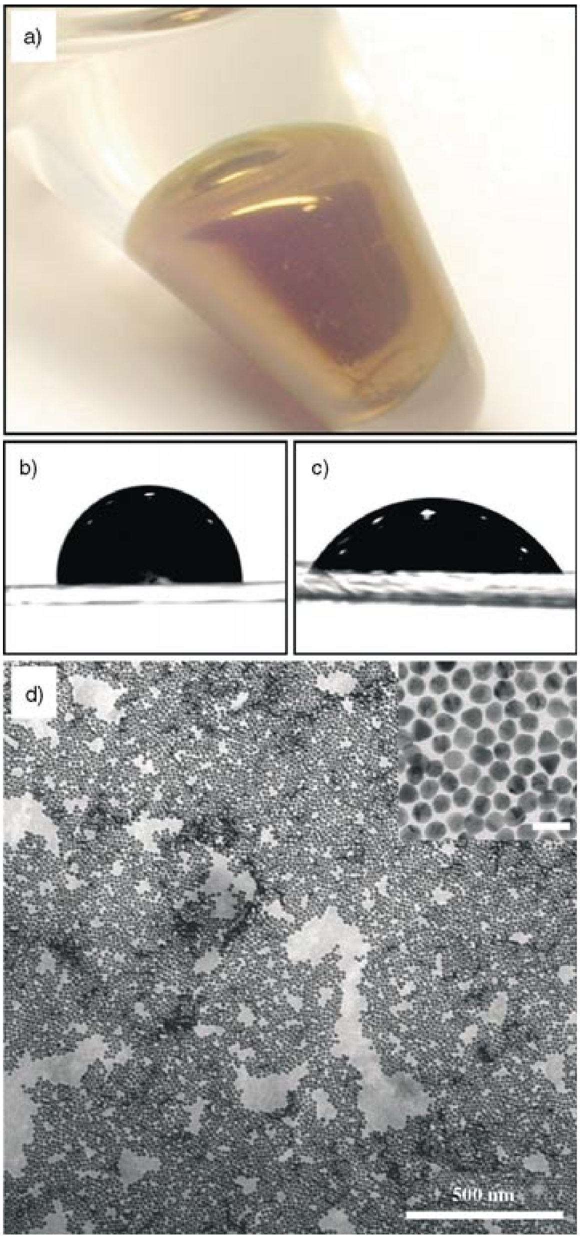

Figure 1. a) Photograph of the self-assembled Au@DTBE nanoparticles at the water/toluene interface in a plastic Eppendorf tube. This tube has been titled such that the colored area corresponds to the water/toluene interface. Owing to the reflectance from the sides, only the blue-purple area represents a transmission image. b,c) Photographs of a 5-μL water droplet, covered with toluene, resting on the surface of a thin film of 12-nm Au@DTBE nanoparticles, transferred from the water/toluene interface on a glass slide (b) and on the surface of a thin film of 12-nm Au-NPs cast on a glass slide (c). d) TEM image of the monolayer of 12-nm Au@DTBE nanoparticles, formed at the water/toluene interface; inset: high-magnification TEM picture, the scale bar is 25 nm.

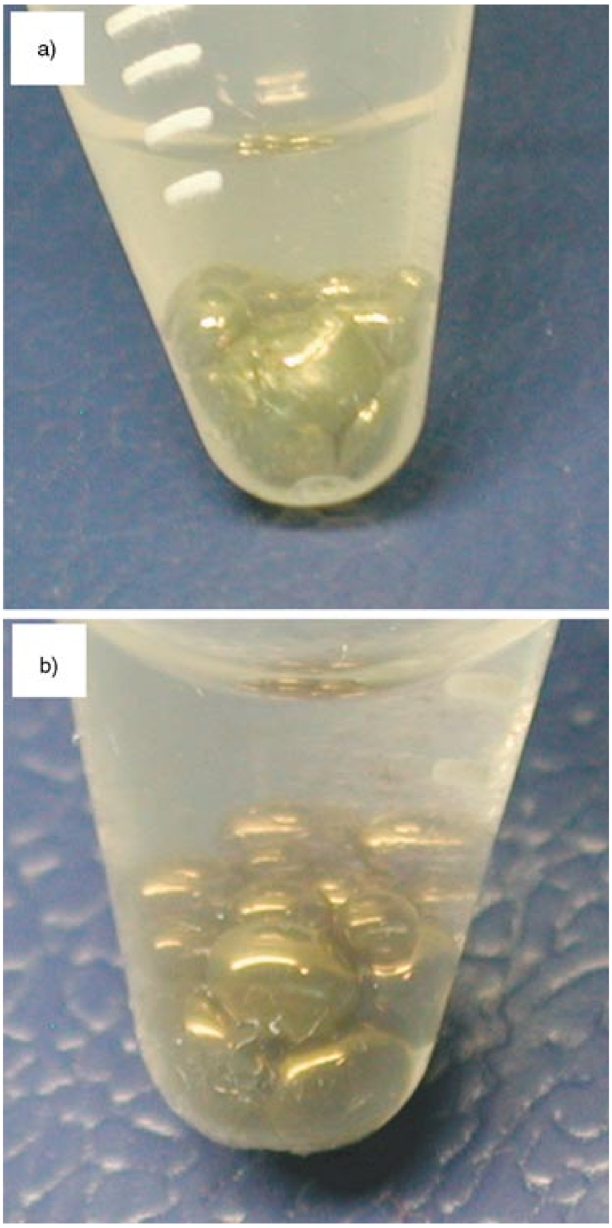

Figure 2. Photographs of thin films of Ag-NPs (a) and of a mixture of Au- and Ag-NPs at a molar ratio of 1:1 (b), formed at the water/toluene interface in a plastic Eppendorf tube.

image.[4a] Moreover, we observed that the transmitted and reflected color of the resultant nanoalloy films varied with the molar ratio of Au@DTBE to Ag@DTBE nanoparticles. The use of interfacial entrapment of nanoparticles to construct composite thin films is an ongoing project in our laboratory.

To gain a better insight into the effect of the terminal group 2-bromopropionate, we conducted interfacial entrapment with hydrophobic nanoparticles. We prepared 4-nm γ-Fe_2O_3 nanoparticles by oxidation of iron(III) acetylacetonate followed by stabilization with oleic acid and oleylamine in toluene.[15] As the long carbon chains of oleic acid and oleylamine capping the γ-Fe_2O_3 nanoparticles are exposed outwards, these nanoparticles are highly hydrophobic and thus may reside only in nonpolar media. We had difficulty in measuring the contact angle of these γ-Fe_2O_3 nanoparticles with the water/toluene interface since the nanoparticles were immediately removed into the toluene phase upon addition of toluene to their thin films cast on a glass slide. The stabilizers on the γ-Fe_2O_3 nanoparticles were replaced with 2-bromo-2-methylpropionic acid (BMPA) by incubating nanoparticles with BMPA for two days.[11c] These BMPA-capped γ-Fe_2O_3 nanoparticles are denoted as γ-Fe_2O_3@BMPA (Scheme 1b (right)). Upon addition of water to a dispersion of γ-Fe_2O_3@BMPA in toluene, γ-Fe_2O_3@BMPA nanoparticles were spontaneously transferred into the water/toluene interface; as for the Au@DTBE nanoparticles, this process was favored by gentle shaking. The inset in Figure 3 shows a typical picture of the interfacial entrapment of γ-Fe_2O_3@BMPA nanoparticles; a yellow layer formed at the water/toluene interface is clearly visible. After transferring this film onto a glass slide, we observed that the contact angle of γ-Fe_2O_3@BMPA nanoparticles with the water/toluene interface is close to 90°, similar to that of Au@DTBE nanoparticles. Unlike for the interfacial entrapment of Au@DTBE nanoparticles, we lack the ability to fabricate monolayers of γ-Fe_2O_3@BMPA nanoparticles at the water/toluene interface. As shown in Figure 3, both monolayers and multilayers of closely packed nanoparticles were observed. Control of the thickness of the films of γ-Fe_2O_3@BMPA nanoparticles formed at the water/toluene interface is underway.

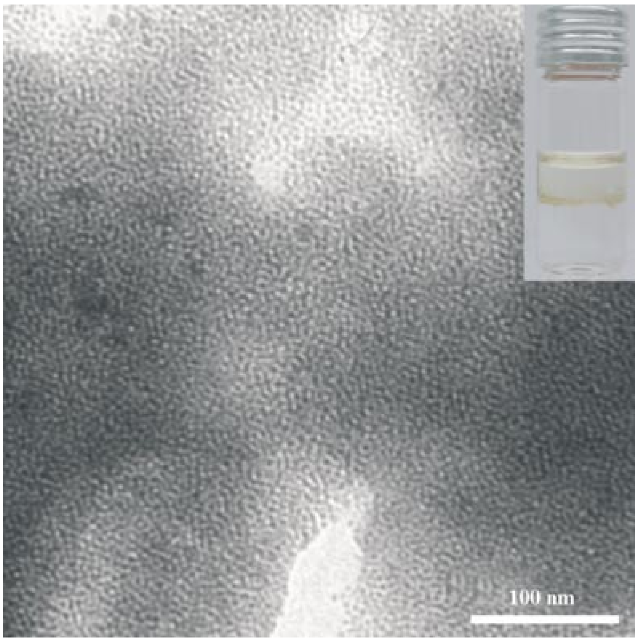

Figure 3. TEM image of the thin film of 4-nm γ-Fe_2O_3@BMPA nanoparticles formed at the water/toluene interface. The yellow layer formed at the water/toluene interface is clearly visible in the photograph shown in the inset.

In summary, we have capped aqueous Au- and Ag-NPs with DTBE and DTBU and nonaqueous γ-Fe_2O_3 nanoparticles with BMPA. The terminal 2-bromopropionate group of these ligands may render the contact angles of the nanoparticles at the water/oil interface close to 90°, driving nanoparticles to the water/oil interface and to self-assemble into closely packed arrays. Meanwhile, the possibility to form nanoalloy films at interfaces has also been demonstrated. The 2-bromopropionate group rather than the length of the hydrocarbon chains of the ligands mainly determine the surface wettability of modified nanoparticles. Thus, our work is an important step towards interfacial entrapment and assembly of nanoparticles for the creation of 2D or 3D nanostructures for electronic, optoelectrical, and magnetic applications. In our laboratory, we are currently capping nanoparticles with ligands containing various carboxylic ester terminal groups to generalize our concept and to establish a relationship between the contact angle of the nanoparticles at the water/oil interface and the terminal group on the ligand terminal. This should provide a means to manipulate nanoparticle solubility in the bulk phase and hence the elasticity of the interface.

Experimental Section

DTBE and DTBU were prepared by acrylation of bis(2-hydroethyl) disulfide and bis(2-hydroethyl) disulfide, obtained by employing the method described by Hawker and co-workers.[16] Briefly, 2-bromo-2-methylpropionyl bromide (14.8 mmol) was added dropwise to a mixture of the disulfide (6.17 mmol) and triethylamine (31.5 mmol) in dichloromethane (150 mL) at 0 °C under an argon atmosphere. The solution was stirred at 0 °C for 1 h and then for another 2 h at room temperature. After the precipitates were filtered off, the organic phase was extracted with 2 N Na_2CO_3 solution saturated with NH_4Cl to remove the excess bromides. Subsequent removal of dichloromethane yielded DTBE and DTBU.

DTBE (4.6 mg) or DTBU (7.2 mg) was dissolved in THF (10 mL) and the solution then added dropwise to an aqueous solution of Au or Ag-NPs (40 mL). After incubating the mixtures for 6–12 h, followed by removal of excess initiators by centrifugation, the initiator-capped nanoparticles were obtained and suspended in water for further use.

A solution of 4-nm γ-Fe_2O_3 nanoparticles in toluene (5 mL) was incubated with a solution of BMPA (1.67 mg) in toluene (5 mL) for two days. The subsequent removal of excess BMPA yielded γ-Fe_2O_3@BMPA nanoparticles and they were suspended in toluene for further use.

UV/Vis absorption spectra were recorded by using a Cary 50 UV-visible spectrophotometer. TEM images were obtained by using a Zeiss EM 912 Omega microscope at an acceleration voltage of 120 kV. Contact angle measurements were implemented with a contact angle measuring system G10 apparatus (Krüss, Germany) at ambient temperature.

Received: June 9, 2004

Keywords: colloids · interfaces · nanoparticles · self-assembly · surface wettability

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