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Sum Frequency Generation on Surfactant-Coated Gold Nanoparticles

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Structures comprising metallic or semiconductor nanoparticles and organic compounds[1] have potential applications in a diverse range of technologically significant fields. Invariably the use of nanoparticles stems from the ability to selectively tune the electrical and optical properties they exhibit through control of parameters such as their composition and the particle size and shape.[2−4] Additionally, a large percentage of the atoms comprising a nanoparticle reside at the surface, consequently many of the optical, transport, and thermodynamic properties of these materials are also surface related.[5] The modification of nanoparticle properties by adsorbed surfactants and organic molecules is therefore of great interest. However, little is known about the structure of surfactants at nanoparticle surfaces, primarily due to the fact that few of the available techniques are capable of extrapolation to nanometer length scale substrates.[6,7] Here we show that the nonlinear optical technique of Sum Frequency Spectroscopy[8] (SFS) may be applied to the nanoparticle/surfactant interface by recording the first spectrum of a surfactant adsorbed on a nanoparticle surface.

A composite nanoparticle/surfactant film was formed at the air/water interface of a Langmuir trough containing an aqueous solution of monodisperse gold nanoparticles previously prepared by the standard technique of citrate reduction of $HAuCl_4$.[9,10] Transmission electron micrographs (TEM's) of nanoparticles isolated by evaporation of the aqueous solution showed that they had an average diameter of 15 ± 2 nm. A film of the dichain surfactant dioctadecyldimethylammonium chloride (DODAC) was spread from chloroform on the surface of the aqueous nanoparticle solution, compressed to the desired area after solvent evaporation, and left to react for 24 h. Due to its extremely low aqueous solubility a chloroform solution of DODAC readily spreads at the air/water interface without any significant solubilization of the surfactant. Hence interactions between the anionically stabilized gold nanoparticles and the cationic surfactant occur primarily at the air/water interface with little bulk interaction and consequent precipitation of macroscopic nanoparticle aggregates. The hybrid nanoparticle/surfactant film was deposited on a silicon wafer by drawing it, at an approximately horizontal angle, through the nanoparticle/DODAC/air interface. Kinetic experiments indicated that film formation was complete after 24 h.

The morphology of the composite nanoparticle/surfactant film was studied by Atomic Force Microscopy (AFM). A single layer of nanoparticles was found to be present on the substrate (Figure 1) with the film height being determined as 14 ± 3 nm. This is in extremely good agreement with the average diameter of the gold nanoparticles as measured by TEM. The AFM image shows that two-dimensional lateral aggregation of the nanoparticles occurred, as may be expected since the cationic surfactant neutralizes the stabilizing citrate charge on the nanoparticles when they diffuse to the surface. The density of the nanoparticle films was found to be almost independent of the average surface area/DODAC molecule used to form the film at the air/water interface. This result is not surprising given that the surfactant occupies a negligible area at the air/water interface in comparison to that occupied by the nanoparticle, implying that each nanoparticle has hundreds of DODAC molecules adsorbed even at low compressions of the surfactant monolayer.

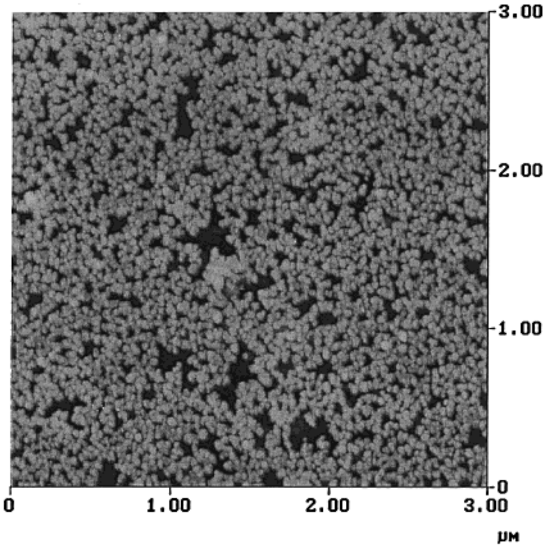

Figure 1. AFM image of a composite gold nanoparticle/DODAC surfactant film formed at the air/water interface (1.00 nm^2/DODAC molecule) and deposited on a silicon wafer substrate.

Sum frequency spectra of the films were recorded in the methyl/methylene C−H stretching region (2800−3000 cm^{-1}) using a nanosecond laser spectrometer. The SF spectrum of a DODAC monolayer deposited on a silicon substrate from a surface density of 0.40 nm^2/molecule is shown in Figure 2a. In accordance with well-characterized surfactant behavior the DODAC molecules are expected to be orientated with their cationic headgroups toward the silicon substrate. The strong resonances at 2960, 2935, and 2875 cm^{-1} arise from the terminal methyl groups of the surfactant alkyl chains. Additionally, weak methylene stretching modes are observed at ≈2910 and 2860 cm^{-1}; their presence was confirmed by modeling the spectra. SF generation does not arise from molecules in a centrosymmetric or isotropic environment. Hence the dominance of the methyl over the methylene resonances implies that the DODAC surfactant monolayer is well ordered and that the methylene groups are in a locally near centrosymmetric environment, i.e., predominantly trans.[11]

The sum frequency spectrum of a gold nanoparticle/DODAC film deposited on silicon is shown in Figure 2b. Although it was formed at the same surfactant surface density as that used to produce the spectrum in Figure 2a, the two spectra are strikingly different. Most notably, the nanoparticle/DODAC film spectrum is enhanced in intensity and the magnitude of this enhancement is resonance dependent. The amplitude of the ≈2960 cm^{-1} asymmetric stretching resonance, for example, is 4.8 times larger

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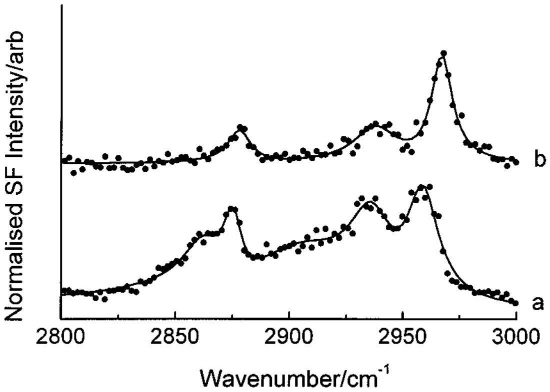

Figure 2. SF spectrum in PPP polarization (sum frequency, visible, infrared beams) of (a) a DODAC monolayer deposited on a silicon substrate from a 0.40 nm^2/DODAC molecule layer at the air/water interface and (b) a composite gold nanoparticle/DODAC film formed at the air/water interface (0.40 nm^2/DODAC molecule) and deposited on a silicon substrate. To enable comparison spectrum b has been normalized to spectrum a through division by a factor of 4.8. The spectra are displaced for clarity. The solid circles are the individual data points and the solid lines are theoretical fits to the data.

in spectrum b than a in Figure 2. There are other significant differences between the spectra. First, the peak positions of the methyl resonances are blue shifted by approximately 6 cm^{-1}. Second, the weak methylene resonances are greatly diminished, if present at all, in the spectrum of the nanoparticle/DODAC film. The SF spectrum in Figure 2b was comparable to that of the film recorded in situ at the air/water interface. These observations lead to the conclusion that spectrum b in Figure 2 is predominantly that of the surfactant adsorbed at the nanoparticle surface.

One possible source of the significant differences that are observed between the SF spectra of a DODAC monolayer and a nanoparticle/DODAC film is variation in the average orientation of the surfactant due to the substrate morphology. To investigate whether the differences in spectra a and b of Figure 2 can be attributed to variation in surfactant orientation a system of DODAC coated gold nanoparticles deposited on a microns-thick evaporated gold substrate was prepared. The orientation of DODAC surfactant in this system is identical with that of the gold nanoparticle/DODAC film system with silicon employed as the substrate. The SF spectrum recorded is markedly different from that of Figure 2b and closely resembles that of a DODAC monolayer adsorbed on evaporated gold. Hence variation in the average molecular orientation of the surfactant may be eliminated as the source of the differences between spectra a and b in Figure 2. Further, the large nonresonant second-order susceptibility ($\chi_{NR}^{(2)}$) of bulk gold which typically acts to amplify resonant SF signals cannot explain the resonance-dependent enhancement observed in the nanoparticle/surfactant system since this effect is almost invariant with infrared frequency.

Since the changes in the relative and absolute intensities of the C−H resonances observed in the spectra of Figure 2 do not arise from conformational effects or from the nonlinear optical properties of gold itself, they must be due to differences in the visible and infrared electromagnetic fields generated at the surfaces when using nanoparticle rather than silicon substrates. The electromagnetic field strengths influence not only the magnitude of the background SF signal but also the relative importance of the individual tensor components of the resonant second-order nonlinear susceptibilities ($\chi_R^{(2)}$'s) and hence the strengths of each resonance. It is interesting to speculate on the consequences of changes in these fields between silicon, gold nanoparticle, and evaporated gold substrates. Silicon is a poor reflector in the infrared and consequently the surface E-field established perpendicular to the surface (*z*-axis) is small. Conversely, the infrared reflectivity of gold is high and increases to nearly 100% at thicknesses of the order of hundreds of nanometers. If the nanoparticle film is considered to be a very thin gold layer on the silicon substrate it follows that the surface infrared E-field produced will have a larger *z* component than would be present on bare silicon, but smaller than that which would exist on thick gold. The absolute and relative intensity of individual resonances would therefore be expected to depend on the degree of interaction with the infrared field in the *z* axis.

A second potential effect arising from the presence of nanoparticles in the film is the nature of the surface plasmon resonance of the system. Silicon has negligible surface plasmon resonance and no enhancement of the surface E-fields is expected by this mechanism. In contrast, bulk gold exhibits strong nonwavelength-specific surface plasmon resonance which results in enhancement of the *z*-axis surface E-field. Unlike bulk gold the surface plasmon resonance of gold nanoparticles is wavelength specific and for 15 nm diameter nanoparticles is a maximum at $\lambda \approx 530$ nm, coinciding with the wavelength of the visible laser beam. Consequently the visible surface E-field will have an enhanced intensity in comparison to silicon and like all surface plasmon fields will contain only a *z* component. Preferential enhancement of resonances with significant *z* components would therefore be expected. Experiments to determine the relative importance of each of these two effects are presently being performed. Specifically, the nanoparticle size (and hence the λ_{max} of surface plasmon absorption) is being varied, and a systematic study of the effect of the possible beam polarization combinations is being made.

In summary we have for the first time measured a sum frequency vibrational spectrum originating from surfactant molecules at the nanoparticle/surfactant interface. While further work is required to fully understand the nature of SF generation on nanoparticle substrates, the potential now undoubtedly exists to determine the polar orientation and degree of conformational order of adsorbed surfactants.

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Supporting Information Available: SF spectra of a DODAC monolayer and a gold nanoparticle/DODAC film deposited on evaporated gold and a description of the SF spectrometer and the modeling procedure employed to fit the data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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