Monolayer structures

DOI: 10.1002/smll.200600736

Phase Separation on Mixed-Monolayer-Protected Metal Nanoparticles: A Study by Infrared Spectroscopy and Scanning Tunneling Microscopy**

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Ligand-coated metal nanoparticles[1,2] (NPs) are a supramolecular assembly of a two-dimensional (2D) monolayer (the ligand shell) wrapped around a 3D metallic core with applications in fields ranging from biology[3] to electronics[4] and plasmonics.[5] The chemical nature of the ligand molecules and the morphology of the ligand shell determines a large fraction of the particles' properties.[1,6] Thus it is important to investigate how molecules arrange when assembled around a particle core. Recently,[7,8] we used scanning tunneling microscopy (STM) to prove that mixed monolayers, which on flat surfaces phase-separate into randomly shaped domains,[9] spontaneously form ordered rings of alternating composition when assembled around a NP core (see Figure 1). Here, we show that it is possible to use infrared (IR) spectroscopy to prove the existence of phase-separated domains on NPs. We reason that Fourier transform IR spectroscopy (FTIR), a simple and common technique, can be used to screen nanoparticles in order to evaluate whether their ligand shell is phase-separated or not, even though it cannot unambiguously distinguish between different domain shapes (a task left for STM). Murray and co-workers have studied the IR spectra of homoligand NPs coated with alkylthiols of various lengths and assigned most of the peaks.[10] Detailed analyses of alkylthiol monolayers are possible because the vibrational spectra of methylene chains have been extensively studied.[11–14]

In aliphatic molecules an upward shift of the CH_2 stretching frequencies (2900–3000 cm^{-1}) as a function of molecular environment has often been observed and is a well-established phenomenon.[12,14] This feature seems to be well understood and can be ascribed to various phenomena such as intramolecular conformational disorder,[12,14] librotorsional modes,[12,14] and twistons. All these phenomena sustain longitudinal and transversal diffusion in polymethylene systems. It has also been suggested,[14] but never fully explained, that similar shifts may also originate from the fact that some kind of intermolecular coupling effect (electronic and/or dynamical) takes place. This non-negligible problem is at present a matter of extensive theoretical and experimental studies.[15] Whatever the origin of the upward shifts may be, we can assume that chains that do not feel such perturbations give rise to a CH_2 symmetric stretch near 2848 cm^{-1}, while the perturbed ones have their frequencies up-shifted to approximately 2852 cm^{-1}. In the absence of any ionic species in sp^3 systems, electronic and/or dynamical perturbations cannot be cooperative (i.e., long range), but

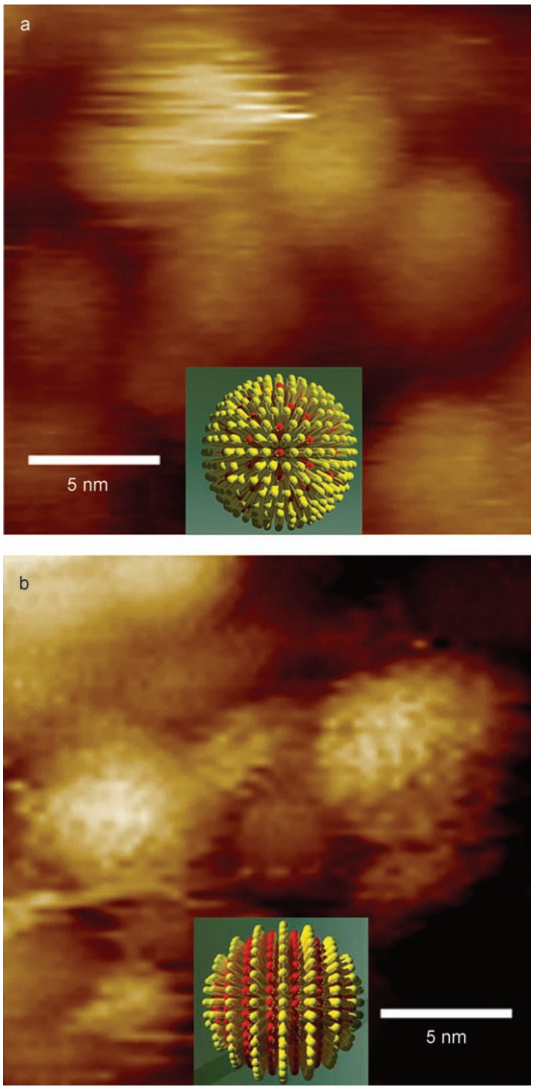

Figure 1. STM height images of a) OT-d17/UT (2:1) and b) OT/MPA (2:1) nanoparticles. The lack of structure of the former is indicative of the absence of a ripple formation. The striation presented on the latter are the signature of the formation of ribbonlike domains of alternating composition.

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[**] This work was financially supported by the National Science Foundation (NIRT DMR-0303973). F.S. is grateful to the Packard Foundation, 3M, and DuPont for their young investigators awards. A.C. acknowledges support from the Rocca Foundation.

Supporting information for this article is available on the WWW under http://www.small-journal.com or from the author.

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are certainly localized on or around each *n*-alkane molecule; conceptually we then expect at least two absorption bands to exist at very close frequencies with their intrinsic width ($\approx$15–25 cm^{-1}) much larger than the experimental resolution and with their intensities proportional to the concentrations of the two "species". Necessarily the two bands are strongly overlapping and the changes of their relative intensities will cause, as is common in the spectroscopy of a two-phase system, an evolution of the observed band shape and, especially, of the observed single-peak frequency, which will shift upward or downward following the prevailing concentration of either the perturbed or unperturbed phases.

In spite of such small shifts, it is possible to use the CH_2 stretching frequencies as a probe to distinguish between a predominantly unperturbed state ($\approx$2848 cm^{-1}) and a state where any of the above perturbations are active ($\approx$2852 cm^{-1}). This, for example, has been experimentally observed in a mixture of an alkane molecules and their deuterated analogues.[14]

Hence, it is possible, in principle, to use the C–H stretching frequencies as probes of the molecular environment, for example, to distinguish between homogeneous mixing and phase separation in a mixed self-assembled monolayer (SAM). Only in the case of homogeneous mixing of two types of molecules (**A** and **B**) as the molar fraction of **B** increases, the probability that an **A** molecule has another **A** molecule as a nearest neighbor decreases linearly. In contrast, in the case of phase separation, as the molar fraction of **B** increases a nonlinear variation in the composition of the nearest neighbors of **A**, and consequently in the CH_2 stretching frequencies, is expected.

To prove our reasoning on homogeneously mixed SAMs, we studied NPs coated with mixtures of varying composition of 1-octanethiol (CH_3-$(CH_2)_7$-SH; OT) and its fully deuterated analogue (OT-d17). This system is an ideal model for homogeneous mixing because the enthalpic driving force for phase separation is minimal. The deuteration of a compound is a common spectroscopic "trick" to investigate and assign specific molecular vibrations. While, to a first approximation, the deuteration of a compound could be thought of as unpertubative to its molecular environment, it has been observed[16] that this isotopic substitution leads to a smaller volume and smaller polarizability of the C–D bond with respect to the C–H bond. The physical reasons for these changes are to be found in the anharmonicity of the chemical bonds and consequently to the different zero-point motion for the C–H or C–D bonds. These changes are very small but meaningful: In particular, the change in polarizability implies a change of the attractive intermolecular interactions with the surrounding molecules; this is the reason why mixtures of two alkanes (one deuterated and one not) are subjected to microphase segregation even when the difference in length of the two molecules is small.[13,17] For hydrogen it has been found that an increase of the attractive intermolecular interactions, via dispersion forces, leads to a weakening of the intramolecular bond and consequently to a downshift of the hydrogen frequency of vibration.[18] In contrast, a relative increase of the repulsive intermolecular dispersion forces leads to a compression of the intramolecular bond and an increase in frequency. Thus, it would be expected for NPs coated with mixtures of one thiol and its deuterated analogue that the C–H stretching frequencies would be affected by the relative increase in the number of close intermolecular interactions between C–H and C–D bonds, which would cause a slight increase of the C–H stretching frequencies (due to reduced polarizability of the C–D bonds) with a linear dependence on the composition only in case of homogeneous mixing. As expected, we found a linear increase in the CH_2 stretching frequency for decreasing OT molar fraction (Figure 2a).

We observed a markedly different trend (Figure 2b) of CH_2 stretching frequencies as a function of composition for a series of NPs coated with OT and 3-mercaptopropionic acid (MPA), known to phase separate[7,8] because of cooperative effects of the different dispersion forces and dipolar interactions between the MPA molecules. As soon as the molar fraction of MPA increases, the frequency of the symmetric and antisymmetric stretching increases (see also Figure S1 of the Supporting information). New boundaries are created, leading to an increase in conformational disorder. Then, for a wide range of compositions, the frequencies remain almost constant (within experimental errors). The invariance in frequency in this region suggests that the intermolecular forces and the conformational disorder of OT molecules do not vary with composition, something that can only be explained by invoking phase separation. It should be noted that in the flat region, the highest frequency observed was for the equimolar composition. STM data show that at this composition the narrowest domains are present.[8] STM images measure the average dimension of two neighboring phases, but do not distinguish between the two. The fact that at this composition the measured spacing is the smallest indicates that this is the composition where the probability of OT molecules having MPA molecules in proximity (or vice versa) is at its highest, thus matching the FTIR data. We had already postulated that when the MPA content exceeds 80%, ribbonlike domains would cease to exist and become isolated rounded domains.[7,8] This situation would lead to OT molecules being found mostly at the boundaries of extremely small domains. The observed upshift in frequency in our plots seems to confirm this picture.

To avoid the overlapping effect of the OT and the MPA CH_2 stretching modes, we synthesized and studied NPs coated with MPA and OT-d_{17} (CD_2 stretching frequency $\approx$2090 cm^{-1}). The trend (Figure 2c) in the CD_2 stretching frequencies was found to be analogous to the one shown in Figure 2b. In these particles, the intensity ratio between the antisymmetric carboxylate stretching peak (MPA) and the peaks in the entire CD stretching region (OT-d17) can be used to estimate the ligand-shell composition (assuming that the relative intensity of the vibrational peaks is mostly unperturbed by the environment). We found this ratio to be in very good agreement with the stoichiometric ratio used to synthesize the NPs (Figure 3).

It should be mentioned that all of the NPs were synthesized using a one-phase method[19] to avoid possible contamination with the phase-transfer agent and to have full con-

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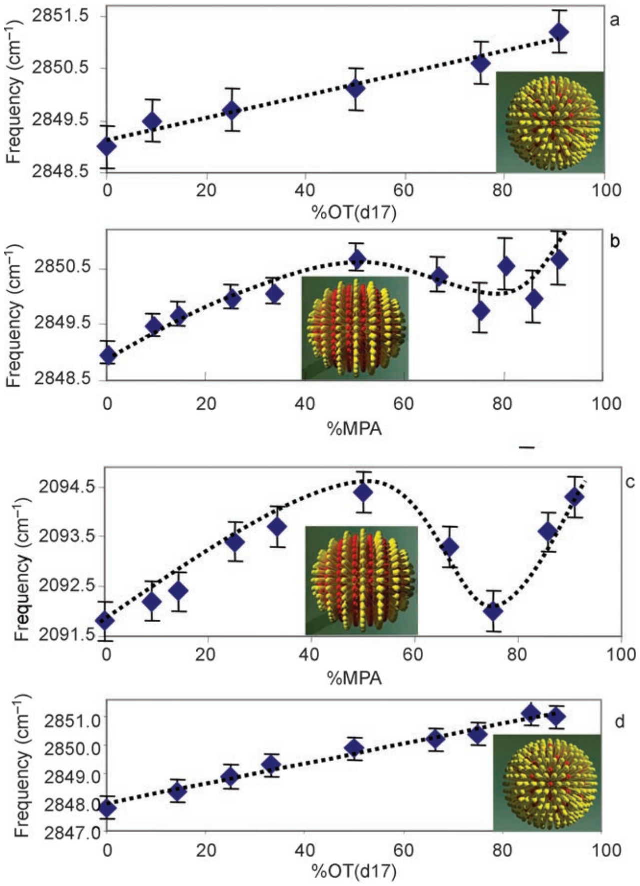

Figure 2. a) Plot of the CH_2 symmetric-stretching frequencies for OT/OT-d17 NPs as a function of OT-d17 composition. The dotted line is an interpolated linear trend; it has a correlation coefficient (R^2) of 0.96. The inset shows a schematic representation of homogeneous mixing in the ligand shell. b) Plot of the CH_2 symmetric-stretching frequencies for OT/MPA NPs as a function of MPA composition. The inset shows a schematic representation of "rippled" phase-separated domains.[7,8] c) Plot of the CD_2 symmetric-stretching frequencies for OT-d17/MPA NPs as a function of MPA composition. The dotted lines are solely meant as a guide for the eye. d) Plot of the CH_2 symmetric-stretching frequencies for OT-d17/UT NPs as a function of OT-d17 composition. The interpolated linear trend $R^2 = 0.98$. Throughout this Communication, the molar composition is based on the stoichiometric ratios used during the particle synthesis. All of the FTIR spectra studied were taken by preparing a KBr pellet containing roughly the same amount of nanoparticles. The pressure used to prepare the pellet was always the same (10 tonne cm^{-2}) to avoid pressure effects in the spectra.[10] Error bars are the largest variation in frequency observed for different scans on the same sample and on samples with the same composition synthesized on different occasions.

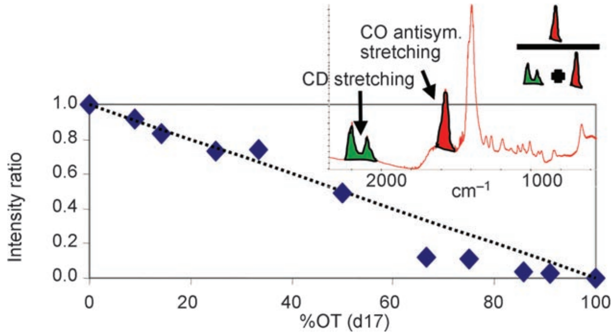

Figure 3. Plot of the ratio of intensity of the C–O stretching peak to the sum of the C–O stretching peak and of the C–D stretching region as a function of stoichiometric fraction of OT(d17) used to synthesize OT(d17)/MPA NPs. The dotted line (which shows perfect correspondence to stoichiometric ratio between the ligands) is designed to guide the eye. The inset provides a qualitative cartoon to explain how the peak intensity ratio was calculated.

trol on the ligand stochiometry; the two-phase synthesis does have not these properties.[1,2] The underlying assumption in this study is that ligand-shell composition variations do not affect size distributions, thus enabling vibrational spectroscopy comparisons across all samples. Transmission electron microscopy (TEM) images show that all of the particles studied have average diameters in the range of 3.5–4.8 nm, all with a size distribution characterized by a ratio of the standard deviation to the average diameter of ≈0.25. A detailed description of the all-size distribution observed can be found in Figure S2 and Table 1S in the Supporting Information. We have not observed any systematic change in the average size with OT/MPA composition. Hence any eventual shift of the C–H frequencies due to the influence of NP size should be so small as to only affect the error bars in our measurements.

To prove the validity of our approach, we used FTIR as a tool to predict and investigate whether phase separation occurs in the ligand shell of all-aliphatic mixed-ligand NPs. A series of NPs coated with mixtures of 1-undecanethiol (CH_3-$(CH_2)_{10}$-SH; UT) and OT-d17 of varying ligand shell composition was studied. The nanoparticles showed a linear trend in CH_2 stretching frequencies (Figure 2 d), thus suggesting that the ligands on these NPs are not phase separated. This was confirmed using STM (Figure 1 a).

Here we have shown that plots of CH_2 stretching frequencies versus composition provide evidence for homogeneous mixing or for phase separation in the ligand shell of monolayer-protected gold nanoparticles. FTIR is a much simpler and more common characterization tool when compared to STM, and thus the approach shown in this Communication could be used in many laboratories to prescreen nanoparticles in order to determine whether the molecules that compose the ligand shell are homogeneously mixed or phase separated. These studies could be also extended to larger, less-soluble particles and to nanomaterials of various shapes.

Experimental Section

Materials and methods: 1-Octanethiol, 3-mercaptopropionic acid, 1-undecanethiol, and sodium borohydride were purchased from Aldrich. 1-Octane-d17-thiol (OT-d17; 98.5 at% D) was purchased from CDN isotopes (Quebec, Canada). Hydrogen tetrachloroaurate(III) hydrate (99.9% $HAuCl_4 \cdot xH_2O$) was purchased from Alfa Aesar. Ethanol (200 proof absolute) was purchased from Pharmco, and acetone was purchased from Mallinckrodt Chemicals. All chemicals were reagent grade and were used as received.

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A Nicolet Nexus FTIR spectrometer was used for measuring the IR spectra of the nanoparticles. Spectra were taken from KBr pellets made by sintering mixtures of small amounts of the nanoparticles and KBr, mechanically prepared at a pressure of 10 tonne cm^{-2}. 256 spectra taken at a 1 cm^{-1} resolution were acquired and averaged for every sample. No smoothing was applied to the spectra, but a baseline correction was always made before the determination of the peak frequencies. STM images were acquired as described in a previously published paper.[8]

Nanoparticle average core sizes were determined using TEM images. A JEOL 200CX was used at 200 kV and approximately 200 NPs were counted for every sample.

Nanoparticle synthesis: Nanoparticles were synthesized using a one-phase method following a previously published report.[19] Briefly, a mixture (in the proper desired ratio) of thiol molecules was added to an ethanol solution (200 mL, kept at 0 °C) of $HAuCl_4$ (0.9 mmol) so that the total thiol concentration was 0.9 mmol. A large excess of $NaBH_4$ (26.43 mmol in 200 mL of ethanol) was added dropwise over 200 min. After the addition of $NaBH_4$ was completed, the solution was stirred for 2 h and kept in a refrigerator for the following 36 h in order to allow the NPs to precipitate. The solution was filtered on a quantitative filter paper (VWR 28297-942) under vacuum and then washed thoroughly with ethanol and acetone to yield a black powder ($\approx$130 mg).

Keywords:
IR spectroscopy · monolayers · nanoparticles · phase separation · scanning tunneling microscopy

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Received: December 28, 2006
Published online on April 5, 2007

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