Studying Nanoparticle-Induced Structural Changes within Fatty Acid Multilayer Films Using Sum Frequency Generation Vibrational Spectroscopy

Jasper Holman,[†,‡] Shen Ye,*[†] David J. Neivandt,[§] and Paul B. Davies*[‡]

Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, U.K., and Department of Chemical and Biological Engineering, University of Maine, Orono, Maine 04469

Received May 24, 2004; E-mail: pbd2@cam.ac.uk; ye@cat.hokudai.ac.jp

Semiconductor nanoparticles suggest exciting possibilities for electronic applications[1] because of the tunability of their electrical and optical properties, which can be controlled by changing the size and shape of the particles.[2,3] Consequently, much effort has been directed toward precise control of these parameters. A promising synthetic approach for the II−VI semiconductor particles is to react metal ions (Cd, Zn, Pb) immobilized in a fatty acid Langmuir−Blodgett (LB) film with a chalcogenide gas such as H_2S or H_2Se.[4] The fatty acid film serves as a restraining matrix that limits the size of the nanoparticle. By combining different surfactants, it is possible to control the size, shape, and nucleation sites of the particles,[5,6] making these composite films potentially suitable for molecular electronics. Furthermore, the use of LB films allows the thickness of the film to be varied with molecular precision. A great deal of research has focused on the formation of CdS nanoparticles within fatty acid films, with the vast majority of the emphasis placed on the properties of the resultant nanoparticles. Little work has focused on the effect of nanoparticle formation on the organic matrix. Here we report the first application of the nonlinear optical technique of sum frequency generation (SFG)[7] vibrational spectroscopy as a tool for investigating the order of the fatty acid molecules in the composite nanoparticle fatty acid multilayer structure.

SFG does not arise from molecular groups in a centrosymmetric environment. This makes it a surface-specific technique as no SFG occurs in isotropic media. It also means that SFG is very sensitive to the local symmetry of a particular molecular group. If hydrocarbons in a monolayer are in an all-trans configuration, the methylene groups reside in a locally centrosymmetric environment and are consequently not observed in the SFG spectrum,[8] while the observation of methylene modes reveals the presence of gauche defects within the layer. On the other hand, the methyl groups reside at an interface and consequently are always observed, but their intensity depends on the ordering of the methyl groups. Second, on a substrate that itself has a large nonlinear polarizability, it is possible to determine the polar orientation of a molecule, i.e., whether it is pointing away from or toward the surface.[9] While SFG is mainly used as a surface-specific technique, it can also be used to study the "bulk" of a film. If a multilayer structure is created with a per-protonated layer within an otherwise per-deuterated film, scanning the IR wavenumber over the C−H stretching range allows for the exclusive detection of the per-protonated layer.[10] Hence, preparing films with the per-protonated layer at different locations within the film allows for the determination of a "bulk" view of the film.

Films built up from a total of nine layers of per-deuterated cadmium arachidate and one layer of per-protonated cadmium arachidate on hydrophobic per-deuterated octadecanethiol (d-ODT) covered gold substrates were prepared by LB deposition of a Langmuir monolayer of arachidic acid (30 mNm^{-1}, 20 °C) on a 5 mM $CdCl_2$ and 0.5 mM $NaHCO_3$ aqueous subphase. At a pH of 6.5 this results in an exclusively Y-type deposition, i.e., head-to-head and tail-to-tail. Four samples were prepared containing a single per-protonated cadmium arachidate layer, namely layers 1, 2, 5, and 10, respectively, counting from the lowermost layer to the surface layer. The CdS-arachidic acid films were formed by reacting the parent cadmium arachidate films with H_2S gas for 4 h. CdS nanoparticle formation was confirmed by UV−vis spectroscopy showing an onset of absorbance around 450 nm, indicative of significant quantum confinement with a diameter of 3 nm.[11] Furthermore, AFM images showed the formation of particulate features of approximately 3 nm in size, consistent with the diameter of CdS nanoparticles formed under these conditions, and significant deformation of the surface not present on the surface of the unreacted film. Previous XRD experiments[12] showed a severe disruption of the film, with the hydrocarbon chains tilting away from the surface normal, and uniform disklike nanoparticle formation.

SFG spectra were recorded in the C−H stretching region (2800−3000 cm^{-1}) using a broadband femtosecond laser system[13] with a co-propagating beam geometry. The SFG spectra of the unreacted films are shown in the left-hand panel of Figure 1. The most striking feature is that the resonances of layers 2 and 10 occur as dips, while those of layers 1 and 5 occur as peaks. This is due to interference between the SFG signals from the gold substrate and the SFG active (per-protonated) arachidate layer and indicates that the methyl groups of layers 2 and 10 point away from the surface while the methyl groups of layers 1 and 5 point toward the surface,[10] as would be expected from Y-type deposition. This is a clear example of one of the unique properties of SFG. The three strong resonances arise from methyl groups, while a weak methylene resonance around 2860 cm^{-1} can be observed for layer 1. This implies that the hydrocarbon chains are in an all-trans configuration, but some gauche defects do occur for layer 1. The resonances of the surface layer are blue-shifted (∼5 cm^{-1}) compared to the ones buried within the film because of the different local environment of the methyl groups (air versus an organic film).[10]

Figure 1 (right-hand panel) shows the SFG spectra of layers 1, 5, 2, and 10, respectively, after reaction. It can be seen that the intensity of the SFG signal from the lowermost layer has been reduced significantly, less so for layers 2 and 5 and not at all for layer 10. Furthermore, relatively strong methylene resonances can
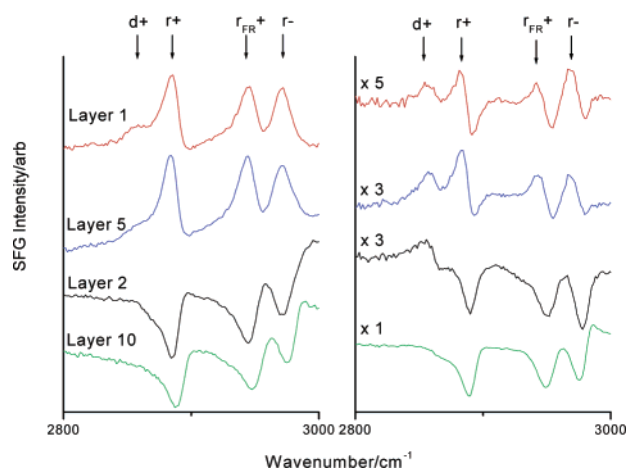
Figure 1. SFG spectra of a single per-protonated cadmium arachidate layer in an otherwise fully per-deuterated 10-layer film deposited onto d-ODT gold before (left) and after (right) reaction with H_2S. The spectra correspond from top to bottom to layers 1, 5, 2, and 10, respectively. The symbols refer to the symmetric methylene stretching mode (d^+), the symmetric methyl stretching mode (r^+), its Fermi resonance (r^+_{FR}), and the asymmetric stretching mode (r^-). Post-reaction spectra have been rescaled as indicated by the multiplication factors. The nonresonant background remained the same post-reaction.

now be observed for the buried layers (1, 2, and 5). For layer 10 no distinct CH_2 resonance can be observed.

The concurrent loss of methyl resonance intensity and the introduction of methylene resonances into the spectra of the fatty acid layers within the film are consistent with spectral changes deriving from the introduction of gauche defects into previously fully trans alkyl chain structures, as commonly observed in systems in the absence of nanoparticles. An alternative interpretation of the spectra of Figure 1, however, exists. Specifically, the local E-fields and nonlinear response of the system may be perturbed by the presence of the CdS nanoparticles within the film, thereby giving rise to spectral features (such as the presence of methylene modes) that do not correlate with alkyl chain conformational changes. This alternate interpretation is, however, countered by the correlation of the magnitude of the spectral changes with depth into the film (arguing against a local effect). Further, it is noted that the uppermost layer (10) is in direct contact with CdS nanoparticles (between layers 9 and 10), yet the spectrum of this layer contains no methylene resonances and is of equal intensity to that measured prior to the formation of nanoparticles. Other evidence that the spectral changes observed in Figure 1 are not due to optical effects arising from the presence of nanoparticles is found in the similarity of SFG spectra recorded on a comparable multilayer system but comprising octadecylammonium chloride rather than cadmium arachidate and spherical rather than disklike CdS nanoparticles (Supporting Information). It is concluded, therefore, that the spectral changes observed in Figure 1 are attributable to conformational changes of arachidic acid within the multilayer structure due to the formation of CdS nanoparticles and not to nanoparticle-induced nonlinear optical effects.

The retention of order within the surface layer is quite surprising since, in a naive picture, it seems reasonable to imagine the extent of the reaction to be an inverse function of the H_2S diffusion path length. Since the surface layer is in direct contact with the H_2S atmosphere the nanoparticle formation will have developed at least as much in the surface layer as within the film. Hence, while the diffusion of H_2S through the matrix is an interesting subject and is currently under investigation, the explanation for the different structural response to nanoparticle formation must lie elsewhere.

A possible explanation is the difference in freedom of movement between the lowermost, bulk, and surface layers. Upon nanoparticle formation the surface layer can move freely in a direction perpendicular to the surface, but the movement of the buried layers and lowermost layer is severely limited. For the lowermost layer the movement would be even more restricted because of the rigid d-ODT layer on gold. This is potentially different from the bulk of the film where the deformation of one layer conveys freedom of movement to the surrounding layers.

The stability of the surface layer is also surprising because one of the key stabilizing forces, electrostatic complexation, is largely removed after the reaction with H_2S. The highly ordered structure of the unreacted film is due to the electrostatic interaction of the carboxylate groups mediated through the cadmium ions and the van der Waals interaction between the long hydrocarbon chains in which the former has been claimed to be the strongest factor.[14,15] However, after reaction with H_2S most of the cadmium ions are converted to uncharged CdS nanoparticles and the carboxylate headgroup is reprotonated,[11] leaving only the van der Waals interaction as a stabilizing factor. As this does not seem to affect the order of the surface layer, it appears that the van der Waals interaction in these films is more important than previously assumed. In summary, we have demonstrated the applicability of SFG to studying these important multilayer films and the unique information that can be obtained. There is a clear distinction in ordering between the surface layer and the bulk of the film after the incorporation of CdS nanoparticles. The retention of order appears to show the importance of the van der Waals interaction in stabilizing these films and the flexibility of the fatty acid molecules.

Supporting Information Available: UV−vis spectra of a 10- and 20-layer film of cadmium arachidate after reaction with H_2S, AFM images of the 10-layer film before and after reaction with H_2S, and SFG spectra of cadmium arachidate and ODA multilayer films before and after nanoparticle incorporation. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Fendler, J. H. *Nanoparticles and Nanostructured Films*; Wiley-VCH: Weinheim, Germany, 1998.
(2) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226−13239.
(3) Heath, J. R.; Shiang, J. J. *Chem. Soc. Rev.* **1998**, *27*, 65−71.
(4) Smotkin, E. S.; Lee, C.; Bard, A. J.; Campion, A.; Fox, M. A.; Mallouk, T. E.; Webber, S. E.; White, J. M. *Chem. Phys. Lett.* **1988**, *152*, 265−268.
(5) Guo, S.; Konopny, L.; Popovitz-Biro, R.; Cohen, H.; Porteanu, H.; Lifshitz, E.; Lahav, M. *J. Am. Chem. Soc.* **1999**, *121*, 9589−9598.
(6) Grieser, F.; Furlong, D. N.; Scoberg, D.; Ichinose, I.; Kimizuka, N.; Kunitake, T. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2207−2214.
(7) Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York, 1984; Chapter 2, pp 27−28.
(8) Guyot-Sionnest, P.; Hunt, J. H.; Shen, Y. R. *Phys. Rev. Lett.* **1987**, *59*, 1597−1600.
(9) Ward, R. N.; Duffy, D. C.; Davies, P. B.; Bain, C. D. *J. Phys. Chem.* **1994**, *98*, 8536−8542.
(10) Holman, J.; Davies, P. B.; Neivandt, D. J. *J. Phys. Chem. B* **2004**, *108*, 1396−1404.
(11) Dhanabalan, A.; Kudrolli, H.; Major, S. S.; Talwar, S. S. *Solid State Commun.* **1996**, *99*, 859−862.
(12) Vitta, S.; Metzger, T. H.; Major, S. S.; Dhanabalan, A.; Talwar, S. S. *Langmuir* **1998**, *14*, 1799−1803.
(13) Ye, S.; Noda, H.; Morita, S.; Uosaki, K.; Osawa, M. *Langmuir* **2003**, *19*, 2238−2242.
(14) Ye, S.; Noda, H.; Nishida, T.; Morita, S.; Osawa, M. *Langmuir* **2004**, *20*, 357−365.
(15) Schwartz, D. K.; Garnaes, J.; Viswanathan, R.; Zasadzinski, J. A. N. *Science* **1992**, *257*, 508−511.

JA046954X