

## Evidence for Novel Interdigitated Bilayer Formation of Fatty Acids during Three-Dimensional Self-Assembly on Silver Colloidal Particles

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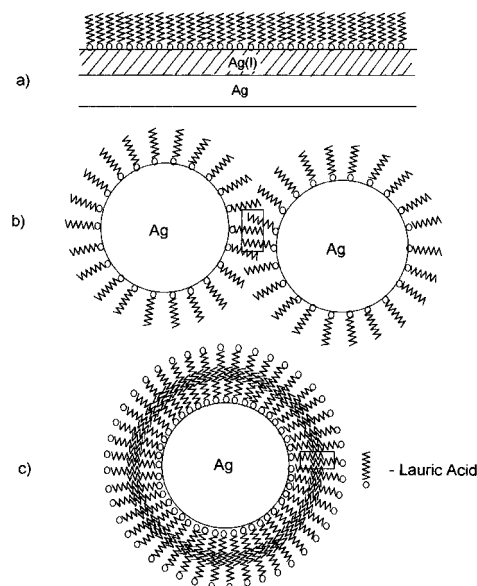
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There is current interest in the study of self-assembled monolayers (SAMs) on planar surfaces<sup>1–3</sup> (hereafter referred to as 2-D SAMs, Chart 1a). Following the important work of Brust *et al.*<sup>4</sup> wherein passivation of gold clusters with covalently bound alkanethiols was demonstrated, attention is being focused on understanding the important similarities/differences between 2-D and 3-D SAMs (formed on curved surfaces such as those afforded by colloidal particles, Chart 1b). While it is accepted that the high curvature of the colloidal particle surface would lead to greater volume and hence mobility of the outermost functional groups (Chart 1b), studies of SAMs of alkanethiols<sup>5–8</sup> and primary amines<sup>9</sup> on gold colloidal particle have concluded that to a large extent, 3-D SAMs are similar to their 2-D counterparts. In this communication, we provide evidence for formation of *interdigitated bilayers* of fatty acid molecules on silver colloidal particles, the process being facilitated by the highly curved colloid surface. This represents an important point of deviation from self-assembly on planar surfaces where *monolayers* of fatty acids on metal oxide surfaces have been reported.<sup>10–12</sup> Bilayer structures have been reported for octadecanethiol SAMs on 2-D gold surfaces followed by adsorption of different cationic and anionic surfactants.<sup>13</sup> To the best of our knowledge, bilayers of fatty acids on 2-D surfaces have not been observed to form spontaneously.

Silver colloidal particles were prepared as described elsewhere.<sup>14</sup> A clear yellow sol formed immediately at pH ~9.5. Transmission electron microscopy (TEM) measurements<sup>15</sup> of the colloid yielded a particle size of  $70 \pm 12$  Å. Assuming complete reduction of the silver salt and an average particle diameter of 70 Å, close packed monolayers of lauric acid are calculated to form on the clusters (the “primary monolayer”, Chart 1b) at a lauric acid concentration of  $\sim 1 \times 10^{-5}$  M (20

Chart 1



<sup>a</sup> (a) Structure of a close packed SAM of fatty acid molecules on silver planar films. (b) Structure of a close packed SAM of fatty acid molecules on a colloidal particle at unity surface coverage. Interdigitation of the primary monolayer of a neighboring cluster is indicated by a rectangle. (c) Bilayer formation of fatty acid molecules due to interdigitation of excess fatty acid in the close packed SAM depicted in part b. The region of interdigitation is indicated by a rectangle.

Å<sup>2</sup> area per lauric acid molecule<sup>16</sup>). Capping of the clusters was effected by adding to 9 mL of the silver hydrosol 1 mL of a solution of lauric acid in absolute ethanol. The concentration of the lauric acid was adjusted to yield overall capping concentrations in the hydrosol of  $5 \times 10^{-6}$ ,  $10^{-5}$ , and  $5 \times 10^{-5}$  M (sols 1–3, respectively). Silver clusters were also capped with  $5 \times 10^{-5}$  M stearic acid molecules for thermal measurements (sol 4). Optical absorption measurements showed a shift in the surface plasmon resonance from 386 nm for bare silver particles to ~405 nm for sols 2–4 indicating fatty acid adsorption.<sup>17</sup> Exceptional long-term stability of sol 3 in comparison to the other sols was observed. Formation of an “interdigitated” secondary monolayer by excess lauric acid molecules in sol 3 (Chart 1c) would lead to carboxylic acid derivatization of the particles and explain the observed long-term stability. We mention here that a surfactant bilayer structure has been proposed earlier for aqueous magnetite colloidal particles.<sup>18</sup> However, realization that purely geometrical effects can lead to bilayer formation on 3-D surfaces as opposed to monolayer formation on 2-D surfaces for fatty acids has not been reached till now nor has information on the nature of the bilayer formed been obtained.

The kinetics of lauric acid SAM formation on planar silver films was studied by quartz crystal microgravimetry (QCM)<sup>19</sup> and is shown in Figure 1 (inset). The equilibrium mass loading was ~160 ng/cm<sup>2</sup>, yielding an area/molecule of ~22 Å<sup>2</sup> indicative of a fairly close packed monolayer. The contact angle of a sessile water drop on the SAM surface was 100°, showing formation of a monolayer exposing a hydrophobic surface due to the alkyl tails.

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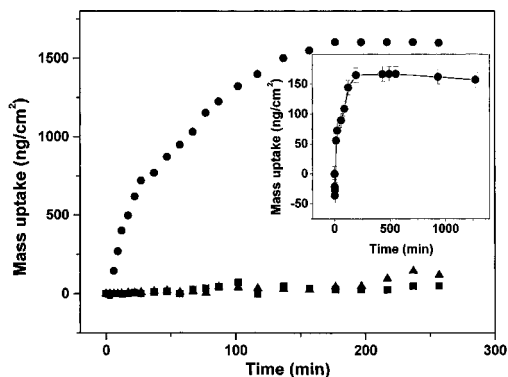
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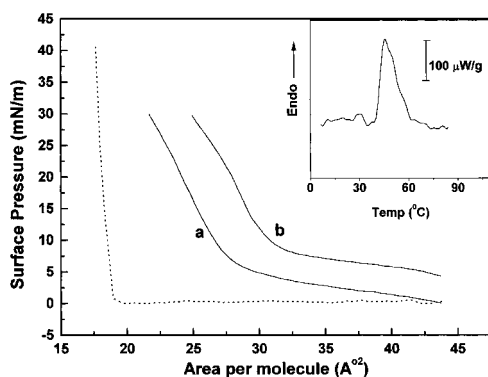
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**Figure 1.** QCM mass uptake with time for the oxidized aluminum coated crystals immersed in sols 1–3 (filled squares, filled triangles, and filled circles, respectively). Inset shows QCM mass uptake with time for lauric acid molecules adsorbed on silver planar films.



**Figure 2.** Pressure–area isotherms of an octadecylamine monolayer spread on sol 3 used as the subphase after different times of equilibration of the monolayer (curve A 15 min and curve B 2 h after spreading the monolayer). The dotted line shows the isotherm for octadecylamine on water at pH 9.5 for comparison. The inset shows the DSC heating curve for stearic acid bilayer capped silver clusters.

Strong coordination of carboxylic acid groups to oxidized aluminum surfaces<sup>10,11</sup> was used to test the bilayer formation hypothesis. *Ex situ* QCM measurements made on oxidized aluminum coated quartz crystals immersed in sols 1–3 for various intervals of time are shown in Figure 1. While negligible mass change is seen for sols 1 and 2 (filled squares and triangles, respectively), a large mass increase in the case of sol 3 (filled circles) is observed which stabilizes after ~150 min of immersion. The equilibrium mass increase of 1600 ng/cm<sup>2</sup> obtained for sol 3 cannot be explained in terms of simple chemisorption of a lauric acid monolayer, which would contribute only ~160 ng/cm<sup>2</sup> to the mass loading. Optical reflectivity measurements corroborated the presence of silver clusters on the QCM surface for sol 3. The contact angle of a sessile water drop on the silver particle covered QCM surface on immersion in sol 3 was ~42°, indicating a hydrophilic surface due to exposed carboxylic acid groups on the clusters.

The carboxylic acid derivatized silver clusters in sol 3 could be attached electrostatically to oppositely charged octadecylamine Langmuir monolayers, as recently demonstrated for bifunctional molecule capped gold clusters.<sup>20</sup> Figure 2 shows the  $\pi$ - $A$  isotherms of an octadecylamine monolayer on sol 3

as a function of time (curve A 15 min and curve B 2 h after monolayer equilibration) where a large time dependent expansion of the monolayer is seen. The dotted line is the  $\pi$ - $A$  isotherm of octadecylamine on water at pH 9.5 for comparison. No expansion in the monolayer was observed for sols 1 and 2 over a 5-h measurement. A control  $\pi$ - $A$  isotherm experiment was carried out by using only a  $5 \times 10^{-5}$  M solution of lauric acid at pH 9.5 with octadecylamine as the Langmuir monolayer. No expansion with time was observed, showing that cluster adsorption at the air–water interface is responsible for the Langmuir monolayer expansion. Good-quality Langmuir–Blodgett films of the octadecylamine–lauric acid capped silver clusters could be formed from sol 3.

Following Murray *et al.*,<sup>5</sup> thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses of the powders of sol 4<sup>21</sup> were used to understand the nature of fatty acid bilayer formation. Sol 4 was chosen since the endotherm corresponding to melting of interdigitated chains in laurylthiol capped gold clusters was reported to occur close to 0 °C.<sup>5</sup> Water adsorbed at the exposed carboxylic acid groups of the lauric acid bilayer may obscure other features present in that temperature region. Silver particles from sol 4 could also be adsorbed on oxidized aluminum films and attached to octadecylamine Langmuir monolayers as shown for lauric acid capped clusters. TGA showed two losses at 134 (12%) and 190 °C (14%) which are attributed to quantitative loss of stearic acid molecules from the secondary and primary monolayers, respectively. The DSC heating curve for the powder is shown in the inset of Figure 2. A broad endotherm corresponding to 18 J/g is observed at a temperature of ca. 45 °C. Assigning this heat to the stearic acid mass fraction in the clusters (determined from TGA) leads to a transition enthalpy of 18.4 kJ/mol, indicating melting of an ordered portion of the alkyl chains. The ordered regions may arise from interdigitated segments of the primary and secondary monolayers (Chart 1c, rectangle). An interdigitated structure is expected to be energetically favorable in an aqueous environment due to the resulting maximization of the hydrophobic interaction between the interdigitated chains.<sup>22</sup> Interdigitation of chains from neighboring alkanethiol capped gold clusters has been proposed by Murray *et al.*<sup>5</sup> and Badia *et al.*<sup>8</sup> (Chart 1b, rectangle). Attributing the observed endothermic transition to melting of the interdigitated regions between the primary and secondary monolayers and taking a contribution of 4 kJ/mol per interdigitated CH<sub>2</sub> segment<sup>5,23</sup> to the melting transition yields ca. 4–5 interdigitated CH<sub>2</sub> groups per stearic acid chain.

In conclusion, self-assembly of fatty acid molecules on silver colloidal particles can lead to an interdigitated bilayer structure (Chart 1c) and highlights an important difference with 2-D self-assembly where steric constraints due to close packing of chains preclude formation of such a structure (Chart 1a). Thus derivatization of colloidal particle surfaces can be achieved without the use of bifunctional molecules thereby expanding the scope for surface modification in 3-D.

**Supporting Information Available:** Experimental data for the optical absorption spectra of Langmuir–Blodgett films of octadecylamine complexed with  $5 \times 10^{-5}$  M capped lauric acid clusters (2 pages). See any current masthead page for ordering and Internet access information.

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(19) QCM measurements were made on thermally evaporated silver/aluminum coated AT cut 6 MHz quartz crystals exposed to air prior to SAM formation with an Edwards FTM5 microbalance. The stability and resolution of the frequency counter was  $\pm 1$  Hz, yielding an overall mass resolution of 12 ng/cm<sup>2</sup>. Frequency changes were converted to mass loading by using the Sauerbrey equation (Sauerbrey, *G. Z. Phys. (Munich)* **1959**, *155*, 206). Lauric acid SAM formation was studied by immersion of the silver coated crystal in  $10^{-4}$  M concentrated solution of lauric acid in absolute ethanol and monitoring the *ex situ* resonant frequency change with time.

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(21) Flocculation of the particles was induced by increasing the ionic strength in the sol. The precipitate formed was filtered, washed with water, and dried in nitrogen atmosphere. Washing with an organic solvent was avoided to prevent dissolution of stearic acid molecules in the secondary monolayer. TGA measurements were performed on the powders with use of a Seiko Instruments model TG/DTA 32 instrument while DSC data were obtained on a Seiko Instruments DSC 220 C calorimeter at a heating rate of 10 °C/min.

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