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# Langmuir−Blodgett Films of Alkane Chalcogenide (S,Se,Te) Stabilized Gold Nanoparticles

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## ABSTRACT

**Gold nanoparticles stabilized by alkanethiolates, alkaneselenides, and alkanetellurides have been prepared by analogous methods. Chloroform solutions of thiolate and selenide stabilized particles were spread and evaporated on the water/air interface where the particles formed well-defined Langmuir films. The films were transferred to solid supports of freshly cleaved mica and were studied by atomic force microscopy (AFM). The particles were found to have an average core diameter of 2 nm. The stability of the particles under ambient conditions increased in the order Te < Se < S.**

Gold nanoparticles stabilized by the adsorption of a monolayer of alkanethiolates[1] are currently studied worldwide for a number of fundamental and practical reasons.[2] Owing to their extraordinary stability under ambient conditions, they lend themselves, unlike most other metal particle systems, to a host of experimental studies and applications including electrochemical investigations of discrete capacitive charging of particles,[3] nanostructure self-assembly,[4] single-electron transistors,[5] and gas sensor devices.[6] Many properties of the particles, such as their chemical reactivity, interparticle electron transfer, and their ability to partake in self-organization processes, depend crucially on the nature of the ligands. The barrier height for electron transfer, for example, can depend on the redox-state of an electrochemically addressable moiety within the ligand shell.[7] The electrical conductivity of thin films of thiolate stabilized gold nanoparticles can be increased significantly if the alkane thiol ligands are replaced by bifunctional molecular wire type molecules, which cross-link the particles.[8,9] Electron transport is further expected to depend on the nature of the chemical bond between the ligand and the metal core, which is determined in most current systems by the gold−sulfur interaction.

The presence of functional end groups and their positions relative to each other within the ligand shell can have a profound influence on the chemical properties of the particles. It has been shown that thiolate ligands readily undergo place exchange reactions with other thiols added to a solution of particles, which has opened a simple and elegant new route to a vast range of functionalized particles.[2] More surprisingly, the ligands display a remarkable “three-dimensional” mobility on the surface of the particle, which roughly represents a nanosphere. This has been exploited to create self-optimizing binding sites for a molecular species present in solution, which effectively acts as a template for the “evolution” of the binding site on the particle surface.[10] Ligand stabilized gold nanoparticles may thus play an important role in the emerging field of adaptive chemistry. From these considerations it becomes obvious that an option for alternatives to the sulfur−gold linkage is desirable because it would enhance the ability to control three important properties of the particles. These are (i) electron transfer between adjacent particles, (ii) the facility with which ligands undergo place-exchange reactions, and (iii) the mobility of ligands on the surface of the particle.

Previously reported alternatives to thiolates include amine[11] and isocyanate[12] ligands. In this communication it is demonstrated that gold nanoparticles stabilized by alkanethiolates, alkaneselenides, and alkanetellurides can be prepared by analogous methods. Because the orbitals are extended on Se and Te relative to S, this exchange should lead to a significant change in electronic coupling between the ligand and the gold core. Likewise, the change in binding energy will lead to differences between Se, Te, and S both with regard to

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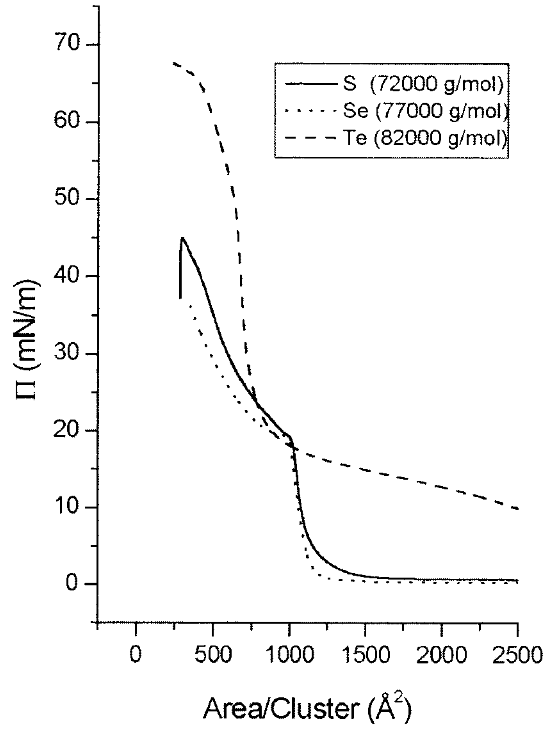

**Figure 1.** Langmuir isotherms of thiolate (solid line), selenide (dotted), and telluride (dashed) stabilized gold nanoparticles.

exchange reactions and ligand shell mobility, allowing increased tuneability of the system for particular purposes.

The particles were characterized by Langmuir isotherms and by AFM studies of Langmuir–Blodgett films on mica. All preparations were carried out by phase transfer of tetrachloroaurate from water to toluene and subsequent reduction with sodium borohydride in the presence of the stabilizing ligand in a two-phase liquid/liquid system. The conditions of the initial report on dodecanethiol stabilized particles by Schiffrin and co-workers[1] were followed closely, except for the use of didodecyl diselenide and didodecyl ditelluride instead of the corresponding selenols and tellurols, which are relatively unstable in air. All three materials were purified by repeated precipitation in ethanol and redissolved in chloroform, giving the typical dark brown solutions characteristic of particles with a core diameter below 3 nm. Didodecyl diselenide was prepared from dodecyl bromide and potassium polyselenide following ref 13. Residual diorganyl polyselenides, which typically pollute crude diselenide material, were removed efficiently by oxidation to dihydroxy dodecylselenonium *p*-toluenesulfonate (mp. 110–112 °C (dec), ethyl acetate), the tosylate salt[14] of dodecylselenenic acid. This compound was subsequently recrystallized and reduced to yield highly pure didodecyl diselenide. Didodecyl ditelluride was prepared by alkylation of polytelluride anions, prepared by reduction of tellurium with sodium in DMF at 50 °C, followed by column purification and crystallization.[15]

Thiol stabilized particles appear to be indefinitely stable, whereas their selenide analogues showed signs of particle growth (appearance of a plasmon absorption peak at 525 nm) after a few days of storage in chloroform and had fully precipitated after one month. Chloroform solutions of telluride stabilized particles showed color changes already a few hours after preparation and precipitated quantitatively within 3 days. Commercial grade chloroform was used throughout allowing an exact assessment of the relative stabilities of the Te-, Se-, or S-capped clusters. In all cases, changing the solvent to, for example, toluene may increase significantly the absolute stability. Langmuir films of all three types of particles were prepared by spreading 800 $\mu$L of a solution containing 0.4 mg/mL of nanoparticles on a water surface of 77700 mm$^2$ using a Langmuir balance. Compression isotherms were obtained at a speed of 10 mm/min. Langmuir–Blodgett films were prepared by horizontal (Schaefer) transfer of the densely compressed monolayers (close to the collaps pressure) onto freshly cleaved mica and subsequently imaged by atomic force microscopy (AFM) using a Nanoscope III scanning probe microscope. The Langmuir isotherms of all three materials are shown in Figure 1.

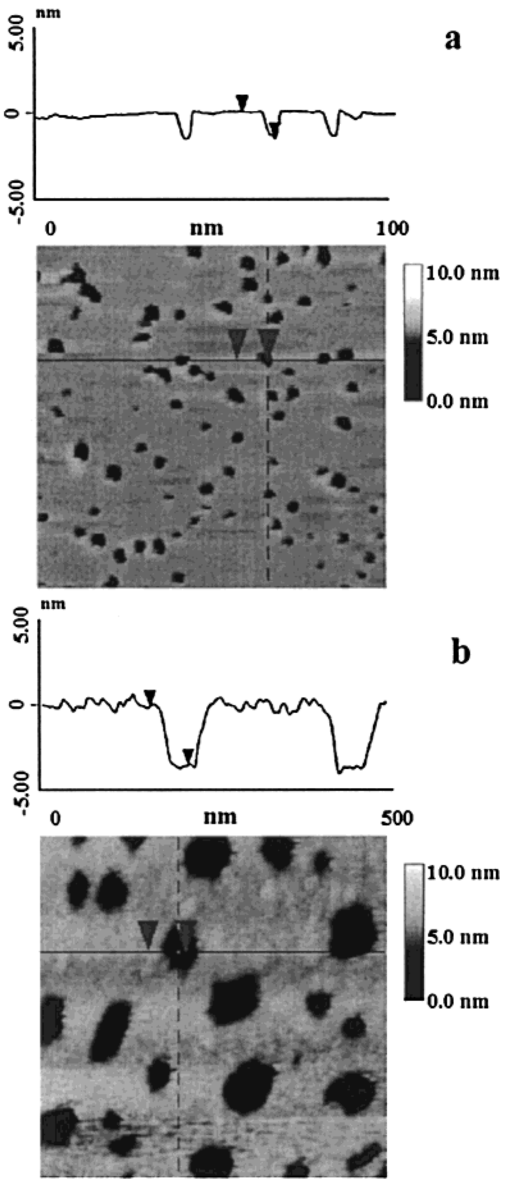

**Figure 2.** AFM images of Langmuir–Blodgett monolayers of thiolate (a) and selenide (b) stabilized gold nanoparticles on mica.

Thiolate and selenide stabilized particles exhibit identical behavior upon compression of the films. The absence of a liquid phase giving rise to a slow increase in pressure at large mean molecular areas, typical for phospholipids, is noteworthy. This indicates that the particles initially form small compact rafts, which are subsequently compressed without the occurrence of a two-dimensional phase transition from a liquid to a solid phase. The compression of solid rafts rather than of a homogeneous liquid phase also explains the presence of voids in the compressed and transferred films as shown by AFM (Figure 2). The Langmuir films collapsed at a surface pressure of 20 $\mathrm{mNm}^{-1}$ for both selenide and thiolate stabilized particles. For the selenide stabilized particles, a monolayer thickness of 3.4 nm has been determined from the depth of the voids, which is readily measured by AFM. This indicates the presence of particles of a core size of approximately 2 nm and an average molecular weight of 72 000 for thiolate stabilized particles and 77 000 for selenide stabilized particles, which are heavier due to the exchange of sulfur with selenium.[16] The voids in the thiolate stabilized monolayer are smaller and correspond to one missing cluster. Because the tip is too broad to reach the bottom of the voids, the depths of these voids appear smaller than the expected 3.4 nm.

Given these values, the area per particle for a compact layer was found to be 10 $\mathrm{nm}^2$ for both thiolate and selenide stabilized particles, consistent with the particle diameter (including the ligand shell) of 3.4 nm as determined by AFM. The compression isotherm of the telluride stabilized particles is markedly different from the two others. It clearly shows the presence of a liquid phase, and the collapse pressure is significantly higher. AFM inspection of transferred films indicated significant coalescence of particles (not shown) and destruction of the layer. This suggests that the particles are not sufficiently stable for well-defined Langmuir monolayers to form. The observation of a liquid phase and the increased collapse pressure are probably due to the presence of free ligands, which are products of particle degradation. These ligand molecules are surfactants, which can form Langmuir films themselves and interfere with the formation of well-defined films of particles.

In conclusion, it has been shown that selenide stabilized gold nanoparticles are sufficiently stable for the preparation of well-defined LB films and comparable in size and properties to thiolate stabilized particles. Telluride stabilized particles can be prepared by an analogous method but lack the stability required for nanostructure self-assembly. Further comparative studies of ligand exchange and mobility in thiolate and selenide stabilized particles are on the way.

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