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Langmuir isotherms of flexible, covalently crosslinked gold nanoparticle networks: Increased collapse pressures of membrane-like structures

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ABSTRACT

A series of hydrophobic gold nanoparticles were prepared by the Brust–Schiffrin method, employing thiols with chain lengths ranging from C6–C18 as capping ligands. Solutions of the purified nanoparticles were cast as monolayers upon the air–water interface of a Langmuir trough. After collecting characteristic compression isotherms and noting collapse pressures for each monolayer film at 20 °C, the impact of covalent crosslinking was studied by introducing a solution of dodecanedithiol in hexanes to the floating film of nanoparticles. It was discovered that characteristic collapse pressures increased significantly for films of nanoparticles with capping ligand alkyl chain lengths of less than 16 carbons. The films were easily transferred to a substrate, and TEM analysis revealed that the films retained a flexible, membrane-like morphology.

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1. Introduction

Recent decades have brought about reliable methods for the synthesis and functionalization of metal nanoparticles [1], but progress towards utilizing nanoparticles in a number of applications has been hindered by a lack of strategies for positioning the particles in durable solid-state arrays. For example the electronic properties of smaller gold nanoparticles are ideal for applications where Coulombic transport is the primary means of electronic communication [2], but precise interparticle spacing within an array has a critical impact on conductivity. Likewise, the optical properties of larger gold nanoparticles have served as the basis for plasmonic waveguiding structures, but again the ability to assemble the particles on a solid substrate is the key [3]. In both cases, it is best that the particles are immobilized upon assembly into a target structure to ensure continued, coherent electronic and/or plasmonic communication.

Herein, we describe a means of fabricating durable cross-linked films of close-packed gold nanoparticle arrays using the air–water interface within a Langmuir trough as a soft template for assembly. To date, there are relatively few examples of crosslinked nanoparticle arrays. Dithiols have been used to anchor gold nanoparticles to solid substrate [4], and to link alternating layers of gold and platinum particles together in a layer-by-layer manner to yield superstructures [5]. Nanoparticles have also been embedded in

dynamic polymeric matrices [6]. Arrays of nanoparticles have been created within Langmuir troughs [7,8], but lateral linkage of nanoparticles to yield a two-dimensional array has not been reported.

The use of a Langmuir trough in these studies is twofold: not only does it serve as a controlled environment for the assembly of nanoparticle films, but it also provides evidence of changes in the mechanical properties of the crosslinked arrays. Here, a series of alkanethiol-capped nanoparticles having similar gold core diameters but different ligand shell thicknesses were synthesized and cast as films upon the aqueous subphase of the trough, and film collapse pressures were determined through the collection of Langmuir isotherms. A similar series of isotherms were collected for nanoparticle films that had been crosslinked by an introduced alkanedithiol. The nanoparticle films were transferred to a solid substrate, and the structural characteristics of both crosslinked and non-crosslinked films were determined by TEM analysis.

2. Materials and methods

All solvents and reagents for nanoparticle synthesis were obtained from commercial sources and used as received. Ultrapure water was collected from a Barnstead Nanopure II purification system with a resistivity of 18.1 MΩ cm and used throughout. All glasswares were cleaned with aqua regia and rinsed with copious amounts of ultrapure water prior to use. Hydrophobic SiO₂ TEM grids were purchased from Dune Sciences, Eugene, OR.

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Gold nanoparticle synthesis: A series of alkanethiol-capped AuNP were synthesized using the biphasic Brust–Schiffrin method [9], using thiols having even-numbered hydrocarbon chains ranging from C6 to C18. Following synthesis, the particles were precipitated from solution and purified by Soxhlet extraction techniques [10].

Dithiol synthesis: 1,12-dithiolododecane was prepared from 1,12-dibromododecane by established literature preparation methods [11].

Nanoparticle film preparation for standard isotherm: A custom-built biphasic KSV Langmuir trough with surface area dimensions of 334 mm × 20 mm was utilized for nanoparticle film fabrication. The temperature-controlled aqueous subphase was maintained at 20 °C by a Julabo F12 recirculating system. Immediately prior to use, the trough assembly was thoroughly cleaned with hexane, ethanol, and ultrapure water. The lower subphase of the trough was filled with freshly collected ultrapure water. A solution of gold nanoparticles was prepared by dissolving 3 mg of anhydrous, alkanethiol-capped gold nanoparticles in 5 mL of hexane. 50 μL of this solution was spread over the surface of the water at a rate of 0.3 $\mu\text{L s}^{-1}$. After the solvent was allowed to completely evaporate, the barriers were compressed symmetrically at a rate of 10 mm min^{-1} . The surface pressure of the film was monitored by a platinum Wilhelmy plate, positioned perpendicular to the barriers at the center of the subphase. Each film was compressed past the point of film collapse, as identified by a significant decrease in slope on the isotherm graph of mean-molecular area (MMA, nm^2) vs. surface pressure (mN/m).

Crosslinked nanoparticle film preparation and isotherm collection: A solution of nanoparticles was prepared by dissolving 3 mg of anhydrous nanoparticles in 5 mL of hexane. A second solution contain 23.5 mg of 1,12-dithiolododecane in 100 mL of chloroform was prepared. 50 μL of the nanoparticle solution was spread over the aqueous subphase of the Langmuir trough at a rate of 0.3 $\mu\text{L s}^{-1}$. After allowing for complete solvent evaporation, the barriers were compressed symmetrically at a rate of 10 mm min^{-1} until the surface pressure reached 0.2 mN m^{-1} . At this point, the compression was paused and 50 μL of the 1,12-dithiolododecane was spread over the film at a rate of 0.3 $\mu\text{L s}^{-1}$. The solvent was

allowed to evaporate and the compression was resumed, continuing past the point of apparent film collapse.

Film deposition and TEM analysis: Both standard and crosslinked films were deposited onto hydrophobic silicon oxide TEM grids using the Langmuir–Blodgett method. TEM grids were cleaned by UV/ozone exposure, rinsed with anhydrous ethanol and ultrapure water, and submerged in the aqueous subphase by a mechanical dipper prior to spreading a solution of nanoparticles over the air–water interface. The isotherm experiments are carried out as described above, pausing the isotherm when a pressure 2 mN/m less than the known collapse pressure for a given film was achieved. The TEM grid was then withdrawn from the aqueous subphase at a rate of 2 mm/min. To ensure high quality film transfer, trough barriers remained active during substrate withdrawal, maintaining the surface pressure of the film during deposition. The transferred films were imaged on a JEOL 2010F transmission electron microscope at an accelerating voltage of 200 kV.

3. Results

After purification, nanoparticles were dissolved in hexane and cast upon SiO_2 TEM grids for size analysis, where the average particle size was found to be 4.3 nm. Collapse pressures of a series of both non-crosslinked and crosslinked nanoparticle films were identified by a decrease in the slope of the corresponding Langmuir isotherms (Fig. 1). Here, we report the average collapse pressure and the standard deviation for each type of nanoparticle film ($n=5$). Films composed of nanoparticles having ligand shells of alkanethiols with chain lengths < C16 tended to form poorly ordered films with low collapse pressures (< 15 mN/m), while films of nanoparticles capped by longer-chain thiols were more robust with collapse pressures exceeding 30 mN/m. However, after crosslinking, films of nanoparticles capped by shorter-chain thiols show increased collapse pressures, while films of nanoparticles capped by hexadecanethiol and octadecanethiol exhibit decreased

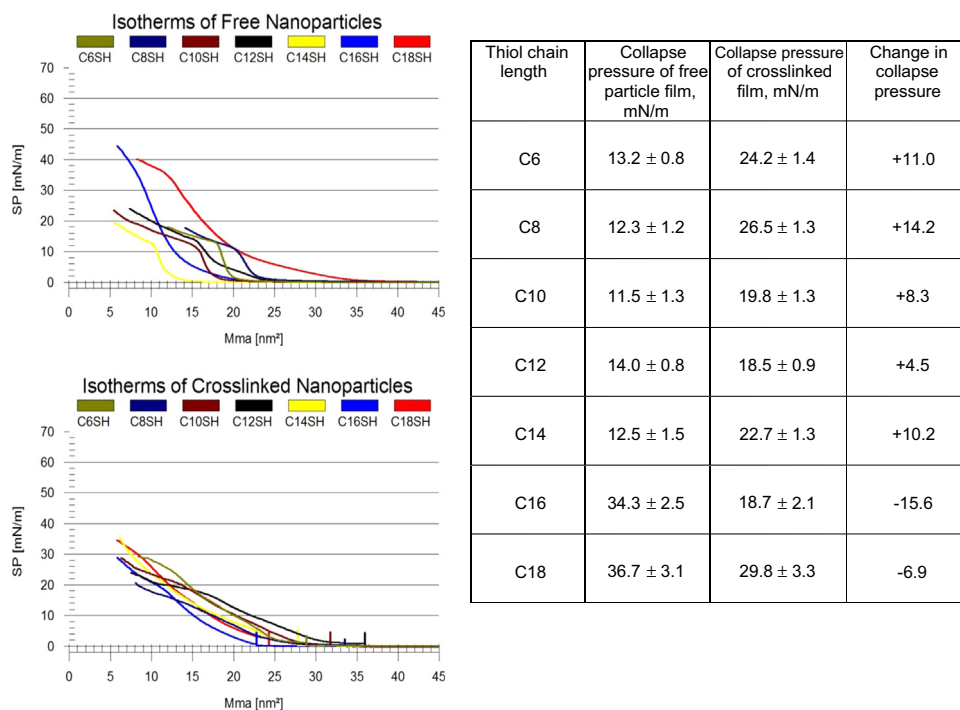


Fig. 1. Langmuir isotherms of free particles (top left) and crosslinked nanoparticles (bottom left). Changes in film collapse pressures are summarized in the table (right).

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