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Molecularly Tuned Size Selectivity in Thermal Processing of Gold Nanoparticles

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The ability to control size and monodispersity is essential for the exploration of electronic, optical, and magnetic properties of materials at the nanoscale.[1] There have been a number of approaches to size and shape control, including two-phase synthesis producing monolayer-protected nanoparticles, seeding, templating, shape-inducing agents, fractional separation, and photochemical methods.[1−3] Fundamentally little is known about the precise control of sizes, shapes, and monodispersity. The viability of achieving both controlled size growth and size monodispersity from the thermal processing of small-sized monolayer-protected nanoparticles as precursors, as demonstrated in our earlier work,[4] has recently gained increasing interest.[5] The control of temperature has provided an important means for processing nanoparticle size and monodispersity.[4,5] In view of the involvements of molecular desorption, nanoscrystal core coalescence, and molecular re-encapsulation processes in the evolution of nanoparticle precursors at elevated temperatures, one fundamental question is whether the size selectivity can be tuned molecularly. This question has never been addressed. The answer to this question would have not only significant impact toward the establishment of the thermal processing method for the precise control of size and monodispersity but also much broader implications to many nanoparticle-based technologies. In this report, we demonstrate for the first time that the size selectivity of nanoparticles in the thermal processing can be tuned molecularly. This novel tuning is accomplished in a proof-of-concept demonstration for monolayer-protected gold nanoparticles by manipulating the chain length and the concentration of alkanethiols in the processing solution. The basic idea stems from two key promises of such molecular tuning: (1) an increase in alkanethiol chain length leads to a gain in stabilization energy due to additional interchain cohesive interactions[6,7] and (2) a change in alkanethiol concentration shifts the evolution equilibrium in terms of shell desorption and re-encapsulation.[4b] We present herein the experimental data to demonstrate quantitative correlations between size selectivity and these two parameters. The key distinction of

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this idea from previous work[4,5] rests with the molecularly tuned size slectivity for the thermally activated size processing route.

The precursor gold nanoparticles encapsulated with decanethiolate (DT) monolayer shells (Au_{2nm}-DT) were synthesized using Brust et al.'s standard two-phase method,[3a] giving an average size of 2.01 ± 0.41 nm. Following solvent evaporation, the Au_{2nm}-DT nanoparticles and other reactants and products from the synthesis solution were dissolved quantitatively in toluene giving a stock solution with known concentrations of Au_{2nm}-DT particles, free DT, and tetraoctyammonium bromide (TOABr). All subsequent heating treatments were preformed on identical samples from this common stock solution. For the study of chain length dependence, alkanethiols ($CH_3(CH_2)_nSH$) of a selected chain length were quantitatively added into the processing solution, giving a constant concentration (232 mM) for all chain lengths. For the study of concentration dependence, different quantities of alkanethiols of a selected chain length were added into the processing solution, giving different concentrations for the same chain length. The reaction tube was placed in a preheated oven set at 149.0 ± 1.5 °C. After 1 hr of thermal treatment, the tube was removed from the oven and allowed to cool before dissolving the nanoparticles in the mostly solid mixture in toluene.

Figure 1 shows a representative set of transmission electron microscopy (TEM) micrographs for samples obtained from thermal processing in the presence of alkanethiols of different chain lengths under constant concentration. The monodispersity of the nanoparticles was determined by directly measuring the diameters of particles in the TEM image using size-analysis software. The total counts of particles were generally in the order of 200−500, from which the average diameter and standard deviation values were determined.

There are several important observations. First, the thermally evolved particles show largely spherical morphology, although shapes with hexagon-like features can be identified. Second, the particles are highly monodisperse (±0.36 nm) with relative standard deviations typically under 5%. Third, the average size of the particles is clearly dependent on the chain length of the alkanethiols used in the thermal processing. The nanoparticle cores for samples evolved using shorter chain thiols were found to be larger than those evolved in the presence of longer thiols. For example, the gold nanoparticles obtained using alkanethiols with $n = 5$ (Figure 1a) show an average core diameter of 7.60 ± 0.43 nm. When the chain length is extended to $n = 15$ (Figure 1c) an average core diameter of 5.86 ± 0.31 nm was obtained. We also note that the size increase of the particles was also accompanied by a systematic increase of the surface plasmon resonance band (see Supporting Information).

Figure 2 shows the correlation between the size of the post-heat treatment nanoparticles and the chain length of the alkanethiols used in the thermal processing. Note that the concentration of the alkanethiols was constant for all chain lengths, making chain length the only independent variable.

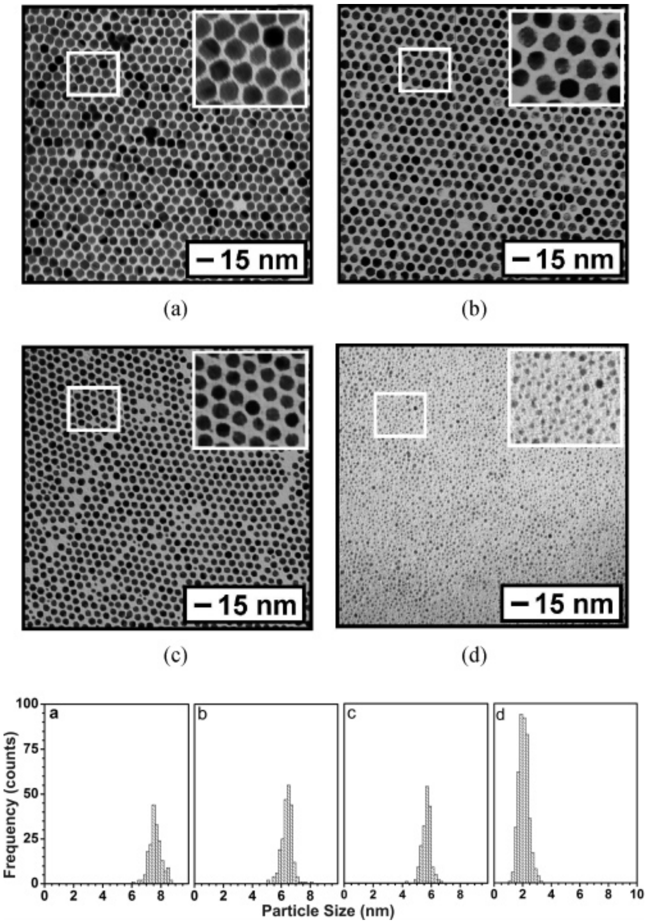

Figure 1. TEM images and particle size distributions of gold nanoparticles produced by thermal processing in the presence of alkanethiols of different chain lengths (n): $n = 5$ (a, 7.60 ± 0.43 nm), 10 (b, 6.41 ± 0.40 nm), and 15 (c, 5.86 ± 0.31 nm). TEM micrograph for the precursor Au_{2nm}-DT (d, 2.01 ± 0.41 nm) is included for comparison.

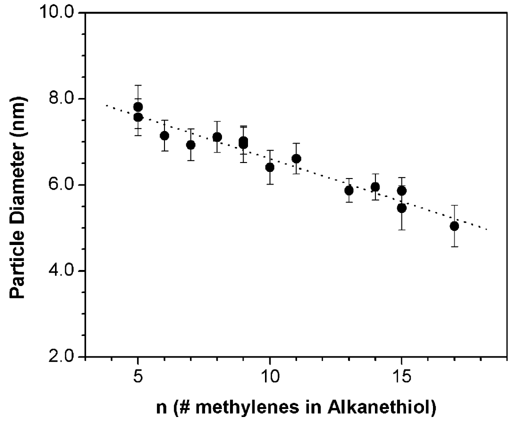

Figure 2. Plot of nanocrystal core size vs alkylthiol chain length (n), i.e., number of methylenes. The concentration of alkanethiols was constant for all chain lengths (232 mM). Linear regression results: particle diameter = $-0.19n + 8.71$ nm ($R^2 = 0.94$; dashed line).

Important information can be extracted from the above correlation. First, the data clearly exhibit a linear trend for the average particle core size versus the chain length of the alkanethiols, demonstrating that the particle size can be manipulated by alkanethiol chain length. Second, by changing the chain length of the alkanethiols from $n = 5$ to $n = 17$, nanoparticle sizes ranging from 5 to 8 nm with good monodispersity can be obtained. Finally, a quantitative piece of information is obtained from the slope of the trend line, that is, ~0.2 nm/methylene. This value suggests that the increase of a methylene unit in the capping alkanethiol can effectively decrease the nanoparticle core size by 0.2 nm.

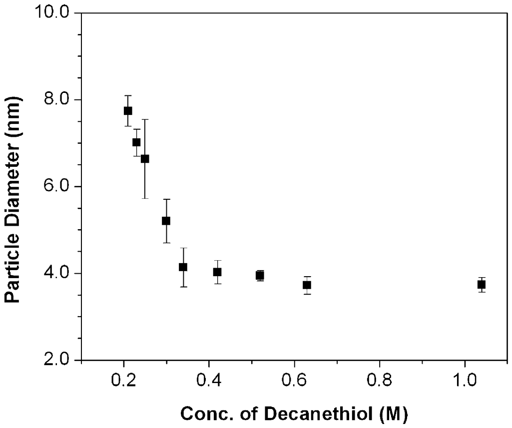

Figure 3. Plot of nanocrystal core size vs decanethiol concentration used in the thermal processing solution.

At a higher concentration (e.g., 310 mM) of the alkanethiols, the slope was found to be smaller (~0.1 nm), which likely reflects the increased rate of re-encapsulation leading to limited growth of the nanoparticle core.

This effect of alkanethiol concentration on the particle size evolution was examined further. Figure 3 shows a representative set of data for the dependence of particle sizes on the concentration of decanethiol added in the pre-heat-treatment solution. It is clear that the evolved core size is strongly affected by changing the concentration in the solution. The observation of a reciprocal relationship with concentration is consistent with a model involving the Langmuir isotherm for the adsorption−desorption equilibrium, a detailed assessment of which is part of ongoing work. Increasing concentration leads to a significant decrease of the particle size for concentrations less than ~0.5 M. At higher concentrations, this effect diminishes. Note that the chain length of the alkanethiols was constant ($n = 9$ methylenes) for all concentrations used, making concentration the only independent variable.

The effect of increasing concentration on the particle size can be understood by considering that the shell desorption is favored at low thiol concentration and that the equilibrium shifts in favor of re-encapsulation as thiol concentration is increased. To understand the origin of the linear correlation between the particle size and the chain length, we considered the energetic aspects involved in the alkanethiolate encapsulation. Assuming a spherical model for the nanoparticle core, ~22 Å^2 for the average surface area per thiolate as known for a densely packed self-assembled monolayer on a planar Au surface,[8] and ~1 kcal/mol of methylenes for the cohesive energy,[9] this estimation (see Supporting Information) showed that, as particle size increases, the increasing number of thiolates in the encapsulation shells leads to an increase in cohesive energy. The longer the chain length of the capping alkanethiolate, the larger the cohesive energy resulting from the chain−chain van der Waals interaction. The result suggests that the cohesive energy is at least partially responsible for the origin of the size−chain length correlation. The discrepancy between the theoretical calculation and the experimental data for the smaller particles formed using longer chain thiols ($n > 14$) is believed to be associated with the less-extensive interdigitation of the alkyl chains on the smaller-sized particles in comparison with larger ones.

The results substantiate that shell desorption, core coalescence and growth, and shell readsorption processes in the thermally activated size evolution of gold nanoparticles in the presence of alkanethiols of different chain lengths are dependent on the relative binding strengths of the capping thiolates and the shell composition. The desorption rate is dependent upon the energy required to not only break the gold−sulfur bond but also break the cohesive van der Waals forces between methylene groups on adjacent alkanethiolates. At thermally enhanced rates of ligand exchange, the shell composition changes and the coalescence of smaller particles into larger particles occurs. The difference in the chain length thus regulates the degree of coalescence and re-encapsulation and ultimately results in equilibrium core size differences.

In conclusion, we have unraveled the remarkable dependence of the particle size on the chain length and concentration of alkanethiols in the thermal processing of pre-synthesized gold nanoparticles, demonstrating for the first time the molecularly tuned size selectivity of the thermal processing route. The findings of a linear relationship between the particle size and the alkanethiol chain length and a reciprocal relationship between the size and the alkanethiol concentration imparts the thermal processing route with the capability of molecularly tuning of particle sizes. This tuning is unique because it demonstrates the important role played by cohesive interactions in regulating interfacial reactivities of preformed nanoparticles in a thermal processing route, in sharp contrast to the manipulation of precursor ratios documented for a chemical synthesis route.[3] These findings should have significant implications to fine-tuning or re-engineering of size and monodispersity of metal nanoparticles for various technological applications.

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Supporting Information Available: (1) Surface plasmon resonance band of the nanoparticles and theoretical consideration; (2) preliminary theoretical consideration of the cohesive energy in relation to the alkyl chain length. This material is available free of charge via the Internet at http://pubs.acs.org.

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