

Extraction and Dispersion of Large Gold Nanoparticles in Nonpolar Solvents

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ABSTRACT

Gold nanoparticles up to 70 nm in diameter could be extracted from aqueous solutions into nonpolar organic solvents by tetrathiolated resorcinarenes 1 and 2. The resorcinarene-coated nanoparticles formed stable dispersions in toluene and chloroform and could be passed through a crosslinked polystyrene column without significant degradation, but exhibited variable resistance to alkanethiol-induced flocculation. Gold nanoparticles encapsulated by resorcinarene 2 were found to be exceptionally stable even in the presence of propanethiol and dodecanethiol, with an approximate dispersion half-life of one month at room temperature.

Key Words: Gold nanoparticles; Surface modification; Resorcinarenes; Flocculation; Colloidal gold; Tetrabenzylthiol resorcinarene; Tetraarylthiol; Particle extractions; Chloroform; Toluene

INTRODUCTION

Functionalized gold nanoparticles have been employed extensively as labels for biomolecular assays (1) and as components in nanostructured assemblies and devices (2). Particles in the mid-nanometer size range may be especially attractive in this regard, as their optical extinction and scattering properties change dramatically with size (3). However, their application as materials is often handi-

capped by their limited dispersion, particularly in organic solvents. Chemisorptive surfactants such as alkanethiols are known to enhance particle dispersion and provide opportunities for further chemical modification (4), but gold nanoparticles beyond a certain size (about 10 nm) are prone to flocculation because their van der Waals interactions can overwhelm the steric stabilization provided by typical surfactants (5). Another factor to consider is the robustness of the surfactant layer against degradation or

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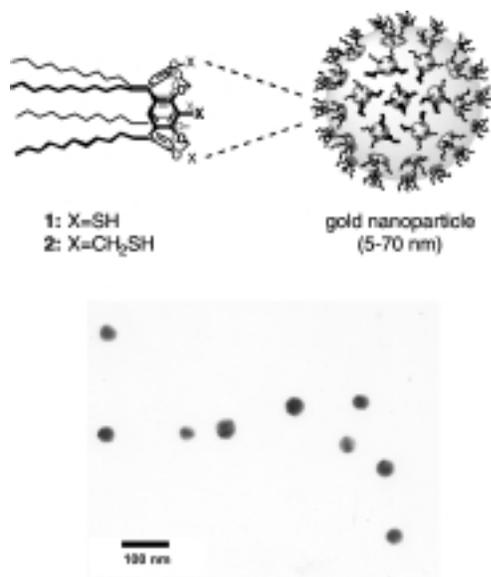


Figure 1. Gold nanoparticle encapsulated by tetrathiolated resorcinarenes. Transmission electron micrograph (Phillips EM-400, 80 keV) of 35 ± 3 nm gold particles dispersed by 2 was obtained by placing a drop of a toluene solution onto a Formvar-coated Cu grid, then removing it a few seconds later by wicking.

desorption, as even strongly chemisorptive surfactants are known to undergo facile exchange in solution (6).

In this article we describe the enhanced robustness of gold nanoparticles stabilized by tetrathiolated resorcinarenes 1 and 2 and their dispersibility in nonpolar organic solvents (see Figure 1). Compound 2 is an exceptionally effective surfactant: it can mediate the extraction of colloidal gold particles as large as 70 nm from aqueous suspensions, and maintain kinetically stable dispersions in nonpolar solvents such as toluene and chloroform. We have previously demonstrated that appropriately modified resorcinarenes are excellent dispersants of gold nanoparticles in hydrocarbon solvents, but exhibit variable degrees of robustness (7). In comparison, nanoparticles encapsulated by 2 are remarkably robust, and can resist degradation or flocculation even after long-term exposure to competing alkanethiol surfactants.

EXPERIMENTAL

Resorcinarenes 1 and 2 were synthesized by modification of known literature procedures (8,9). Gold nanoparticles of narrow size dispersity were prepared as aqueous suspensions by citrate reduction of gold chloride (10^{10} – 10^{11} particles/mL) (10), then treated with milli-

molar solutions of 1 or 2 in THF. The resorcinarene-encapsulated nanoparticles could be extracted into toluene or chloroform upon adding minute amounts (1–5 mol% of surfactant concentration) of tetra-*n*-octylammonium salts, which presumably exchange with inorganic counterions in the electrostatic double layer. Extracts were dried over molecular sieves and concentrated until optical densities between 0.1 and 0.2 were achieved at plasmon resonance (532 nm) (11). Dispersions of encapsulated nanoparticles with minimal free surfactant could also be prepared by washing the aqueous solution with hexanes prior to the extraction procedure above. All extractions and dispersions were performed in silanized glassware to minimize surface adsorption.

RESULTS AND DISCUSSION

Tetrabenzylthiol resorcinarene 2 was capable of extracting and dispersing gold particles as large as 34 nm into toluene and as large as 70 nm into chloroform solutions (12,13). These nanoparticle dispersions appeared to be indefinitely stable at room temperature even with the removal of excess surfactant, retaining over 90 % of their optical density after one month (see below). Tetraarylthiol 1 was less effective but could still extract and disperse 19- and 42-nm gold particles into toluene and chloroform, respectively. The basis for the difference between 1 and 2 is not yet established but may be related to the surfactants' strength of adsorption. The four thiol groups of 2 are unencumbered and therefore should be able to strongly passivate the gold surface by cooperative adsorption, whereas those of 1 are sterically hindered by neighboring methylene units and may be unable to adsorb in a tetradentate fashion, resulting in weaker passivation (see Figure 2).

The resorcinarene-coated nanoparticles were evaluated by gel permeation chromatography (GPC), which has been used to provide a qualitative measure of structural stability for encapsulated nanoparticles (14)

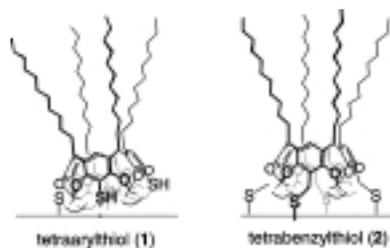


Figure 2. Steric differences between resorcinarenes 1 and 2 adsorbed on gold nanoparticle surfaces.

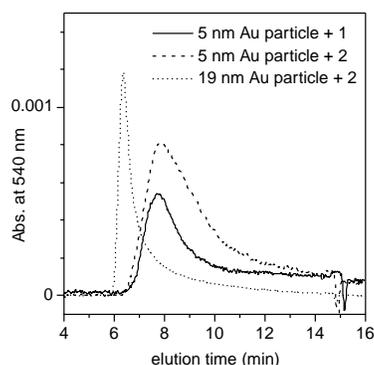


Figure 3. Gel permeation chromatography (GPC) traces of 5- and 19-nm gold particles stabilized by 1 or 2. Peaks were monitored by optical absorbance at 540 nm. The abrupt change in absorbance after 15 min correlates with the elution of toluene.

and other nanostructured assemblies (15). 5- and 19-nm particles encapsulated by 1 or 2 were loaded onto a crosslinked polystyrene column (Styragel HR 4E, Waters) and eluted with chloroform at a flow rate of 0.75 mL/min. GPC peaks were produced with retention times and peakshapes in accord with their size and polydispersity and exhibited only minor tailing (see Figure 3) (14,16). It is worth mentioning that the hydrodynamic volumes of the resorcinarene-encapsulated nanoparticles did not correlate well with those of polystyrene size standards as estimated by the Marc-Houwink equation (17), although this is hardly surprising given their completely different compositions. GPC analysis of nanoparticles using 0.1 mM surfactant in chloroform as the eluent produced essentially identical peakshapes, demonstrating that the resorcinarene-encapsulated nano-

particles were stable against surfactant desorption during elution.

The nanoparticle dispersions were also evaluated for long-term stability in the presence of other alkanethiol surfactants by monitoring their optical density at 532 nm (see Figure 4). It has been demonstrated previously that the displacement of resorcinarenes by single-chain alkanethiols would result in the flocculation of gold particles larger than 10 nm with a concomitant loss of optical density (7). Indeed, dispersions of 19-nm particles stabilized by 1 in toluene were degraded by the addition of propanethiol (C3SH) or dodecanethiol (C12SH): the dispersion half-life was reduced from 214 hrs (1.5 weeks) in the absence of competing surfactant to 100 hrs (4.2 days) in the presence of 1.7 mM C3SH (see Figure 4a). In comparison, addition of 1–3 mM C3SH or C12SH to 19-nm gold particles stabilized by 2 caused only a gradual decrease in optical density, with an approximate dispersion half-life of one month at room temperature (see Figure 4b). Transmission electron micrographs of the resorcinarene-stabilized nanoparticles after one month exposure to PrSH indicated an intermediate degree of flocculation; however, the particles retained their individuality and were easily redispersed upon agitation. Nanoparticles dispersed by 2 in chloroform exhibited similar levels of robustness. It should be noted that nanoparticles encapsulated by 2 were also stable to other chemisorptive agents such as PPh_3 and could withstand heating to at least 70°C, but were vulnerable to oxidation by iodine and degradation by corrosive ions such as cyanide and fluoride.

In summary, we have developed a methodology for enhancing the dispersibility and robustness of gold nanoparticles up to 70 nm in organic solvents and in

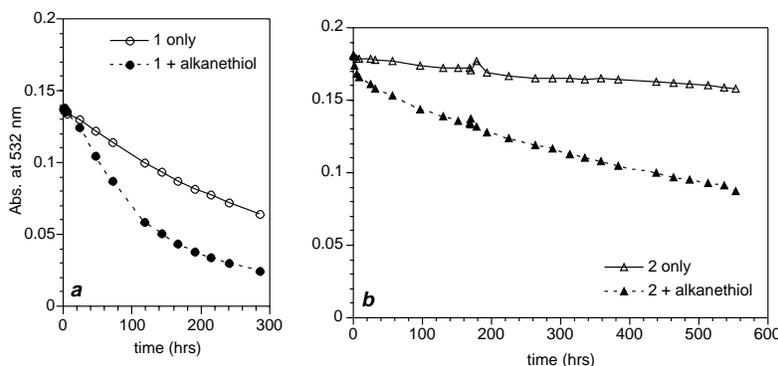


Figure 4. Dispersion stability studies of resorcinarene-encapsulated gold nanoparticles. (a) 19-nm gold particles stabilized by 1 in toluene (1.8 mM) in the absence and presence of C3SH (1.7 mM). (b) 19-nm gold particles stabilized by 2 in toluene (2 mM) in the absence and presence of C3SH (1.7 mM). Additional alkanethiol (C12SH, 1.7 mM) was added after one week.

the presence of competing surfactants. Surfactants such as resorcinarenes 1 or 2 should provide increased processing control for dispersing larger nanoparticles into polymer-matrix composites and in the fabrication of ordered nanostructured materials, as recently demonstrated by the self-organization of large gold nanoparticles into planar arrays (18). The superior dispersive properties of the resorcinarenes may also be useful for other nonaqueous particulate systems which require enhanced steric stabilization, such as electro- and magnetorheological fluids (19).

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 12. All diameters were determined as statistical averages by particle size analysis of transmission electron micrographs with coefficients of variance between 10–15%.
 13. Gold nanoparticles up to 100 nm could be extracted into CHCl_3 by resorcinarene 2 with higher concentrations of tetra-*n*-octyl ammonium bromide (0.2 mM). However, these dispersions were more limited in their stability.
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