

Resorcinarene-Encapsulated Nanoparticles: Building Blocks for Self-Assembled Nanostructures

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Abstract

Calix[4]resorcinarene-derived surfactants are highly effective at stabilizing metal nanoparticles of different sizes, creating opportunities to fabricate well-defined nanostructures with size-tunable materials properties. The resorcinarenes have a critical role in the dispersion of nanoparticles under various solvent conditions and in the robustness of the protective surfactant layer. Magnetic cobalt particles stabilized by resorcinarenes self-assemble into nanostructured “bracelets” in toluene. Resorcinarene surfactants can also promote the self-organization of gold nanoparticles as large as 170 nm into two-dimensional arrays. These nanostructured films possess novel optoelectronic properties such as surface-enhanced Raman scattering (SERS), and are expected to have useful applications for chemical sensing.

Introduction

Supramolecular chemists have had a long-standing fascination for self-assembled systems, and have become adept at using a variety of intermolecular forces to create multicomponent assemblies of ever-increasing size and complexity. As supramolecular science continues its progression toward nanoscale dimensions, chemists will encounter forces of a different genre: long-range van der Waals interactions, electrostatic double-layer forces, and various short-range repulsive interactions which can be used to stabilize self-assembled nanostructures [1]. Whereas scientists and engineers working on the submicron length scale are faced with the challenge of developing technologies to decrease the unit size and density of functional materials and devices [2], those who work and think at the molecular level must learn to harness forces in the nanoscale regime to address this next level of supramolecular materials science.

Self-assembly processes are being used with increasing frequency in nanostructured materials synthesis, the quintessential example being the self-organization of metal nanoparticles into two-dimensional (2D) arrays such as that shown in Figure 1 [3]. Numerous examples of nanoparticle superlattices in hexagonal close-packed formation have been reported, the great majority of these having been stabilized by single-chain fatty acids or alkanethiols and organized at the air-water interface [4]. However, this approach to self-organization has apparently been limited to metal particles whose unit size is less than 10 nm. Particles larger than this threshold size become difficult to manipulate because their

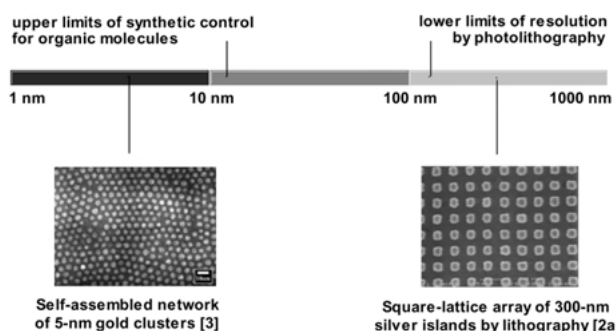


Figure 1. “Bottom-up” self-assembly processes have been successful at producing nanostructured materials with repeat distances of 10 nm or less, whereas “top-down” lithographic approaches can produce lattices with periodicities over 100 nm with relative ease. The fabrication of nanostructured materials with periodicities in the mid-nanometer size range is still a developing area of materials synthesis. Electron microscopy images used with permission of the authors.

size-dependent van der Waals interactions can overwhelm the short-range steric repulsion provided by the surfactant layer [5]. This affects not just the particles’ ability to self-organize under controlled conditions, but also their long-term stability in nonpolar media. For example, dispersions of alkanethiol-coated gold nanoparticles in toluene are thermodynamically unstable for particles larger than 10 nm, which quickly precipitate from solution [6].

In order to expand the range of metallic nanoparticles which can be fabricated into well-defined nanostructured materials by self-assembly, interparticle attractive forces must be countered by greater short-range repulsion. This can be achieved by designing surfactant layers with intrinsic

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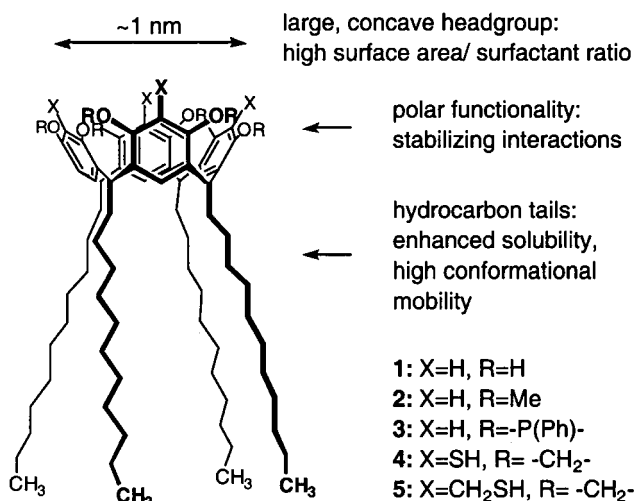


Figure 2. Resorcinarene derivatives as nanoparticle encapsulants.

ically high configurational entropy [1]. Indeed, single-chain surfactants with small headgroups are a poor choice of material, because their hydrocarbon chains are known to form well-ordered monolayers with minimal entropy [7]. On the other hand, increasing the spacing between chains should greatly increase their conformational freedom, resulting in improved steric stabilization.

This strategy has been demonstrated by using calix[4]resorcinarenes to stabilize dispersions of metal nanoparticles in organic solvents (see Figure 2). There are several advantages to using macrocyclic surfactants such as the resorcinarenes for this purpose: (i) their large headgroups require fewer surfactant molecules per unit area, reducing the entropic cost of encapsulation; (ii) their adsorption to the nanoparticle surface can be greatly stabilized by multiple binding interactions; and (iii) the macrocyclic base can be appended by several hydrocarbon tails at fixed spacings. This last feature ensures that the hydrocarbon chains will always possess a certain degree of conformational freedom, regardless how densely packed the resorcinarenes are on the nanoparticle surface.

Dispersion studies of encapsulated gold nanoparticles

Initial studies on the use of resorcinarenes for stabilizing nanoparticles in organic solvents were encouraging [6]. Crystalline gold nanoparticles as large as 20 nm were generated as aerosols and captured in millimolar solutions of C11 resorcinarene **1** or its octamethyl ether **2**, forming stable purple dispersions in mesitylene. The stability of the nanoparticle dispersions were evaluated by monitoring changes in absorption generated by the surface plasmon resonance of the gold nanoparticles at 538 nm. Stabilization was most likely mediated by the cooperative chemisorption of multiple oxygen atoms to the gold surface. This adsorption proved to be quite weak however, as the resorcinarene-encapsulated nanoparticle dispersions were rapidly degraded by attempts to isolate them from solution or by their exposure to competing alkanethiol surfactants.

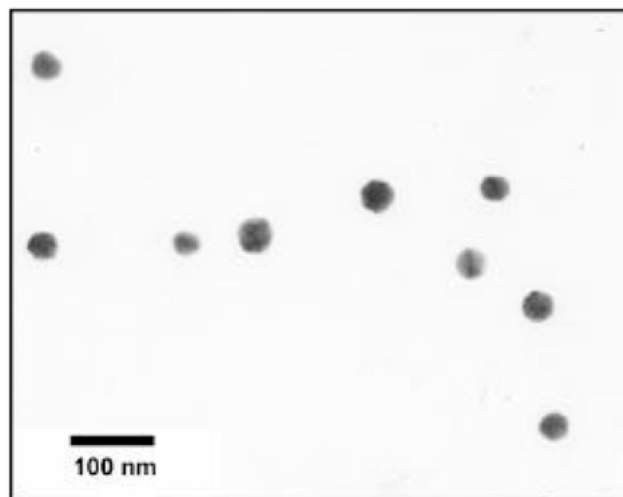


Figure 3. TEM image (Philips EM-400, 80 keV) of 35 ± 3 nm Au particles extracted by resorcinarene **5** into toluene [9].

Phosphorus- and sulfur-substituted resorcinarenes were then investigated for increasing the robustness of the encapsulated nanoparticles [8, 9]. Resorcinarenes **3–5** were found to be capable of extracting gold colloid from aqueous solutions, and nanoparticles encapsulated by some of these surfactants could be isolated by precipitation or gel-permeation chromatography without significant degradation, in contrast to the earlier studies (see Figure 3). Tetra(*P*-phenyl)phosphonite ester **3** was determined to be hydrolytically sensitive, but tetraarylthiol **4** and tetrabenzylthiol **5** proved to be chemically robust surfactants and were capable of stabilizing gold nanoparticles as large as 70 nm in organic solvents. The tetrathiol-stabilized nanoparticles demonstrated resistance against desorption and alkanethiol-induced aggregation: 19-nm gold particles stabilized by **5** in toluene remained well-dispersed in the presence of propanethiol or dodecanethiol, with an approximate half-life of one month at room temperature.

Dispersion and self-assembly of magnetic nanoparticles

The resorcinarene surfactants were also able to stabilize dispersions of magnetic nanoparticles in organic solvents. Thermolysis of $\text{Co}_2(\text{CO})_8$ in degassed toluene solutions mediated by tetraphosphonite ester **3** produced cobalt nanoparticles of various size ranges, depending on initial reaction conditions [10]. Repeated magnetic precipitation and washings yielded nanoparticles with reasonable size dispersity. The dispersibility of cobalt nanoparticles in toluene was enhanced by resorcinarene **1** in comparison with other surfactants such as single-chain carboxylic acids. Dispersions of 15–30 nm cobalt particles ($M_s \sim 24$ emu/g) were stable for weeks at room temperature, whereas 50–60 nm particles ($M_s \sim 250$ emu/g) precipitated within hours. Magnetic dipole–dipole interactions between the 25–30 nm cobalt particles were sufficiently strong at room temperature to direct their assembly into oligomeric chains and loops, as determined by transmission electron microscopy

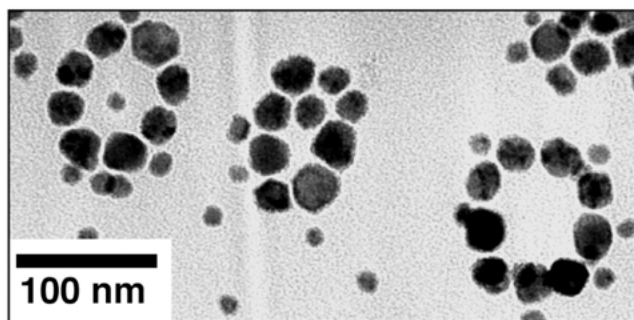


Figure 4. TEM image (JEOL 2000 FX, 200 keV) of Co nanoparticles encapsulated by resorcinarene **1** in toluene [10]. The larger (25–30 nm) particles have self-assembled into nanosized “bracelets”.

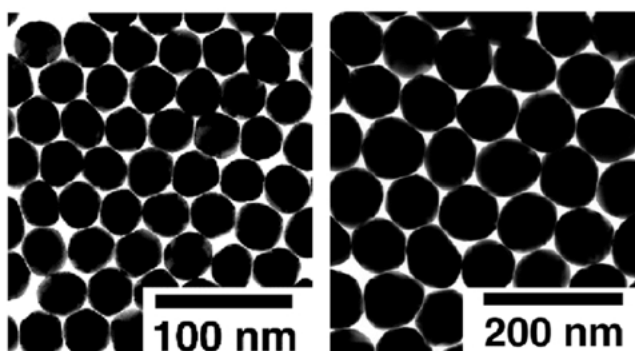


Figure 5. TEM images (Philips EM-400, 80 keV) of self-organized 2D arrays of 34 ± 2 nm (left) and 87 ± 7 nm (right) Au nanoparticles stabilized by resorcinarene **4** [11]. The arrays were formed at the air-water interface and transferred onto Formvar-coated Cu grids.

(see Figure 4). The bracelet-like assemblies were observed to be the predominant aggregate form under several different sample preparation conditions, suggesting cooperative magnetic interactions.

Self-organization and optical properties of gold nanoparticle arrays

The enhanced dispersibility of the large gold nanoparticles by tetrathiol resorcinarenes **4** and **5** suggested that these surfactants could also facilitate the formation of periodic 2D arrays by self-assembly. Colloidal gold particles of narrow size dispersities ranging from 16 to 170 nm were treated with **4** and spread onto air-water interfaces, then transferred onto hydrophilic surfaces by horizontal (Langmuir-Schaefer) deposition or by vertical retraction of immersed substrates [11]. These methods produced monolayers with good long-range order irrespective of particle size (see Figure 5). In comparison, attempts to organize 20-nm dodecanethiol-encapsulated gold particles into 2D arrays at the air-water interface resulted in the formation of multilayer aggregates. This demonstrated that the resorcinarenes were indeed essential for the self-assembly of the nanostructured films.

Careful analysis of the TEM images revealed an inverse correlation between particle size and the average spacing between particles, which decreased from approximately

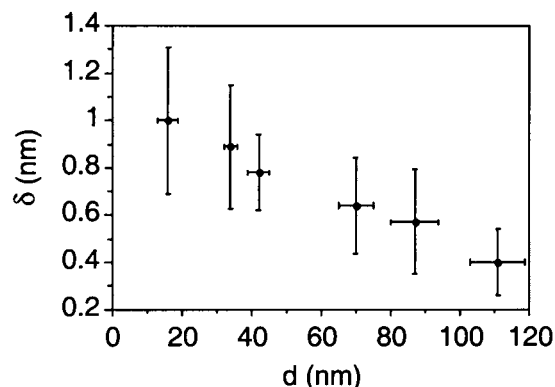


Figure 6. Particle diameter-spacing relationship for the self-organized 2D gold nanoparticle arrays, as determined by TEM image analyses [11]. Error bars are equal to one standard deviation from the mean.

10 Å for the 16-nm particle array to about 4 Å for the 170-nm array (see Figure 6) [11]. This trend is due to the increase in van der Waals attraction as a function of particle size [1], countered partially by the increasing short-range repulsion of the surfactant layer. Interestingly, the interparticle spacings are much less than the expected thickness of a monolayer of resorcinarene **4**, which is well over 1 nm in length with its chains fully extended [12]. Steric repulsion at such close range may therefore be dependent on both loss of conformational chain entropy and increased torsional strain on the resorcinarene headgroup, which has a van der Waals thickness of approximately 5 Å in its undeformed state. A second possibility for the close spacing could be related to the limited mobility of the tetrathiol surfactants on the nanoparticle surface; the force of compression may be sufficient to induce partial depletion of the surfactants from the regions of greatest contact.

Both particle size and interparticle spacing play an important role in the optical properties of the large gold nanoparticle arrays [13]. The extinction maxima of the nanostructured films were observed to shift by hundreds of nanometers from visible to near-infrared wavelengths with increasing periodicity (see Figure 7a) [11]. The films' reflectivities also varied markedly as a function of structure, with maximum specular reflectances at optical wavelengths observed for the mid-nanometer sized (40–70 nm) particle arrays. Nanostructured arrays with smaller periodicities were absorptive at visible wavelengths, whereas arrays with larger periodicities were increasingly effective light scatterers.

Very excitingly, the nanoparticle arrays exhibited size-tunable surface-enhanced Raman scattering (SERS), an analytical technique which can integrate high chemical sensitivity with spectroscopic precision and has enormous potential for trace chemical detection [14]. Strong Raman signals were easily obtained by irradiating approximately one femtomole of adsorbed **4** at near-infrared excitations (see Figure 7b) [15]. The SERS intensities varied dramatically with periodic structure and the wavelength of excitation, generally increasing with both. Comparison of the SERS signals at 813 cm^{-1} with unenhanced Raman signals from thin films of resorcinarene enabled the calculation of empirical enhancement factors (G) ranging from 10^4 to 10^7 (see

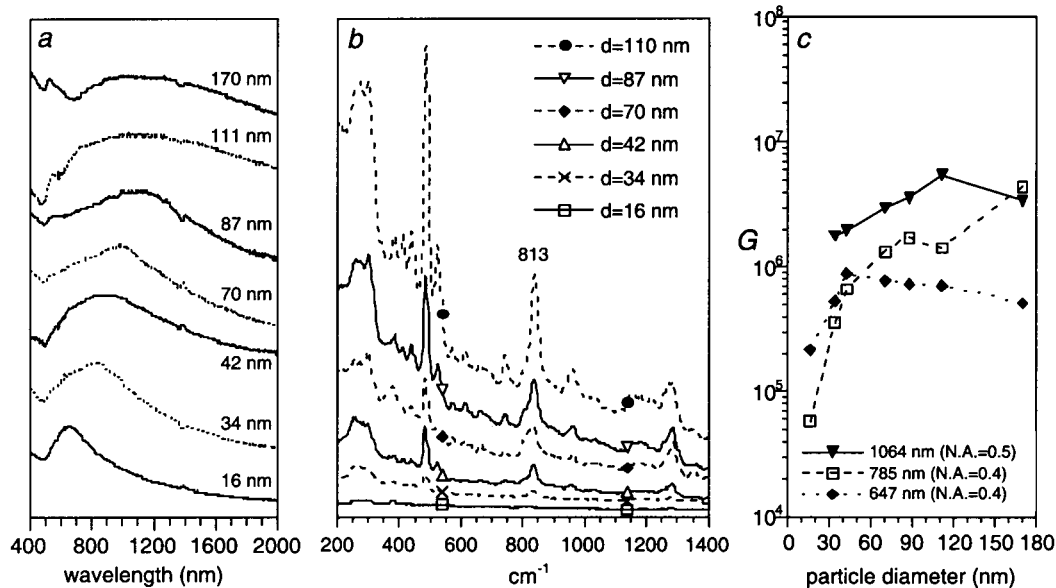


Figure 7. Size-tunable optical properties of the resorcinarene-encapsulated gold nanoparticle arrays [11, 15]. (a) Optical extinction spectra of the gold nanoparticle arrays on quartz substrates. (b) Surface-enhanced Raman spectra of resorcinarene **4** adsorbed on arrays of varying periodic structure (laser excitation at 785 nm, 10 mW; N.A. = 0.75; exposure time = 30 sec). Spectra in (a) and (b) have been shifted for clarity of presentation. (c) Empirical signal enhancement factors (G) as a function of excitation wavelength (647, 785, and 1064 nm) and array periodicity ($d = 16$ –170 nm). G values were based on integrated signal intensities at 813 cm^{-1} .

Figure 7c). However, theoretical studies on nanostructured metal surfaces suggest that electromagnetic field effects contributing to SERS are highly localized in the regions between particles, implying that the SERS signals are due to the excitation of a very small number of molecules located within these interstitial sites [16].

The self-organized gold nanoparticle arrays are capable of detecting other organic analytes in the gas or solution phase, generate reproducible SERS intensities, and are stable in air and water at ambient temperatures. The nanostructured films can be transferred onto a variety of substrates, and may be useful for probing biological systems. Very recently, we have determined that the nanoparticle arrays can be used as substrates for live cells, suggesting their application as real-time sensors of biochemical transport [17]. Such features illustrate the opportunities that become available by the fabrication of nanostructured materials via self-assembly processes.

References

- (a) J. Israelachvili: *Intermolecular and Surface Forces*, 2nd edn, Academic Press, New York (1992). (b) D.F. Evans and H. Wennerström: *The Colloidal Domain: Where Physics, Chemistry, Biology, and Technology Meet*, 2nd edn, Wiley-VCH, New York (1999).
- (a) M. Kahl, E. Voges, S. Kostrewa, C. Viets and W. Hill: *Sens. Actuat. B* **51**, 285–291 (1998). (b) S. Hong, J. Zhu, C.A. Mirkin: *Science* **286**, 523–525 (1999). (c) G.-Y. Liu, S. Xu and Y. Qian: *Acc. Chem. Res.* **33**, 457–466 (2000).
- R.P. Andres, J.D. Bielefeld, J.I. Henderson, D.B. Janes, V.R. Kolagunta, C.P. Kubiak, W.J. Mahoney and R.G. Osifchin: *Science* **273**, 1690–1693 (1996).
- C.P. Collier, T. Vossmeier and J.R. Heath: *Annu. Rev. Phys. Chem.* **49**, 371–404 (1998).
- Metal nanoparticles possess planar facets which also increase with particle size such that the interactions are between planar rather than curved surfaces, contributing further to the van der Waals attraction.
- K.B. Stavens, S.V. Puzstay, S. Zou, R.P. Andres and A. Wei: *Langmuir* **15**, 8337–8339 (1999).
- (a) L.H. Dubois and R.G. Nuzzo: *Annu. Rev. Phys. Chem.* **43**, 437–463 (1992). (b) A. Badia, L. Cuccia, L. Demers, F. Morin and R.B. Lennox: *J. Am. Chem. Soc.* **119**, 2682–2692 (1997).
- A. Wei, K.B. Stavens, S.V. Puzstay and R.P. Andres: *Mater. Res. Soc. Symp. Proc. Ser.* **581**, 59–63 (1999).
- R. Balasubramanian, J. Xu, B. Kim, B. Sadtler and A. Wei: *J. Dispersion Sci. Tech.* **22**, 485–489 (2001).
- S.V. Puzstay, S.L. Tripp and A. Wei: Unpublished results.
- B. Kim, S.L. Tripp and A. Wei: *J. Am. Chem. Soc.* **123**, 7955–7956 (2001).
- (a) E.U.T. van Velzen, J.F.J. Engbersen, P.J. de Lange, J.W.G. Mahy and D.N. Reinhoudt: *J. Am. Chem. Soc.* **117**, 6853–6862 (1995). (b) W.C. Moreira, P.J. Dutton and R. Aroca: *Langmuir* **10**, 4148–4152 (1994).
- For a detailed investigation on the influence of interparticle spacing in the optoelectronic properties of metal nanoparticle arrays, see: (a) C.P. Collier, R.J. Saykally, J.J. Shiang, S.E. Henrichs and J.R. Heath: *Science* **277**, 1978–1981 (1997). (b) J.J. Shiang, J.R. Heath, C.P. Collier and R.J. Saykally: *J. Phys. Chem. B* **102**, 3425–3430 (1998).
- K. Kneipp, H. Kneipp, I. Itzkan, R.R. Dasari and M.S. Feld: *Chem. Rev.* **99**, 2957–2975 (1999).
- (a) A. Wei, B. Kim, B. Sadtler and S.L. Tripp: *Chem. Phys. Chem.* **2**, in press (2001). (b) B. Kim, S.L. Tripp and A. Wei: *Mater. Res. Soc. Symp. Proc. Ser.* **676**, in press (2001).
- (a) P.K. Aravind, A. Nitzan and H. Metiu: *Surface Sci.* **110**, 189–204 (1981). (b) N. Liver, A. Nitzan and J.I. Gersten: *Chem. Phys. Lett.* **111**, 449–454 (1984). (c) F.J. Garcia-Vidal and J.B. Pendry: *Phys. Rev. Lett.* **77**, 1163–1166 (1996). (d) H. Xu, J. Aizpurua, M. Käll and P. Apell: *Phys. Rev. E* **62**, 4318–4324 (2000).
- B. Kim and A. Wei: Unpublished results.