

## Letters

### Encapsulation of Neutral Gold Nanoclusters by Resorcinarenes

Kevin B. Stavens,<sup>†</sup> Stephen V. Pusztaý,<sup>‡</sup> Shouzhong Zou,<sup>‡</sup>  
Ronald P. Andres,<sup>\*,†</sup> and Alexander Wei<sup>\*,‡</sup>

Departments of Chemistry and Chemical Engineering, Purdue University,  
West Lafayette, Indiana 47907-1393

Received September 3, 1999

A new strategy for encapsulating neutral nanoclusters is presented which employs surfactants with large concave headgroups and multiple contact sites. Au nanoclusters ranging from 3 to 20 nm in diameter were generated in the vapor phase and dispersed into dilute solutions of resorcinarenes **1–3**, where they were stabilized for up to several months. The resorcinarenes were readily displaced by dodecanethiol, which resulted in the precipitation of the larger particles as determined by UV–vis absorption spectroscopy and transmission electron microscopy. The chemisorption of resorcinarenes to the Au cluster surface is most likely mediated by multiple Au–O interactions, which is supported by surface-enhanced Raman spectroscopy.

Nanometer-dimension inorganic clusters have generated enormous interest in recent years because of their size-dependent physical properties. Of particular interest are their tunable electronic, magnetic, and photonic behaviors due to quantum confinement effects, with nanocluster-based devices being envisioned as the next generation in electronics miniaturization.<sup>1</sup> Quantized electromagnetic phenomena are highly sensitive to perturbations arising from point-charge defects, so an important requisite for the fabrication of cluster-based nanodevices is the ability to stabilize and manipulate charge-neutral nanoclusters. One approach is to generate

aerosols of bare metal nanoclusters by gas-phase condensation of a pure metal vapor and then capture them in a neutral surfactant solution.<sup>2</sup> Chemisorptive surfactants such as the alkanethiols have been successful in stabilizing small (<10 nm) gold nanoparticles against agglomeration in hydrocarbon solutions; however, alkanethiol-passivated clusters over 10 nm in diameter do not exhibit long-term stability and precipitate at ambient temperatures.<sup>3</sup> This behavior is due largely to the rapid increase in the attractive van der Waals force between particles as a function of their size,<sup>4</sup> but entropic effects also play an important role. In the case of the alkanethiols

\* Corresponding authors. Address correspondence to: Prof. A. Wei, Department of Chemistry, 1393 Brown Building, Purdue University, West Lafayette, IN 47907-1393. Tel: (765) 494-5257. E-mail: alexwei@purdue.edu.

<sup>†</sup> Department of Chemical Engineering.

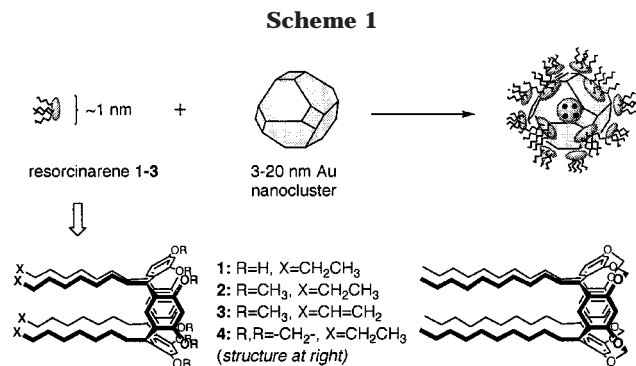
<sup>‡</sup> Department of Chemistry.

(1) (a) Andres, R. P.; et al. *Science* **1996**, *272*, 1323–25. (b) Andres, R. P.; et al. *Science* **1996**, *273*, 1690–93. (c) Service, R. F. *Science* **1996**, *271*, 920–22. (d) Alivisatos, A. P. *Science* **1996**, *271*, 933–37. (e) Klein, D. L.; et al. *Nature* **1997**, *389*, 699–701. (f) Feldheim, D. L.; Keating, C. D. *Chem. Soc. Rev.* **1998**, *27*, 1–12. (g) Smith, C. G. *Science* **1999**, *284*, 274.

(2) Chao, L. C.; Andres, R. P. *J. Colloid Interface Sci.* **1994**, *165*, 290–95.

(3) Osifchin found that alkanethiol-passivated gold clusters with diameters larger than ~7 nm do not form stable colloidal solutions in hydrocarbon solvents: Osifchin, R. G. PhD Thesis, Purdue University, 1994. The flocculation of alkanethiol-coated Au nanoclusters with diameters larger than 10 nm has also been studied in some detail as a function of surfactant: Weisbecker, C. S.; et al. *Langmuir* **1996**, *12*, 3763–72.

(4) Israelachvili, J. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: New York, 1992; Chapter 10.

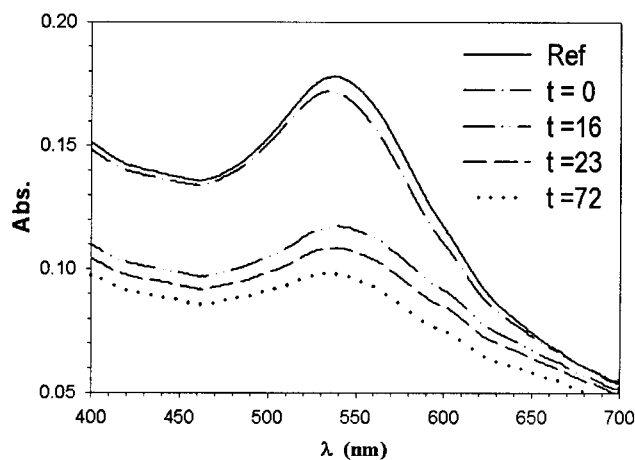


the small headgroups encourage a dense packing of the hydrocarbon chains, which tends to promote flocculation.

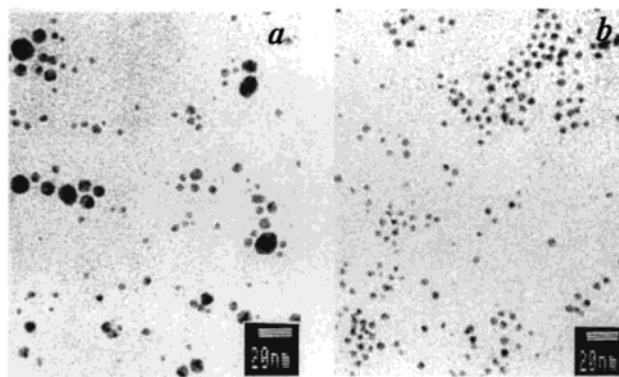
In this Letter we present a new strategy for nanocluster encapsulation and stabilization by using surfactants with larger headgroups and multiple contact sites for adsorption (see Scheme 1). This design confers several advantages: (i) multidentate binding of the surfactant to the nanocluster; (ii) a lower surfactant/particle ratio, reducing the entropic cost of self-assembly;<sup>5</sup> (iii) greater mobility of the pendant hydrocarbon tails, increasing the solubility of the encapsulated materials. We demonstrate this approach by capturing and stabilizing neutral gold nanoclusters of up to 20 nm in diameter with resorcinol-derived calix[4]-arenes (resorcinarenes).<sup>6</sup> The large, concave headgroups (ca. 1 nm diameter) are ideally suited for encapsulation on the multinanometer scale and allow the hydrocarbon chains sufficient mobility for maintaining high solubility.

Gold nanoclusters of controlled size ranges were generated as aerosols using a distributed arc cluster source (DACS)<sup>7</sup> and were bubbled directly into dilute (0.1–1.2 mM) solutions of resorcinarenes **1–3**<sup>8</sup> in mesitylene, which turned deeply purple. This encapsulation procedure was noteworthy in several respects. First, the resorcinarenes were several times more efficient at capturing nanoclusters than dodecanethiol (C12SH) at equimolar surfactant concentrations. At 520 nm, the characteristic Mie resonance for isolated gold particles, solutions of  $3.7 \pm 1.5$  nm Au clusters captured in 1.2 mM of **1** or **2** absorbed five to six times more strongly than solutions of clusters captured in 1.2 mM C12SH. Second, both large (>10 nm) and small (<10 nm) nanoclusters remained well dispersed in millimolar solutions of **1** and **2** at ambient temperature over a period of several months, with minimal loss of absorption intensity or precipitation. Third, 3–15 nm Au clusters stabilized by **3** gradually precipitated from solution when treated with 1 molar equiv of C12SH relative to **3**, as determined by UV–vis absorption spectroscopy (see Figure 1). Transmission electron micrographs of the solutions before and after C12SH addition strongly suggest that displacement of **3** by alkanethiol at the particle surface led to the precipitation of the larger clusters (see Figure 2). This underscores the resorcinarenes' exceptional ability to maintain the nanoclusters in a dispersed solution state.

Evidence for a specific mode of chemisorption is provided by surface-enhanced Raman spectroscopy (SERS), a powerful and highly sensitive method for characterizing monolayer adsorbates on noble metal particles.<sup>9</sup> Au



**Figure 1.** UV–vis absorption spectra of 3–15 nm Au nanoclusters dispersed into a 0.1 mM mesitylene solution of **3** (reference). Treatment with 1 molar equiv of dodecanethiol ( $t = 0–72$  h) resulted in a loss of absorbance over time.



**Figure 2.** Transmission electron micrographs (JEOL 2000 FX, 200 keV) of 3–15 nm Au nanoclusters generated as bare gold clusters in the DACS and dispersed in a 0.1 mM mesitylene solution of **3** before (a) and after (b) addition of dodecanethiol. Samples were obtained by casting a few drops of the solution on a carbon film TEM grid and allowing the solvent to evaporate.

clusters (15 nm) encapsulated by **2** were gently precipitated by addition of one volume of CH<sub>3</sub>CN to remove excess surfactant and then redissolved in mesitylene and drop-coated onto a glass surface. This substrate was observed to generate strong Raman signals, many of which were substantially different in frequency and/or intensity from those produced by polycrystalline samples of pure **2**<sup>10</sup> (see Figure 3a,c). Although we are presently unable to make an unambiguous assignment of all the group frequencies, there are two pieces of evidence which are strongly suggestive of a specific mode of chemisorption. First, several of the peaks in Figure 3a are significantly broadened, most notably those at 720 and 856 cm<sup>-1</sup> ( $\Delta\nu_{1/2} \sim 30$  cm<sup>-1</sup>). This broadening is commonly attributed to inhomogeneities due to chemisorption on different surface lattices or a decrease in vibrational excited-state lifetimes, both of which can strongly affect the bandwidths of the vibrational modes of surfactants which are directly adsorbed onto the metal surface.<sup>11</sup> Second, to compare the Raman signals in Figure 3a with those produced by **2** physisorbed nonspecifically to colloidal Au surfaces, charge (chloride)-stabilized 15–20 nm Au clusters were

(5) Whitesides, G. M.; et al. *Acc. Chem. Res.* **1995**, *28*, 37–44.

(6) Timmerman, P.; et al. *Tetrahedron* **1996**, *52*, 2663–704.

(7) Mahoney, W. J.; Andres, R. P. *Mater. Sci. Eng.* **1995**, *A204*, 160.

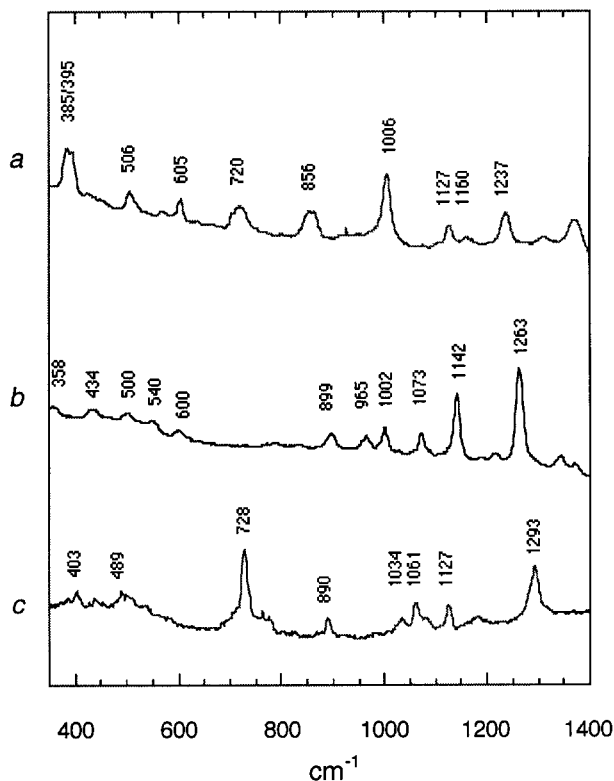
(8) (a) Aoyama, Y.; et al. *J. Am. Chem. Soc.* **1989**, *111*, 5397–404.

(b) van Velzen, E. U. T.; et al. *Synthesis* **1995**, 989–97.

(9) (a) Freeman, R. G.; et al. *Science* **1995**, *267*, 1629–32. (b) Freeman, R. G.; et al. *J. Phys. Chem.* **1996**, *100*, 718–24. (c) Vo-Dinh, T. *Trends Anal. Chem.* **1998**, *17*, 557–82.

(10) Amorphous thin films of **2** were also analyzed by Raman spectroscopy, but these failed to give reproducibly strong or well-defined signals.

(11) Weaver, M. J.; Zou, S. In *Advances in Spectroscopy 26*; John Wiley and Sons: Chichester, 1998; Chapter 5, and references therein.



**Figure 3.** Raman spectra (500 mW diode laser,  $\lambda=785$  nm, integration time=30 s) of resorcinarene **2** (a) adsorbed onto the surface of 15 nm Au nanoclusters; (b) as a thin film on top of charge-stabilized 15–20 nm Au nanoclusters; (c) in bulk polycrystalline phase.

precipitated onto a glass slide and coated with a thin film of **2**. This sample produced completely different Raman scattering frequencies and intensity patterns than those generated by the encapsulated nanoclusters (see Figure 3b).<sup>12</sup> These differences in Raman frequencies and intensities presumably arise from orientational effects during surface adsorption.<sup>13</sup>

(12) It is possible that the Raman signals in Figure 3b originate from adsorbates other than **2**. However, the precipitated Au colloid did not produce any strong signals at wavenumbers higher than 350  $\text{cm}^{-1}$  prior to addition of **2**.

Stabilization of the Au nanoclusters by the resorcinarenes is most likely mediated by chemisorption through multiple Au–O interactions, which is remarkable considering the relatively low affinity of oxygen for gold.<sup>14</sup> However, the eight oxygen atoms along the rim of the resorcinarene headgroup can adsorb to the Au surface in a cooperative fashion, in accordance with the now-classic concept of preorganization in supramolecular chemistry.<sup>15</sup> Further evidence for the importance of Au–O chemisorption is provided by the observation that tetra-*O*,*O*-methylene resorcinarene derivative **4**,<sup>8b</sup> whose oxygen lone pairs are prevented from chemisorbing cooperatively due to steric hindrance, completely failed to capture or stabilize Au nanoparticles.

Although resorcinarenes **1–3** have proven to be excellent stabilizing agents of Au nanoclusters in solution, removing excess surfactant or increasing solvent polarity leads to the rapid degradation of the resorcinarene-encapsulated material, suggesting facile chemical exchange. Appropriate modification of the resorcinarene headgroup is anticipated to increase the robustness of the encapsulation shell, so that charge-neutral nanoparticles can be isolated and characterized as discrete chemical entities. With this modification, encapsulation of neutral Au nanoclusters by resorcinarene-based surfactants will provide a significant advance in the controlled fabrication of nanometer-scale devices.

**Acknowledgment.** The authors gratefully acknowledge financial support from DARPA (DAAH04-96-1-0437: K.B.S., R.P.A.), the Purdue Research Foundation (fellowship to S.V.P.), and the Research Corporation Innovation Award program (RI-0333: A.W.) and acknowledge Professor Michael Weaver for helpful discussions and the use of his laser system.

LA9911786

(13) Gao, X.; et al. *J. Phys. Chem.* **1990**, *94*, 6858–64 and references therein.

(14) Masel, R. I. *Principles of Adsorption and Reaction on Solid Surfaces*; John Wiley and Sons: New York, 1996; Chapter 3.

(15) (a) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1039–1134. (b) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH Publishers: New York, 1995.