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Synthesis of nanometer-sized hollow polymer capsules from alkanethiol-coated gold particles

Minglang Wu, Stacy A. O'Neill, Louis C. Brousseau, Wyatt P. McConnell, David A. Shultz,* Russell J. Linderman* and Daniel L. Feldheim*

Department of Chemistry, North Carolina State University, Raleigh, NC 27695, USA.
E-mail: Dan_Feldheim@NCSU.edu; Russell_Linderman@NCSU.edu; David_Shultz@NCSU.edu

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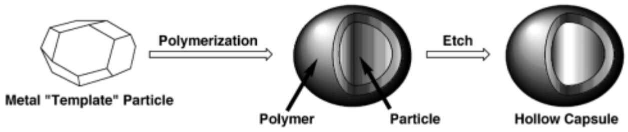
A tripodal alkythiolate ligand has been assembled on gold nanoparticles, which upon metathesis polymerization and particle etching, yields crosslinked spherical hollow polymer capsules.

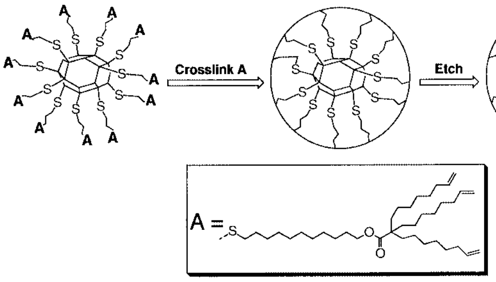
In previous reports, we have shown that gold particles are useful templates for the synthesis of hollow nanoscopic poly(pyrrole) and poly(*N*-methylpyrrole) capsules.[1] In that work, polymerization was initiated in an aqueous suspension of gold particles. Owing to the insolubility of pyrrole-based polymers in water, a polymer shell formed around the particle, which upon gold etching could be converted to a hollow capsule (Scheme 1). The hollow core volume and shell thickness were easily tuned *via* template diameter and polymerization time, respectively; guest entrapment within the host polymer capsule was demonstrated by attaching the guest to the gold particle prior to polymer formation and particle etching.



Scheme 1

Here, we demonstrate an alternative strategy for the formation of hollow polymer capsules. The strategy is similar to that reported by Mirkin and coworkers recently in which a surface-bound ω-substituted alkanethiol was polymerized to form polymer/gold composite particles.[2] In our work, the alkene-terminated tripodal ligand **A** was designed and synthesized in order to maximize polymer crosslinking. Crosslinking is important in forming structurally rigid hollow capsules following removal of the gold particle. Moreover, as demonstrated below, polymerization of **A** leaves alkene functionalities that may be further modified to manipulate the chemical properties of the resulting polymer capsule (Scheme 2).

The tripodal ligand was prepared in seven steps from 1-decen-1-ol and 11-bromo-1-undecanol.[3] Selective hydrolysis of the ester/thioacetate intermediate using methanolic potassium hydroxide in the presence of air gave high yields of the triene functionalized disulfide. Formation of triene functionalized thiol derivatized gold nanoparticles was then accomplished directly from the disulfide using procedures reported previously.[4] The thiol derivatized nanoparticle was purified by precipitation from toluene with ethanol–methanol followed by filtration. TEM images revealed spherical nanoparticles, *ca.* 5 nm in diameter. IR spectral analysis of the thiol-derivatized nanoparticle clearly indicated the presence of the ester at 1725 cm^{-1} (compared to 1731 cm^{-1} in the free ligand) and, as shown in Fig. 1(a), the terminal alkene CH bending modes at 908 cm^{-1} (compared to 908 cm^{-1} in the free ligand) and C=C stretching modes (1632 cm^{-1}) are observed. The free disulfide ligand exhibited a triplet in its ^1H NMR spectrum at δ 2.67 for the methylene protons adjacent to sulfur. However, upon complexation to the gold nanoparticle, the signal at δ 2.67 was no longer observed, as expected.[4b] As shown in Fig. 2(a), the terminal alkene protons were observed in the ^1H NMR spectrum of the thiol derivatized nanoparticle as very broad multiplets



Scheme 2

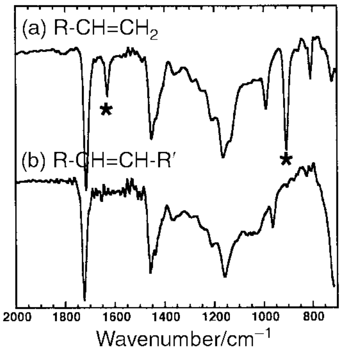


Fig. 1 (a) IR spectrum (neat film) of alkene-terminated thiol-derivatized gold nanoparticles. * Indicates terminal C=C stretching and alkene CH bending modes. (b) IR spectrum (neat film) of thiol-derivatized nanoparticles after reaction with Grubbs catalyst. Note lack of terminal C=C stretching and alkene CH bending modes, while other spectral features remain intact.

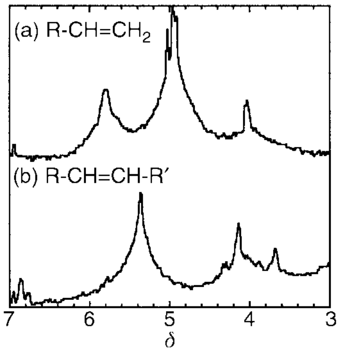


Fig. 2 (a) ^1H NMR spectrum (alkene region) of alkene-terminated thiol-derivatized gold nanoparticles. Alkene resonances appear as broad signals at δ *ca.* 4.9 and 5.9. (b) ^1H NMR spectrum (alkene region) of thiol-derivatized nanoparticles after reaction with Grubbs catalyst. Note new alkene resonances at δ *ca.* 5.3.

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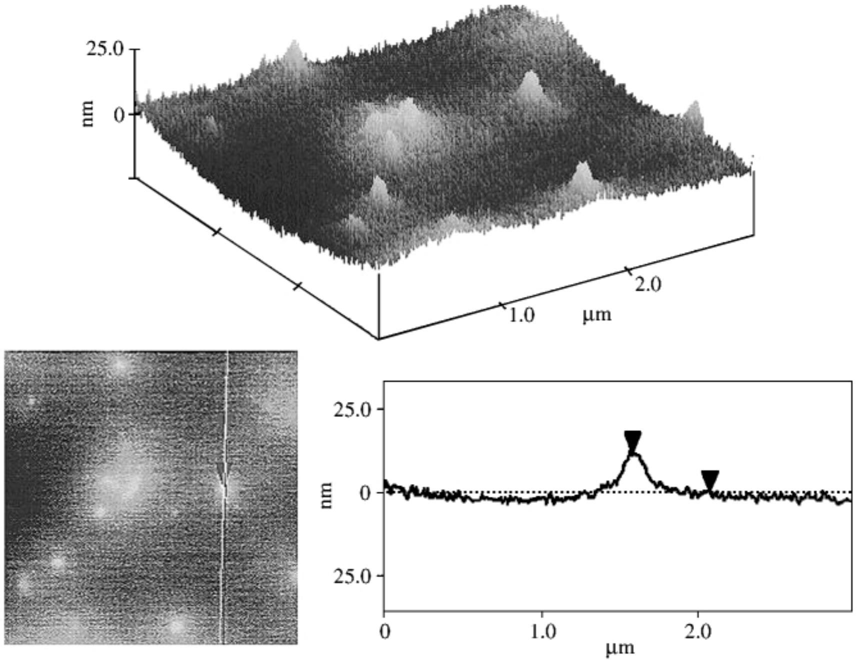

Fig. 3 Atomic force images of hollow polymer capsules. See text for details.

centered at δ *ca.* 5.9 and 4.9 which corresponded very well with the chemical shifts observed in the free triene ligand.

Metathesis of the thiol derivatized nanoparticles was then carried out using *ca.* 7 mol% of Grubbs catalyst[5] per alkene in benzene at room temp. Precipitation of the product from benzene by the addition of ethanol provided a purple waxy solid. The assumption that intramolecular polymerization to form a highly crosslinked polymeric surface occurred is strongly supported by the spectral data of the polymerized nanoparticles. As shown in Fig. 1(b), the IR spectrum shows a lack of *both* the C=C terminal alkene stretches at 1632 cm^{-1} and the alkene CH bending modes at 908 cm^{-1} for the polymerized particles. The changes in the IR spectrum are paralleled by the changes in the ^1H NMR spectrum: the signals for the terminal alkene protons collapsed to a single broad peak at δ *ca.* 5.3, as shown in Fig. 2(b). The signals for the terminal alkene protons collapsed to a single broad peak at δ 5.4.

Removal of the gold from the thiol derivatized particles under the same conditions used for the polypyrrole capsules [0.1 M KCN, 0.002 M $K_3Fe_2(CN)_3$] was not possible. However, sonication of a THF–water solution of KCN, $K_3Fe_2(CN)_3$ and the particles produced a change from purple to brown, indicative of particle etching. Treatment of the brown particles with hydrogen peroxide was necessary to effect complete removal of the gold. ^1H NMR spectra of the hollow polymerized tripodal ligand also indicated the absence of gold by virtue of the now sharp and well defined spectrum.[4b] Treatment of the nanoparticles with hydrogen peroxide efficiently oxidized the polyalkene particle to a polyol particle as evidenced by signals in the range δ 3.6–4.2 in the ^1H NMR spectra.

The fate of the sulfur atoms in the linker is unclear from the data in hand although it is very likely that the sulfur has been oxidized along with the alkenes. In addition, the internal ester linkage may have been partially cleaved. IR data shows hydroxy groups at 3350 cm^{-1}, and a significantly diminished CO stretch at 1723 cm^{-1}.

Atomic force microscopy confirmed that the structural integrity of the polymer capsules was maintained following gold dissolution (Fig. 3).[6] Qualitatively, AFM revealed the presence of spherical capsules, which were relatively impressible compared to gold particles or hollow polypyrrole capsules. Quantitatively, the dimensions of the capsules were 10.47 ± 2.54 nm based on the relative height of 25 capsules. This value agrees well with the diameter expected based on the size of the template gold particle (*ca.* 5 nm) and the length of alkythiol spacer.

In summary, a method has been described for converting alkylthiolate monolayers on gold particles into hollow polymer capsules. The synthetic design of the tripodal ligand provides the potential to ultimately control the functionality present on the surface of the particle as well as that present internally.

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Notes and references

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6 AFM samples were prepared by drop casting a THF solution of capsules onto a freshly cleaned gold-coated glass slide and allowing the solvent to evaporate. Gold substrates were cleaned by dipping in H_2SO_4–H_2O_2 (3 : 1) for *ca.* 2 min followed by sonication in deionized H_2O.