

Hybrid Nanoparticles with Block Copolymer Shell Structures

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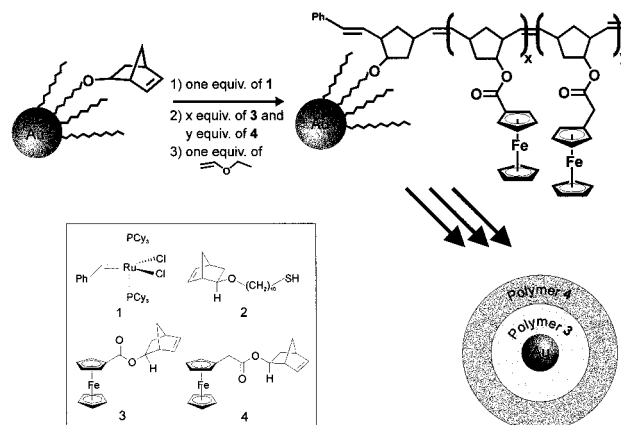
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In recent years, there has been considerable interest in developing methods for assembling nanoscale building blocks into periodic, functional materials.¹ These methods rely on access to both novel building block compositions and assembly strategies. With regard to the former, both inorganic and organic compositions are now available. Importantly, some of these building blocks are accessible in macroscopic quantities and in monodisperse form. For example, a variety of methods exist for preparing monodisperse samples of CdS,² CdSe,² and Au³ particles with diameters ranging from 1 to 40 nm. Studies involving these well-defined inorganic particles have led to not only a greater understanding of quantum confinement effects but also the development of new and useful spectroscopic methods⁴ and detection technologies.⁵ Similarly, a great deal has been learned from the synthesis, characterization, and study of polymer particle compositions.⁶ However, far less is known about such systems with nanoscale dimensions (<100 nm). The development of synthetic methods for preparing structures consisting of inorganic cores and organic polymer shells on this length scale could give entry into a new and versatile class of hybrid metal–organic nanoparticle building blocks. Herein, we wish to report the use of transition-metal-catalyzed ring-opening metathesis polymerization (ROMP) and surface-functionalized gold nanoparticles (GNPs) for the preparation of a new class of nanoparticles with chemically tailorable shell properties (Scheme 1).

Our method takes advantage of several recent advances in both polymer chemistry and materials synthesis. Specifically, it relies on the recent development of a family of functional-group-tolerant ruthenium carbene catalysts for ROMP, such as Cl₂Ru(PCy₃)₂-CHPh, **1**.⁷ It also draws on new synthetic methods for preparing 3 (±1)-nm-diameter GNPs, which are soluble in organic media.⁸ Furthermore, in immobilizing the norbornenyl initiation sites on the surface, we have taken advantage of well-established chemistry

Scheme 1



involving alkanethiol adsorption on gold.⁹ These immobilized norbornenyl groups allow one to selectively grow polymer blocks off the surface of a GNP with a surface-immobilized ROMP catalyst. Since this is a living polymerization process,⁷ the attributes of this strategy are numerous, including exceptional control over polymer length and chemical composition as well as particle size, solubility, and shape.

There are two key steps in the synthesis of metathesis-ready GNPs. The first involves the synthesis and characterization of 1-mercapto-10-(*exo*-5-norbornene-2-oxy)decane, **2** (Supporting Information), which contains a ROMP-active norbornene segment attached to a long-chain alkanethiol. The *exo*- rather than the *endo*-isomer was chosen to optimize ROMP activity.¹⁰ The second step involves immobilization of **2** on 3-nm Au particles. Here, we modified the method of Schiffrin et al.⁸ for preparing GNPs capped with linear alkanethiols by reducing HAuCl₄ (2.24 mmol) in the presence of a 3:1 mixture of 1-dodecanethiol (1.68 mmol) and **2** (0.56 mmol) to yield GNPs modified with the two adsorbates. The dodecanethiol diluent molecule was employed to minimize surface cross-linking of norbornenyl groups and propagating polymer. The ¹H NMR spectrum of the modified particles in CDCl₃ confirms that the norbornene adsorbates are, indeed, attached to their surfaces (Figure 1A,B). The two resonances at approximately δ 5.9 and 6.2 are highly diagnostic of the two norbornenyl olefinic protons and compare well with those observed in the ¹H NMR spectrum of **2** (δ 5.9 and 6.2) in CDCl₃.

Metathesis of the norbornene rings on the GNPs with catalyst **1** (1 equiv)¹² is achieved in less than 10 min in CDCl₃. Evidence for this activation process is the loss of the olefinic resonances at δ 5.9 and 6.2 (Figure 1C). Subsequent addition of 20 equiv of the redox-active complex **3** to this solution leads to polymerization of **3**, as evidenced by the appearance of broad resonances at δ 5.7–5.2 in the ¹H NMR spectrum of the particle–polymer hybrids (GNP–poly₃) (Figure 1D). These resonances are characteristic of polymers synthesized from norbornenyl-containing starting

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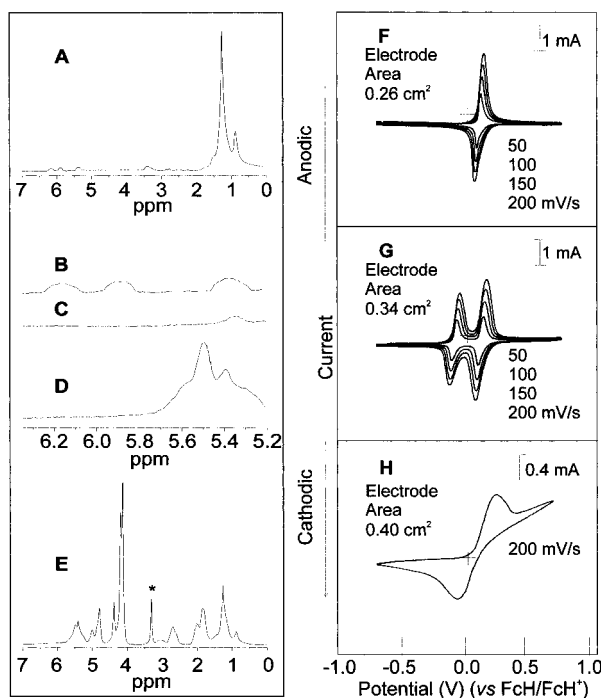


Figure 1. ^1H NMR spectrum (line broadening = 1 Hz) of (A) GNPs functionalized with a 3:1 mixture of 1-dodecanethiol and **2** (δ 7 to 0 ppm), (B) GNPs functionalized with a 3:1 mixture of 1-dodecanethiol and **2** (δ 6.3 to 5.2 ppm), (C) **2**-modified GNPs after treatment with 1 equiv of **1** (δ 6.3 to 5.2 ppm), (D) **2**-modified GNPs after the addition of 20 equiv of **3** to the ROMP-activated GNPs (δ 6.3 to 5.2 ppm), and (E) the GNP-poly**3**-poly**4** hybrid system (δ 7 to 0 ppm). Cyclic voltammetry of (F) the GNP-poly**3** system, (G) the GNP-poly**3**-poly**4** hybrid, and (H) poly**3**.

materials.⁷ After 30 min, there is no evidence of monomer **3**, indicating that polymerization is complete. The polymers can be terminated irreversibly by the addition of a slight excess of ethyl vinyl ether, a known ROMP termination agent for catalysts such as **1**.¹¹ Significantly, the particles treated in this manner can be precipitated from CDCl_3 with *hexanes*, a solvent in which the **2**-modified GNPs are completely redispersible. The GNP-poly**3** hybrids can be redispersed in a variety of more polar organic solvents such as CH_2Cl_2 and THF. These solubility properties mirror those of the untethered ferrocenyl homopolymer, which was independently synthesized from **1** and **3** under nearly identical conditions (poly**3**, Supporting Information). As a control experiment, a solution consisting of the untethered ferrocenyl-containing poly**3** and the **2**-modified GNPs in a ratio comparable to that used for the GNP-poly**3** experiment was prepared. When a precipitation experiment was carried out for this control system, the **2**-modified GNPs remained soluble in hexanes (as evidenced by ^1H NMR spectroscopy), while the homopolymer precipitated as expected. The difference in solubility between the **2**-modified GNPs and the GNP-poly**3** hybrids is strong evidence that the polymers formed via surface polymerization are, indeed, tethered to the surfaces of the GNPs.

As a further demonstration of the generality and scope of our strategy for preparing hybrid nanoparticles, block copolymers of two different norbornenyl ferrocenyl derivatives, **3** and **4**, were grown successively from the surfaces of **2**-modified particles treated with catalyst **1**. In this experiment, after the activation of the particles with **1** (1 equiv),¹² 20 equiv of **3** was syringed into the solution and allowed to react with the GNPs for 20 min. That was followed by the addition of 20 equiv of **4** with subsequent stirring for 20 min (Scheme 1). Compound **4** was chosen as the second polymer building block because it can be easily differentiated from **3** by cyclic voltammetry. The methylene group located between the carbonyl and the ferrocenyl moiety in **4** makes it

approximately 220 mV easier to oxidize than **3**. Moreover, this methylene group provides a spectroscopic tag that allows one to follow the polymerization reaction by ^1H NMR spectroscopy (Figure 1E, note the asterisked resonance). The growth of the broad resonance at δ 3.3, coupled with the complete loss of resonances associated with the starting monomer **4**, indicates complete conversion of **4** to a block of poly**4** onto the GNP-poly**3** particles (i.e., GNP-poly**3**-poly**4**). The living catalyst can be quenched with ethyl vinyl ether and the GNP-poly**3**-poly**4** hybrids isolated as described for the GNP-poly**3** system above.¹³

Cyclic voltammetry of the GNP-poly**3** hybrids cast onto the surface of an Au/Si electrode in 0.1 M TBAPF₆/CH₃CN exhibits a reversible wave associated with ferrocenyl oxidation/reduction at 180 mV vs FcH/FcH⁺ (Figure 1F). The GNP-poly**3**-poly**4** system also exhibits reversible electrochemistry, with the expected two distinguishable waves associated with oxidation/reduction of the two different types of ferrocenyl moieties within the particle-immobilized block copolymer shell ($E_{1/2s} = -40$ mV for the block of poly**4** and 180 mV for the block of poly**3** vs FcH/FcH⁺) (Figure 1G). A comparison of the integrated current associated with these two waves allows one to evaluate the relative amounts of **3** and **4** in the GNP-poly**3**-poly**4** structure. Based on this analysis, we calculate a 1.4:1 ratio for **3** and **4** in the block copolymer.¹⁴ The ideal response associated with these waves¹⁵ and the lack of evidence for mediated electron transfer between the interior block of **3** and the electrode surface indicates that, in these structures, both polymer blocks are accessible to the electrode surface and solvated to the extent that ions can move in and out of the block copolymer structure. Significantly, both the homopolymers and the block copolymers formed from the polymerization of **3** and **4** exhibit broad waves characteristic of sluggish electron transfer and poor polymer solvation (Figure 1H, poly**3** is given as an example). Taken together, all of the data presented herein unambiguously confirm that the polymers grown off the surfaces of the GNPs remain attached to the particle surfaces. Finally, TEM analysis of the GNP-poly**3** hybrids and GNP-poly**3**-poly**4** hybrids indicates that the hybrid particles maintain their 3 ± 1 -nm-diameter Au cores.

These results indicate that the particle synthesis strategy reported herein can be used to prepare a new class of nanoparticles that can be functionalized with polymeric layers of virtually any norbornenyl-containing monomer. Indeed, the strategy could be easily extended to other inorganic nanoparticle templates as well as optically active or electroactive norbornenyl groups. Traditional inorganic nanoparticles already have become the basis for many useful probe-type applications.^{1,4,5} The hybrid structures presented herein, with their high degree of synthetic tunability, are likely to become equally or even more important as diagnostic probes in chemical and biochemical detection strategies. Moreover, they are a new and versatile type of building block that chemists and material scientists can easily incorporate into many existing particle assembly strategies.

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Supporting Information Available: General experimental details, details of the synthesis and characterization of **2**-**4**, details of the synthesis of GNP-poly**3** and poly**3**, and TEM images (Figure S-1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) Elemental analysis performed on GNP-poly**3**-poly**4**. Calcd: C, 55.0; H, 5.1. Found: C, 54.95; H, 5.4.

(14) The reason that this is not a 1:1 ratio may be that there are small differences in polymer solvation and, therefore, different degrees of electrochemical accessibility for the two layers or, alternatively, that there is a stoichiometry error due to the small amount of reagents used.

(15) The peak current is linearly dependent upon the scan rate.