# Redox-active polymer-nanoparticle hybrid materials*

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*Abstract*: Ring-opening metathesis polymerization was used to modify organic soluble gold nanoparticles with redox-active polymers. A gel-permeation chromatography study revealed that each nanoparticle is modified with approximately 11 polymer chains. Electrochemical studies of nanoparticles modified with block copolymers of two different redox-active groups revealed that each monomer is electrochemically accessible, while no current rectification was observed.

## INTRODUCTION

There has been considerable recent interest in preparing materials with periodicity at the nanometer scale [1,2]. Such materials have found numerous applications, ranging from novel spectroscopic methods to new detection technologies [3–7]. Many methods have now been developed for the preparation of monodisperse nanoparticles of CdS, CdSe, and Au [8–10]. Similarly, many researchers have described the synthesis and characterization of nanoparticle-polymer composite materials [11–16]. The development of controlled, templated polymer growth from the surface of nanoparticles is a powerful new approach to the preparation of hybrid inorganic-organic nanoparticles with chemically tailorable physical properties. Such hybrid materials are going to open up a variety of new fundamental and device applications in the fields of catalysis, molecular diagnostics, and interfacial electron transfer.

Specifically, polymers can be used to modify the nanoparticles and yield hybrid materials with a desirable combination of properties that are not easily achieved by other means. Because polymers can be readily made in large quantities and with numerous functionalities, they are uniquely versatile modifiers for nanoparticles. For example, the solubility properties of the resulting hybrids depend greatly on those of the polymer modifier, allowing for synthetic programmability of this important parameter. Furthermore, the ability to control the growth of the polymer chains in a living fashion allows chemists to fabricate monodisperse, structurally precise nanocomposites for further study.

Recently, we reported on the successful growth of polymers directly from the surface of nanoparticle templates [17]. Shortly thereafter, others reported similar and complementary methods for the preparation of such materials [18,19]. Our methodology was based on two recent developments as depicted in Fig. 1: First, we relied on the work of Brust *et al.* for the synthesis of organic soluble gold nanoparticles on the 2–3 nanometer scale [20]. Second, we built upon the recent developments in the field of ring-opening metathesis polymerization (ROMP), a powerful strategy for the synthesis of monodisperse polymers and block copolymers [21–23]. Specifically, norbornenyl-modified compounds are useful monomers in ROMP due to the high ring strain of the norbornenyl group and the wide variety of readily accessible norbornene monomers with differing functionalities. Furthermore, the Grubbs' catalyst **1** has quickly become the standard initiator for this reaction due to its high activity and robust functional-
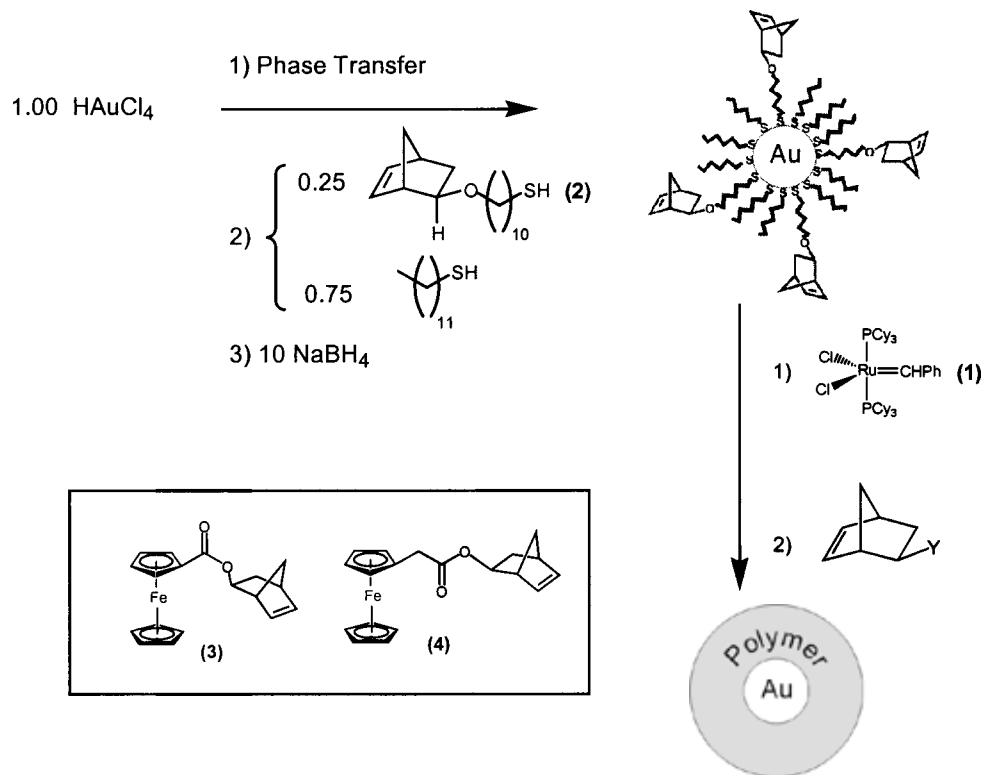
**Fig. 1** The synthesis of gold nanoparticle-polymer hybrid materials.

group tolerance. A linkage between nanoparticle chemistry and ROMP was initiated with the synthesis of 1-mercapto-10-(*exo*-5-norbornen-2-oxy)-decane, **2**, a norbornenyl-modified alkane thiol. Attachment of this molecule to the surface of gold nanoparticles, followed by the treatment of the **2**-modified nanoparticles with **1**, allowed for the controlled polymerization of the redox-active norbornene monomers **3** and **4** to yield the desired hybrid materials. In this report, we supplement our earlier study of this system by discussing new results on the characterization of the size of the hybrid materials. A further study of the redox chemistry of nanoparticles modified with block copolymers of **3** and **4** is also presented.

## RESULTS AND DISCUSSION

In our first experiment, the **2**-modified nanoparticles [17] were activated with **1**. Next, 20 equiv of **3** were injected into the reaction mixture and allowed to polymerize on the surface, yielding **GNP-poly3**, an apparently monodisperse metal-core/polymer-shell structure. Perhaps the best evidence for the proposed structure of these materials was provided by gel-permeation chromatography (GPC, see Fig. 2). Others have used GPC to characterize latex [18] and gold [24] nanoparticles. In the former, latex particles modified with polymers were characterized, while in the latter, gold nanoparticles modified with alkane thiol monolayers were studied. The gel-permeation chromatogram of the **2**-modified GNPs showed one relatively narrow peak consistent with an average molecular weight ($M_n$) of 8 000 (versus polystyrene standards). Injection of the **GNP-poly3** hybrid likewise resulted in one narrow peak, but this peak was shifted to a *higher* $M_n$ of 74 000. This difference in molecular weight corresponds to
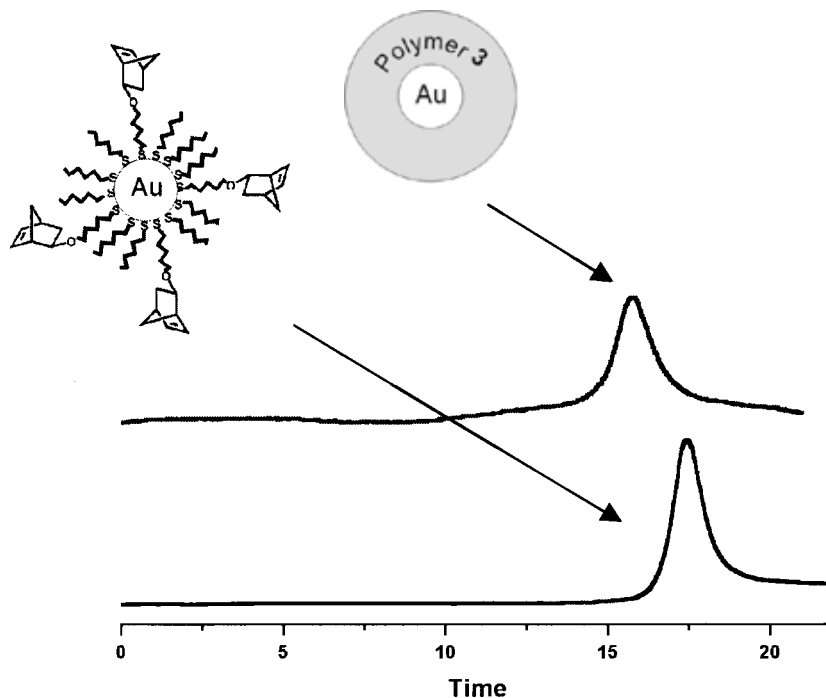
**Fig. 2** GPC analysis of **GNP-poly3** and the **2**-modified gold nanoparticles (solvent= THF, column dimensions = 30 cm × 7.5 mm × 3/8 in (length × I.D. × O.D), flow rate = 1.0 mL per min).

approximately 11 polymer strands per particle. We arrive at this number with the assumption that the polymer chains consist of 20 units of **3** and that a direct correlation exists between the standards and our structures. This result is quite consistent with other data obtained for this system, such as elemental analysis and ^{1}H NMR spectroscopy. The most important information extracted from the GPC is that there is a single peak with a larger $M_n$ compared to the starting material, signaling the presence of only one type of macromolecular material.

We next turned our attention to the synthesis of block copolymers of **3** and **4** directly from the surface of the gold nanoparticles. Because of the methylene spacer group separating the carbonyl group of **4** from the ferrocene ring, **4** is approximately 220 mV easier to oxidize than is **3** [17]. In these experiments, the activated nanoparticles were treated with 20 equiv of one monomer, followed by the injection of 20 equiv of the second monomer. The isolated materials, either **GNP-poly3-poly4** or **GNP-poly4-poly3**, contain polymers with well-defined blocks. Since the second monomer is not injected until consumption of the first is complete, the polymer structure is of the form AA••AAABBB••BB. Given this structure, we theorized that current rectification should occur in **GNP-poly4-poly3** if the polymer chains are rigid and that no interaction exists between the inner **poly4** block and the electrode surface (Fig. 3). Furthermore, only the redox wave associated with the oxidation and reduction of **4** should be obtained in the **GNP-poly3-poly4** case, since the interior block of **poly3** would not be accessible to the electrode. However, as depicted in Fig. 4, the electrochemical response from **GNP-poly4-poly3**, when cast upon a gold electrode, was essentially identical to the response received from **GNP-poly3-poly4** under similar conditions. In both cases, a completely reversible redox wave associated with both **3** and **4** were obtained, indicating 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 polymer structure. This is not surprising, considering the well-known flexibility of norbornene polymer chains. We are
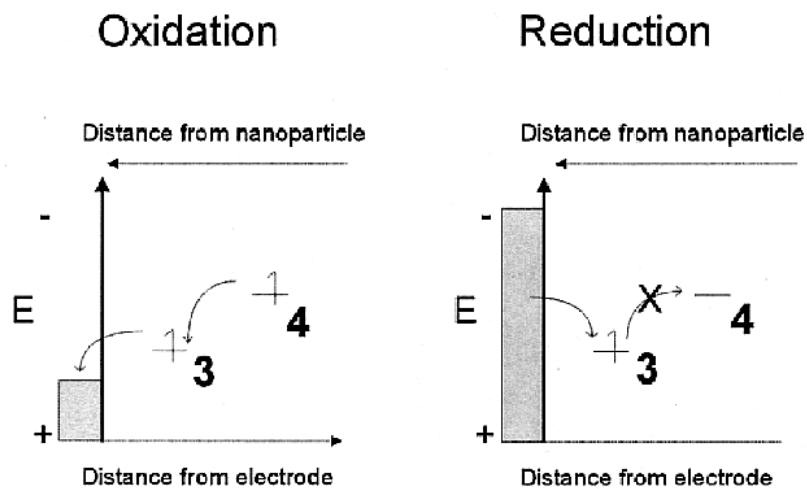
## Oxidation

Distance from nanoparticle

E

4

3

Distance from electrode

## Reduction

Distance from nanoparticle

E

X →

3      4

**Fig. 3** Predicted current rectification for the **GNP-poly4-poly3** structure.

Polymer 4

Polymer 3

Au

Polymer 3

Polymer 4

Au

|1 mA

|50 *u*A

0.0    0.5    1.0    1.5

**Potential (V) (*vs* Ag wire)**

0.0    0.5    1.0    1.5

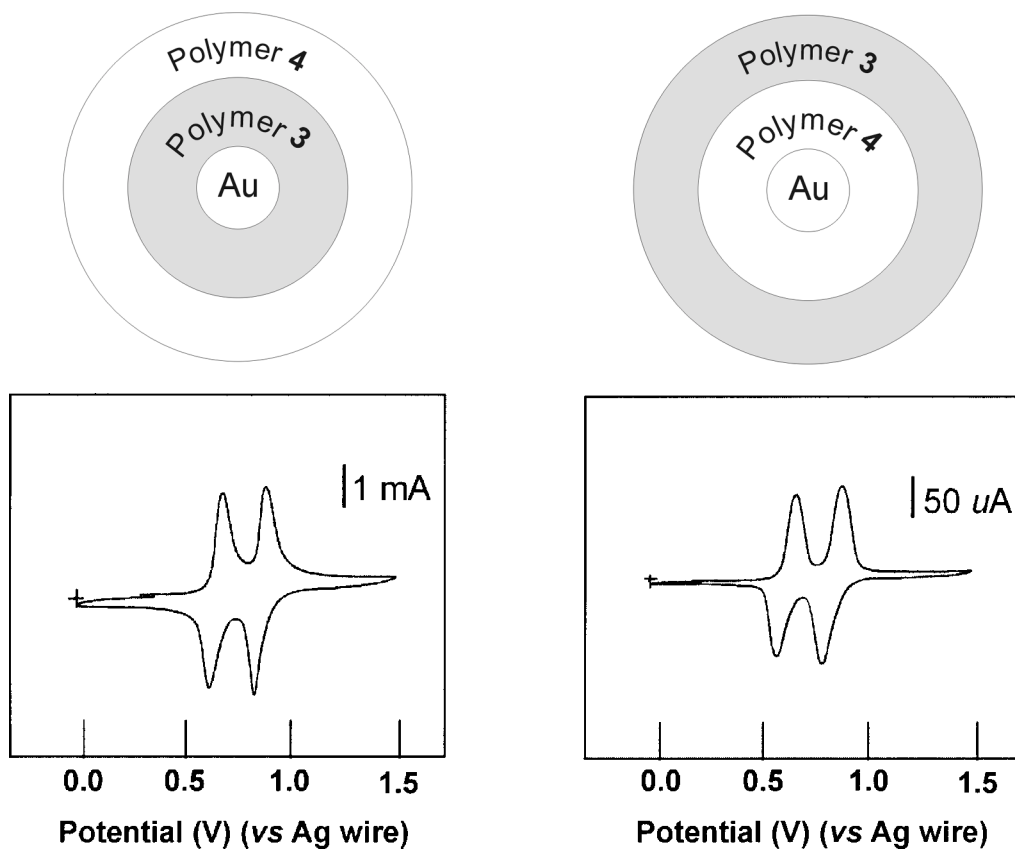**Potential (V) (*vs* Ag wire)**

**Fig. 4** Cyclic voltamagram of **GNP-poly3-poly4** and **GNP-poly4-poly3**. The scans were carried out in 0.1 M TBAPF$_6$/CH$_3$CN at a scan rate of 200 mV/s using a Au electrode, a Pt counter electrode, and a Ag reference electrode.

currently preparing a series of **GNP-poly3-poly4** and **GNP-poly4-poly3** with varying block lengths to determine how adjusting this parameter will change the electrochemical response of the hybrid materials.

## CONCLUSIONS

To summarize, GPC studies of gold nanoparticle-polymer hybrids revealed that, on average, each nanoparticle was functionalized with 11 polymer strands. Regardless of whether the nanoparticle was functionalized first with a block of **3** and then **4** or vice versa, the same electrochemical response was obtained from the material when it was cast onto an Au electrode. This behavior indicates that both polymer blocks are accessible to the electrode. Further fundamental studies such as those presented herein will allow for the optimization of the value of these novel materials with respect to both fundamental and device applications. Moreover, the degree of synthetic tunability in these systems increases with each new ROMP development, allowing for the isolation of heretofore unattainable hybrid materials.

## ACKNOWLEDGMENTS

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