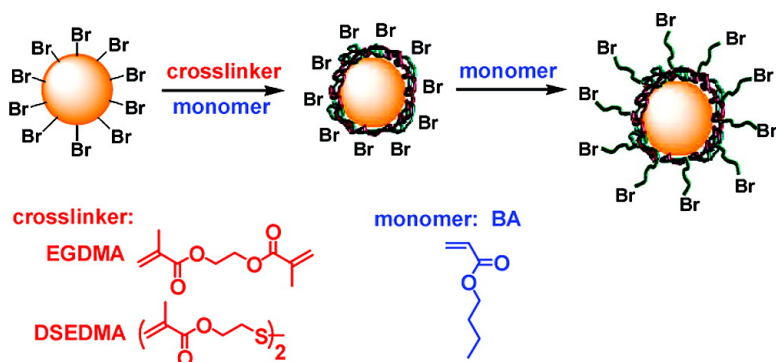


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One-Pot Synthesis of Robust Core/Shell Gold Nanoparticles

Hongchen Dong, Manzhou Zhu, Jeong Ae Yoon, Haifeng Gao, Rongchao Jin, and Krzysztof Matyjaszewski*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received May 21, 2008; E-mail: km3b@andrew.cmu.edu

Thiol stabilized gold nanoparticles (Au-NPs) have attracted significant research interest in recent years due to their great potential in diverse fields such as nanoelectronics, nanooptics, catalysis, biology, and biomedicine.¹ A polymer stabilized shell around the Au-NPs is additionally attractive due to versatile composition and functionalities of polymers. "Grafting-onto" method and "grafting-from" method have been extensively applied to attach polymers to the Au-NP surface. Especially the latter method, via surface-initiated controlled radical polymerization, provides a robust procedure to readily tune the grafting density and length of the surface-tethered polymer brushes.² Until now, most of the surface polymers are bound to Au-NPs via weak Au-S bonds, whose low bond dissociation energy (~40 kcal/mol)³ significantly hampers the stability of the surface-tethered polymer layers on the Au-NPs, especially at higher temperature (>60 °C).⁴ Therefore, most of the surface-initiated polymerizations were performed at ambient temperature to avoid the Au-S bond cleavage, which consequently limits the choices of applicable monomers. The stability of the Au-S bonding could be improved through the introduction of multiple thiol-anchoring groups at the polymer chain ends and/or shell cross-linking of polymeric micelles encapsulating Au-NPs. However, these methods suffer from some limitations and require multiple-step organic synthesis.⁵ Magnetic nanoparticles could also be stabilized by introducing cross-linked polymer shells, although the cross-linked shell without dangling hairs limited the dispersability of the nanoparticles.⁶

In this communication, we report a simple and general strategy for preparing robust Au-NPs through a one-pot synthesis of a cross-linked shell and linear tethered polymer brushes from the Au-NP surface. The introduction of dual protecting polymer layers, i.e. an inner cross-linked shell and outer linear polymer brushes grafted from the inner shell, effectively stabilized the core/shell Au-NPs under harsh conditions, such as elevated temperatures because the cross-linked polymer shell prevented the dissociation of linear polymers from the nanoparticles (Scheme 1). The one-pot synthetic method was achieved based on surface-initiated atom transfer radical polymerization (ATRP)⁷ of a monomer and a cross-linker, which significantly enhanced the stability of the gold/polymer nanocomposite and expanded its applications to many fields, where an adequate tolerance to high temperature is essential.

The basic concept of this one-pot synthesis of the gold/polymer nanocomposite is to form a thin cross-linked polymer shell around the surface of each Au-NP before the growth of linear polymer brushes from the shell. To accomplish such a requirement, a two-step monomer addition procedure was applied, in which all of the cross-linker and a small portion of the vinyl monomer were added at the beginning and a second batch of monomer was added at the high cross-linker conversion. A monomer/cross-linker pair with unequal reactivities was selected for the surface-initiated copolymerization, in which the reactivity of the monomer, *n*-butyl acrylate (BA, $r_{BA} = 0.3$), is much lower than that of the dimethacrylate

Scheme 1. One-Pot Synthesis of Robust Core/Shell Gold Nanoparticles Stabilized with Cross-Linked Shell and Well-Defined Tethered Polymer Brush



Table 1. Copolymerization of BA (M) and Cross-linker (X) with Two-Step Monomer Addition on Surfaces of NPs^{a,d}

entry	I/X/BA ^{first} /BA ^{second}	conv. (%) before BA ^{second} addition ^b	conv. (%) after BA ^{second} addition ^b	X mol % in cross-linked shell/ linear chain ^c
1 ^c	1/10/100/900 (at 28 h)	68.0(X)/ 24.0(M)	77.0(X)/ 8.6(M)	22.1/1.2
2 ^c	1/10/100/900 (at 39 h)	58.4(X)/ 18.4(M)	71.3(X)/ 7.0(M)	24.1/2.0
3 ^c	1/10/100/3000 (at 24 h)	100.0(X)/ 66.6(M)	100.0(X)/ 6.0(M)	13.1/0
4	1/0/3000/0	6.9(M)	—	—

^a Entries 1 and 2 were carried out with initiator-modified silica NPs ($D \sim 20$ nm), entries 3 and 4 with initiator-modified Au-NPs ($D \sim 5$ nm). NP-Br (I)/CuBr/CuBr₂/PMDETA = 1:4:0.2:4.2 at 65 °C in anisole. BA^{first}: first addition of BA. BA^{second}: second addition of BA. ^b Determined by ¹H NMR in CDCl₃. ^c Calculated from BA and X conversions. ^d The cross-linker was EGDMA in entries 1 and 3, and DSEDMA in entry 2.

cross-linker ($r_{MA} = 2.2$, MA: methacrylate).⁸ Therefore, the cross-linker was consumed faster than the monomer and was preferentially incorporated into the cross-linked shell. The subsequent polymerization of the remaining BA monomer formed the linear hairy brush layer. In addition, the concentration of the nanoparticles was kept low (1.7–7.2 mg/mL) to prevent interparticle coupling reactions.

First, the ATRP from initiator-modified silica particles (~20 nm diameter) was used as a model for the Au-NP system to explore optimal reaction conditions. In Table 1, entry 1, the molar ratio of BA to ethylene glycol dimethacrylate (EGDMA) was 10 at the beginning of polymerization. The consumption of EGDMA was ~4 times faster than that of BA (Figure S1 in SI). After 28 h, the conversion of EGDMA reached 68%, when a second large portion of BA was injected into the reaction solution. According to the monomer and cross-linker conversions determined by ¹H NMR, the cross-linked polymer shell contained 22.1 mol% of EGDMA units and 77.9 mol% of BA units, where the linear polymer chain was composed of 98.8 mol% of BA and only 1.2 mol% of EGDMA. After removal of silica particles by HF etching, the GPC trace of the detached polymer layer showed two peaks. One has $M_n = 1.89 \times 10^6$ g/mol, corresponding to the entire cross-linked polymer layer

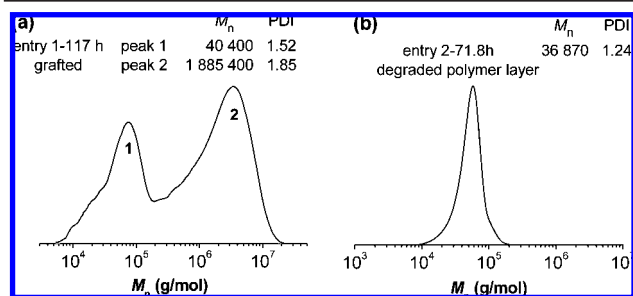


Figure 1. GPC traces of (a) the grafted polymer layer in Table 1, entry 1 and (b) the degraded grafted polymer layer in Table 1, entry 2.

tethered with linear PBA chains, and the other has $M_n = 40\,400$ g/mol, corresponding to the dangling noncross-linked chain (Figure 1a).

To further investigate the polymer layer structure, a degradable cross-linker, bis(2-methacryloyloxyethyl) disulfide (DSEDMA), was used for copolymerization with BA (Table 1, entry 2) under similar conditions as those in entry 1. The cross-linked polymer shell was degraded by tri-*n*-butylphosphine. The individual polymer chains had a similar molecular weight ($M_n = 36\,900$ g/mol) to that of dangling non-cross-linked chains in entry 1 (Figure 1b). The narrow molecular weight distribution ($M_w/M_n = 1.24$) indicates a well controlled copolymerization. Dynamic light scattering measurements of the modified silica NPs in tetrahydrofuran (THF) showed that the diameter of the nanoparticles before the second monomer addition was 67.9 ± 3.5 nm and increased to 172.6 ± 5.9 nm after the polymerization was stopped. Therefore, the thickness of the cross-linked shell was estimated to be 23.8 nm, and the linear polymer chain was 52.4 nm (Figure S2 in SI).

According to the model reactions discussed above, ATRP of BA and EGDMA was conducted using initiator-modified Au-NPs (Table 1, entry 3). The cross-linked polymer shell contained ~ 13.1 mol% of EGDMA and 86.9 mol% of BA, where the linear polymer chain was only composed of BA units. A control sample, Au-NPs modified with only linear PBA brushes, was also prepared via ATRP of BA (Table 1, entry 4). Both types of core/shell Au-NPs were well dispersed in common organic solvents (e.g., THF, dimethylformamide (DMF), and toluene), yielding red solutions. The TEM image of the polymer-modified Au-NPs (Figure S3 in SI) indicated that there was no cross-linking between particles.

The UV-vis spectra of both polymer-modified Au-NPs in toluene exhibited a distinct surface plasmon absorption band at ~ 540 nm (Figure 2a and b). The solutions of the dual polymer layer-modified Au-NPs and the control were simultaneously immersed into an 80 or 110 °C oil bath to compare their thermal stabilities. After 1 h at 110 °C or 3.5 h at 80 °C, almost all of the Au-NPs in the control sample precipitated from solution and could not be redispersed into solution even with sonication, indicating irreversible aggregation of the particles (Figure 2c). In striking contrast, the dual polymer layer-modified Au-NPs were extraordinarily stable even after 24 h at 110 °C, as evidenced by the characteristic plasmon band at 540 nm (Figure 2b). Obviously, the cross-linked shell protected the Au-NPs from aggregation at high temperatures, resulting in the stable Au-NPs for an extended period of time.

In conclusion, we developed a simple and general procedure to prepare thermally stable Au-NPs via a one-pot surface-initiated

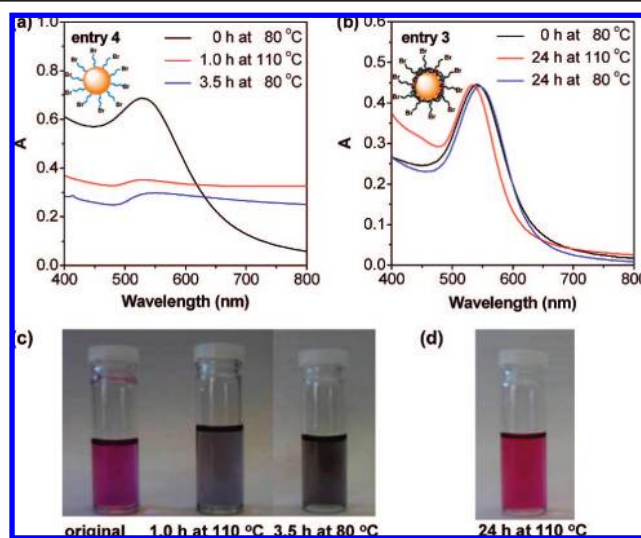


Figure 2. UV-vis spectra and appearances of (a and c) Au-NPs modified with linear PBA brushes (Table 1, entry 4) and (b and d) with a cross-linked shell and tethered PBA brushes (Table 1, entry 3) in toluene at 80 °C and in DMF at 110 °C for varied time.

ATRP. The gold core was protected with a cross-linked polymer shell, and linear polymer brushes were subsequently grafted from the shell. The cross-linked polymer shell prevented the dissociation of linear polymer brushes from the nanoparticles at elevated temperature. Our synthetic method could be readily extended to the preparation of other types of inorganic/polymer nanocomposites with significantly improved stability.

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Supporting Information Available: Detailed experimental procedures and characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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