

Shape control synthesis of polymeric hybrid nanoparticles via surface-initiated atom-transfer radical polymerization

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ABSTRACT: Polymeric hybrid nanoparticles were synthesized via surface-initiated atom-transfer radical polymerization (SI-ATRP) method on the surface of gold nanoparticles in cyclohexanone. Tetraoctyl ammonium bromide (TOAB) as a phase transfer agent was used to transfer the gold nanoparticles into cyclohexanone, which will be replaced by disulfide initiator on the surface of gold nanoparticles. Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and UV-vis spectroscopy were utilized to characterize the product to make sure the experiment had been conducted. The results showed that the polymeric gold hybrid nanoparticles with different structures could be controlled by adjusting the ratio of initiator and gold nanoparticles in ATRP. If the ratio is very little, asymmetric polystyrene-gold hybrid nanoparticles were synthesized, and a single gold nanoparticle was attached with a polystyrene sphere. If the ratio becomes larger, core-shell polystyrene-gold nanocomposite particles were obtained resulting in gold nanoparticle encapsulated by a uniform polymer shell. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43584.

KEYWORDS: hybrid nanoparticles; gold nanoparticles; janus particle; polystyrene; radical polymerization

Received 23 November 2015; accepted 28 February 2016

DOI: 10.1002/app.43584

INTRODUCTION

Polymeric hybrid nanoparticles are always achieving considerable attention due to their fascinating optic, electronic, magnetic, and catalytic properties which leads to a wide range of applicants in biosensing, catalysis, detection, and nanomotors.^{1–3} In particular, a large variety of novel functional materials have been obtained by incorporating gold nanoparticles into polymer matrices, such as polymeric-gold nanoparticles,^{4–6} anisotropic DNA-functionalized gold nanoparticles,⁷ and fluorosurfactant-capped gold nanoparticles.⁸ Among them, polystyrene-gold hybrid nanoparticles have been proved to have potential applications in detection and biosensing.^{9,10}

Many preparation methods of polymeric hybrid gold nanoparticles had been reported on the polymer immobilizing on gold nanoparticles via thiol, including utilizing the initiator with thiol end-group to start surface-initiated atom-transfer radical polymerization (SI-ATRP),^{11,12} taking emulsion method to form polymer on the surface of gold nanoparticles,¹³ or modulating self-assembly of nanoparticles.¹⁴ Among them, the surface-initiated living radical polymerization (SI-LRP) is becoming a popular method to prepare polymeric hybrid gold nanoparticles, especially to core-shell nanoparticles. It is because that SI-LRP technique has advantage to control the thickness of the polymer shells.⁴

One-step Pickering emulsion polymerization had been used to get asymmetric polystyrene-gold nanoparticles at low AuNP concentrations and core-shell polystyrene-gold nanoparticles at high AuNP concentrations.^{15,16} However, there are almost no definitely chemical bonds between gold nanoparticles and polystyrene spheres in Pickering emulsion polymerization. The surface-initiated living radical polymerization also can be used to synthesize hybrid nanoparticles with different structures, such as core-shell and asymmetric nanoparticles.¹⁷ The core-shell or asymmetric structures would be prepared through adjusting the proportion of disulfide initiator and gold nanoparticles. Besides, the bonds of Au-S also can be obtained definitely and controllably.¹⁸ For SI-LRP, an initiator with thiol usually is introduced onto the surface of gold nanoparticles through chemical binding. Then, the polymer chains grow along the direction of initiators immobilized on the gold surface in the polymerization to form the core-shell hybrid nanoparticles.

In this work, the core-shell or asymmetric structures has been prepared through adjusting the proportion of disulfide initiator and gold nanoparticles. In addition, in order to simplify the experimental steps and reduce the toxicity of tetrahydrofuran (THF) or dimethylformamide (DMF), gold nanoparticles were transferred into organic phase with the help of tetraoctyl ammonium bromide (TOAB) as a phase transfer agent. Due to the low boiling point of THF, the reaction temperature of

polymerization is limited. The high boiling point of cyclohexanone (155.6 °C) was chosen. At last, 3-mercapto-1-propanol was selected to prepare initiator with thiol and react with gold nanoparticles more easily.

EXPERIMENTAL

Materials

Chloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), sodium citrate, cyclohexanone, tetraoctyl ammonium bromide (TOAB), pyridine, sulfuric acid, dichloromethane, n-hexane, ethyl acetate, absolute methanol, copper (I) bromide, glacial acetic acid, styrene, and silica gel (for column chromatography, 300–400 μm) were all purchased from Sinopharm Chemical Reagent Co., Ltd. 3-Mercapto-1-propanol, 2-bromoisobutyl bromide, 2-isopropyl bromide butyrate, and *N,N,N,N,N*-Pentamethyldiethylenetriamine (PMDETA) were all purchased from TCI. Copper (I) bromide (CuBr) was purified by washing with glacial acetic acid and absolute ethanol three times and drying in a vacuum oven at 100 °C. Styrene was washed with 5% NaOH aqueous solution, dried over anhydrous MgSO_4 , and distilled under reduced pressure. High purity N_2 was obtained from Chunyu Company of Shanghai.

Synthesis of 3-Mercaptopropanol 2-Bromo-2-Methylpropionate

The 3-mercapto-1-propanol 2-bromo-2-methylpropionate was synthesized as reported.^{19,20} About 0.32 mL of 3-mercapto-1-propanol and 0.52 mL of 2-bromoisobutyl bromide was added dropwise into 15.0 mL of dichloromethane. Then, 0.55 mL of anhydrous pyridine was added into the reaction mixed solution and was stirred at 0 °C for 1 h. At last, the reaction mixture was raised up to room temperature and kept for 16 h. The white precipitates suspending in the solution was removed by filtration. The crude product was purified by silica gel column chromatography using 60/1 (v/v) hexane/ethyl acetate and distilled under reduced pressure to obtain thiol-terminated initiator as a colorless oil.

Synthesis of Initiator-Coated AuNPs

Gold nanoparticles (~15 nm) were prepared using the method reported by Frens.²¹ Aqueous solution of HAuCl_4 (1×10^{-4} g/mL, 25 mL) was boiled under gentle stirring. After a few minutes, a freshly prepared aqueous sodium citrate solution (0.01 g/mL, 0.5 mL) was added dropwise with vigorous stirring. The mixture turned red in a few minutes. After further vigorous stirring for 0.5 h, the product was collected by centrifugation and redissolved in the water.

Cyclohexanone (15 mL) was added into the gold nanoparticles in aqueous solution (10 mL). Then TOAB (0.43 g) as a phase transfer agent was added into the mixed solution under stirring.²² The color of solution changed immediately and the upper was pink. The upper solution was collected and was washed with dilute sulfuric acid and deionized water, respectively, to remove impurities.

About 0.2566 g of disulfide initiator was dissolved in 100 mL of cyclohexanone, some of which was added dropwise into gold nanoparticles in organic phase. After stirring at room temperature for 24 h, the crude products were centrifuged several times

and then dispersed in cyclohexanone to remove free disulfide initiator. Initiator-coated AuNPs had been obtained successfully for the next work.

Surface-Initiated ATRP

In a typical synthesis, cyclohexanone (15 mL), definite amount of 0.15 mL of PMDETA (0.1 mM), 0.09 mL of 2-bromoisobutyl bromide (0.13 mM), styrene (0.4 mL), and CuBr (0.0046 g) were added into a Schlenk flask under N_2 atmosphere. After a few minutes, the initiator-coated AuNPs were added into the mixed solution. The polymerization was carried out at 70 °C under magnetic stirring. The SI-ATRP polymerization was conducted at 70 °C for 4 h under N_2 atmosphere and stopped by exposed to air. The product was collected by centrifugation and washed with a mixture of methanol and water three times. The final precipitate was dispersed in ethanol aqueous solution.

Characterization Techniques

Transmission electron microscopy (TEM) images were obtained by a JEOL 200CX electron microscope equipped with a Model GATAN782 CCD camera at an operating voltage of 120 kV. The samples for TEM studies were prepared by placing one droplet of the sample deposited onto carbon-coated copper grids.

An UH4150 spectrophotometer (Hitachi technologies, Japan) equipped with an automatic sampling system is utilized to analyze the UV–vis absorption of the samples at room temperature. The slit width was 4 nm during the measurements.

Fourier transform infrared (FTIR) spectra were measured by VERTEX 70 using potassium bromide (KBr) pellets.

Hydrogen nuclear magnetic resonance ($^1\text{H NMR}$, CDCl_3) spectroscopy was obtained by an AVANCE 500 MHz Nuclear Magnetic Resonance spectrometer (BRUKER, Switzerland).

RESULT AND DISCUSSION

The polystyrene–gold hybrid nanoparticles have been prepared successfully via SI-ATRP (shown in Figure 1). The Figure 1(A) shows the gold nanoparticles in cyclohexanone, and the definite amount of disulfide initiator dispersed in cyclohexanone was added dropwise. About 24 h later, the disulfide initiator would attach on the surface of gold nanoparticles due to the presence of bonds of Au–S [as shown in Figure 1(B)].²³ If the proportion between gold nanoparticles and initiator is changed, the initiator density on the surface of gold will influence the polymer brush thickness¹⁹ and the formation of hybrid nanoparticles structure. Three kinds of structures of nanoparticles were showed in Figure 1(C–E) due to the different initiator densities on the surface of gold nanoparticles. When the mole ratio was suitable, the asymmetric particles containing one gold nanoparticle and one PS sphere will be obtained [shown in Figure 1(E)]. If we added less disulfide initiators into gold nanoparticles, we will get the PS spheres without gold nanoparticles [shown in Figure 1(D)]. When the mole ratio increases a little, we can also get the asymmetric particles contain a few gold nanoparticles and one PS sphere. When the mole ratio continues to increase, we will get the core–shell nanoparticles [shown in Figure 1(C)]. That is to say that the key to success of the

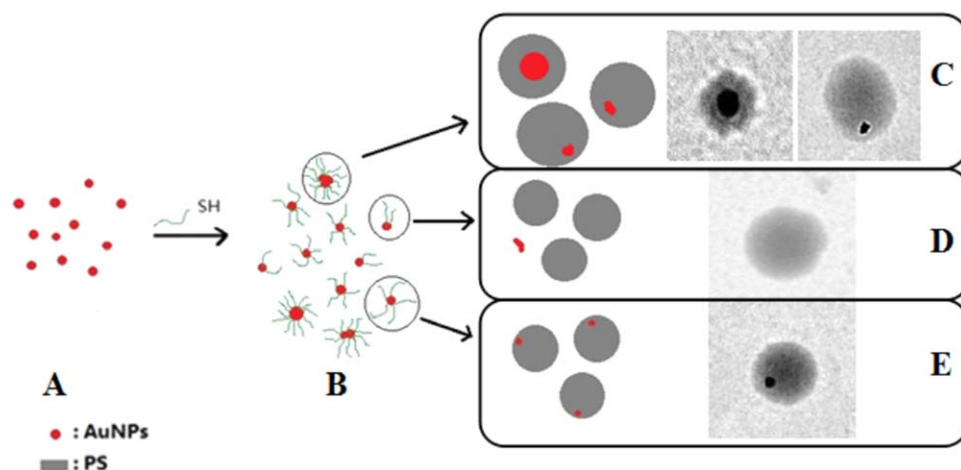


Figure 1. Schematic diagram of preparation of the polystyrene–gold hybrid nanoparticles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

experiment is trying to find an appropriate proportion between gold nanoparticles and initiator. In addition, the synthesis of disulfide initiator and the conditions of polymerization are also very important to the results. The details influences will be interpreted in the next work.

The initiator with thiol have been synthesized as reaction formula [shown in Figure 2(a)] reported in the literatures.²³ The disulfide initiator was used to acquire monomer resulting in formation polymer brush on metal substrates through the bond of Au-S. Figure 2(b) shows nuclear magnetic resonance (¹HNMR) spectroscopy which was used to characterize the initiator with thiol.¹⁹ The final product has four main bonds of carbon–hydrogen in Figure 1(a), which corresponds to peaks in Figure 1(b) [δ (ppm): 4.28–4.30 (t, 2H, $-\text{CH}_2-\text{O}-\text{CO}-$), 2.62–2.66 (q, 2H, $-\text{CH}_2-\text{HS}$), 1.92 (s, 6H, 2- CH_3), 1.96–2.01

(m, 2H, $-\text{CH}_2-$)]. Especially, the peak in 4.28–4.30 ppm shows the chemical shift due to protonation of b in molecular formula, which also indicates that the esterification reaction has been conducted successfully.

Figure 3 shows the Fourier transform infrared spectra of $\text{HS}(\text{CH}_2)_3\text{OH}$ and $\text{Br}(\text{CH}_3)_2\text{COO}(\text{CH}_2)_3\text{SH}$. Similar work had also been conducted to confirm the component of the initiator with thiol via infrared analysis.²⁴ The dot curve is infrared spectrum of 3-mercapto-1-propanol dispersed in dichloromethane. An obvious absorption peak appears at the wavenumber of 3325 cm^{-1} , which is the characteristic peak of hydroxyl group. The absorption peak at the wavenumber of 1051 cm^{-1} indicates that the compound is one kind of primary alcohol. The most important absorption peak is located at 2553 cm^{-1} , which is the characteristic peak of thiol. All the peaks confirm that it is the structure of 3-mercapto-1-propanol.

The solid line is the infrared spectrum of initiator with thiol. After reaction of synthesis, the absorption peaks at the wavenumber of 3325 and 1051 cm^{-1} are disappeared. It suggests

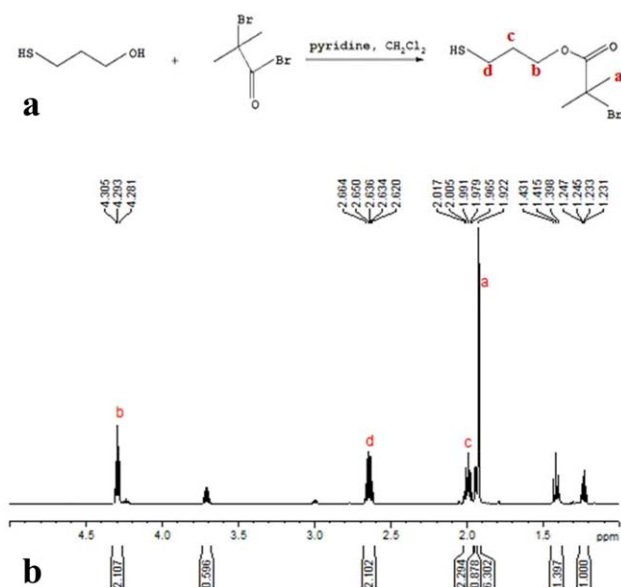


Figure 2. Reaction formula (a) and hydrogen nuclear magnetic resonance (¹HNMR) spectroscopy (b) of disulfide initiator. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

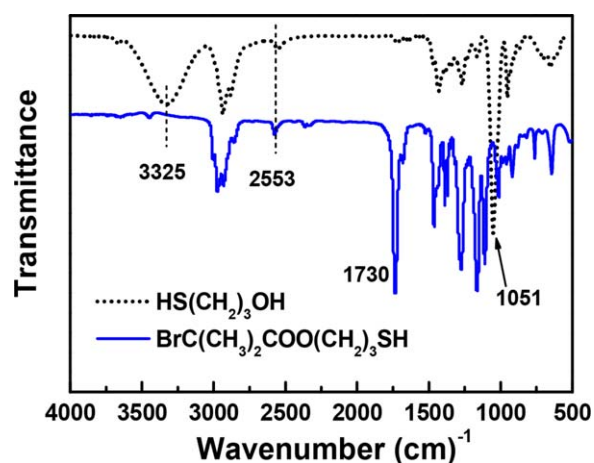


Figure 3. Fourier transform infrared spectra of $\text{HS}(\text{CH}_2)_3\text{OH}$ and $\text{Br}(\text{CH}_3)_2\text{COO}(\text{CH}_2)_3\text{SH}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

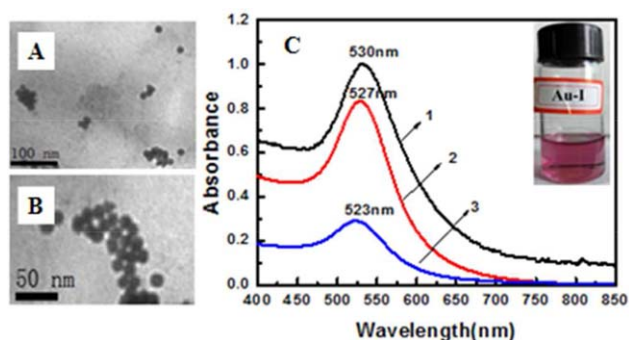


Figure 4. TEM pictures of initiator-coated AuNPs in cyclohexanone (A, B); plasma resonance absorption spectra of gold nanoparticles (C): 1: initiator-coated AuNPs in cyclohexanone; 2: AuNPs in cyclohexanone; 3: AuNPs in water. Inset shows the picture of initiator-coated AuNPs stored for a month. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that hydroxyl group has been consumed during the reaction. Besides, a strong absorption peak at 1730 cm^{-1} appears which illustrates that ester groups have been generated. Combined with ^1H NMR information, it can be suggested that the reaction had been conducted. Specially, there is still a small peak at 2553 cm^{-1} . Therefore, the presence of thiol and other data above mentioned indicated that initiator with thiol has been synthesized successfully.

Figure 4(A,B) show the TEM pictures of initiator-coated AuNPs in cyclohexanone, in which gold nanoparticles is about 15 nm. The nanoparticles tend to aggregate. The plasma resonance absorption spectra of gold nanoparticles in different solvents were shown in Figure 3(C). The curve 1 shows the absorption spectrum of initiator-coated AuNPs in cyclohexanone, which absorption peak is located at 530 nm. The curve 2 is the absorption spectrum of gold nanoparticles in cyclohexanone and its absorption peak is 527 nm. The curve 3 represents the absorption spectrum of gold nanoparticles in aqueous phase and its absorption peak is 523 nm. There is a red shift of 4 nm when gold nanoparticles were transferred into cyclohexanone from water because the localized refractive index changes from water ($n = 1.33$) to cyclohexanone ($n = 1.45$).²⁵ There is also 3 nm red shift on the surface plasmon resonance peak of gold nanoparticles coated by initiators compared with that of the AuNPs due to the thiol absorption on the AuNP surfaces.²⁵ Besides, this red shift also indicates that disulfide initiators had been attached on the surface of gold nanoparticles through the bonds of Au-S.

It is unstable for gold nanoparticles in cyclohexanone. The mixture will become colorless after several hours because there are no chemical bonds between gold nanoparticles and TOAB. However, the color of initiator-coated AuNPs in cyclohexanone stored for a month is still pink as before [inset of Figure 4(C)]. It indicates that the initiators had attached on the gold nanoparticles through the bonds of Au-S to form a protective layer around the gold nanoparticles. Accordingly the stability of solution increases.

Initiator-coated AuNPs dissolved in cyclohexanone was put into ATRP system. The mixture was stirred at 70°C under N_2 atmos-

phere for 4 h. The final product of hybrid nanoparticles was obtained by adding methanol, centrifugation, and repeated washing with a mixture of ethanol and water. Figure 5 shows the TEM pictures of gold–polystyrene hybrid nanoparticles synthesized by ATRP with different amounts of disulfide initiator. When 0.0025 mL disulfide initiator was added, the mole ratio between gold nanoparticles and disulfide initiator was nearly 1/100, it is difficult to find the gold nanoparticles in the Figure 5(A). It might be because the quantity of the initiator was so little that the gold nanoparticles could not maintain stability in the polymerization system and aggregate.

Figure 5(B) shows TEM pictures of asymmetric polystyrene–gold hybrid nanoparticles with 0.025 mL of disulfide initiator. The gold nanoparticles are slightly embedded in the surface of PS sphere to form eccentric structure of snow man when the mole ratio was 1/1000. Many hybrid nanoparticles include one Au nanoparticle banded with a PS sphere. In addition, some hybrid particles contain no gold nanoparticles, which is not obvious. Similar to initiator-coated AuNPs, the diameter of the gold particles is about 15 nm and the PS sphere is approximately 100 nm.

If more disulfide initiator (0.25 mL) was added into the gold nanoparticles in cyclohexanone, the asymmetric polystyrene–gold hybrid nanoparticles were also acquired as shown in Figure 5(C). As we know, the disulfide initiator was attached on the surface of gold nanoparticles to replace TOAB. However, more disulfide initiator adding may cause gold nanoparticles aggregation. Once the aggregate of gold nanoparticles was wrapped by disulfide initiators, the whole system was stable. After SI-ATRP, aggregate of gold nanoparticles appears asymmetric polystyrene–gold hybrid nanoparticles. Therefore, the asymmetric hybrid nanoparticles were also obtained through SI-ATRP at this amount of disulfide initiator.

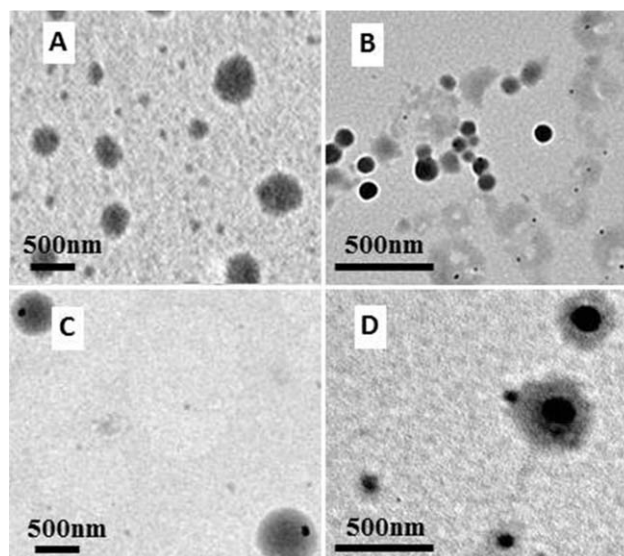


Figure 5. TEM pictures of gold–polystyrene hybrid nanoparticles (Molar ratio of gold nanoparticles and disulfide initiator: (A) 1/100; (B) 1/1000; (C) 1/10,000; (D) 1/20,000).

If further more disulfide initiator was added into the gold nanoparticles in cyclohexanone, a core-shell structure would be obtained. The gold nanoparticle lies in the center and PS is shell [shown in Figure 5(D)]. This is consistent with results reported that polymeric hybrid nanoparticles had a core-shell nanostructure with gold cores and polymer shells.^{26,27} Therefore, in order to gain asymmetric or core-shell structure of the polymeric-gold hybrid nanoparticles, it is very important to know the proportion of gold particles and initiator of SI-ATRP.

CONCLUSIONS

In summary, we have demonstrated that polymeric gold hybrid nanoparticles were synthesized via SI-ATRP method on the surface of gold nanoparticles. The polymeric gold hybrid nanoparticles with different structures can be controlled by adjusting the ratio of initiator and gold nanoparticles in ATRP. When 0.025–0.25 mL of disulfide initiator was added into gold nanoparticles in cyclohexanone, asymmetric polystyrene-gold hybrid nanoparticles were synthesized, and a single gold nanoparticle was attached with a polystyrene sphere. If the disulfide initiator is excessive, core-shell polystyrene-gold nanocomposite particles are obtained resulting in gold nanoparticle encapsulated by a uniform polymer shell.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant no. 51203088) and Innovative Foundation of Shanghai University.

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