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Efficient Synthesis of Single Gold Nanoparticle Hybrid Amphiphilic Triblock Copolymers and Their Controlled Self-Assembly

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S Supporting Information

ABSTRACT: We report on a robust approach to the size-selective and template-free synthesis of asymmetrically functionalized ultrasmall (<4 nm) gold nanoparticles (AuNPs) stably anchored with a single amphiphilic triblock copolymer chain per NP. Directed NP self-assembly in aqueous solution can be facilely accomplished to afford organic/inorganic hybrid micelles, vesicles, rods, and large compound micelles by taking advantage of the rich microphase separation behavior of the as-synthesized AuNP hybrid amphiphilic triblock copolymers, PEO−AuNP−PS, which act as the polymer−metal−polymer analogue of conventional amphiphilic triblock copolymers. Factors affecting the size-selective fabrication and self-assembly characteristics and the time-dependent morphological evolution of NP assemblies were thoroughly explored.

Inorganic nanoparticle (NP) assemblies have aroused significant interest in the past decade because of their collective properties and enhanced electronic, magnetic, and optical characteristics relative to those of individual NPs and the corresponding bulk materials.[1] In regard to their fabrication, directed self-assembly of NPs by utilizing specific molecular interactions in the presence or absence of templates or by exerting external fields/stimuli represents a major strategy.[2] In the context of NP building blocks, the tuning of chemical properties, grafting densities, number of types, and spatial distribution of functional moieties at the surface of the NPs is quite critical for gaining more delicate control over NP-ensembling structures.[3] For conventional spherical NPs with isotropic bulk and surface properties, their self-assembly can be achieved via the “bricks and mortar” strategy using synthetic polymers, proteins, DNA, or viruses as the sticking or structuring motif.[4]

In addition, anisotropic NP building blocks, including shape anisotropy, structural anisotropy, or an anisotropic distribution of surface functionalities, can further enrich the design flexibility and freedom in controlling NP self-assembly.[2j,5] Janus NPs, as coined by de Gennes,[6] represent a special category of anisotropic NPs possessing a biphasic geometry of distinct surface functionalities or core compositions. Although anisotropic NPs have previously been fabricated via a variety of methodologies, most of these techniques are subject to limitations such as relatively low efficiency and unsatisfactory yield.[2j,5] More importantly, the fabrication of ultrasmall (<5−10 nm) anisotropic NPs has remained a considerable challenge when a liquid−liquid interface or Pickering emulsion is used as the template. For gold NPs (AuNPs) as a specific example, there exist only a few reports concerning the preparation of <10 nm anisotropic AuNPs, mainly via the Langmuir−Blodgett technique[7] or using polymer single crystals as the immobilizing template,[8] which are considered difficult to scale up.

In addition to the fabrication of anisotropic AuNPs asymmetrically anchored with two types of surface functionalities, the capability to control the number of surface functional groups precisely is also quite crucial for screening novel and more versatile NP self-assembly strategies.[9] An extreme case involves AuNPs monofunctionalized with a single chemically distinct moiety or a single chain. Such monofunctionalized AuNPs can be also viewed as a special type of anisotropic NPs. Though the fabrication of AuNP surfaces anchored with a single DNA or peptide chain or a single carboxyl functionality has been achieved via gel-electrophoresis separation or solid-phase chemistry approaches,[10] for anisotropic AuNPs monofunctionalized with a single synthetic polymer chain, this has remained quite a challenging task, possibly because of the lack of appropriate separation and purification techniques. The only two existing relevant reports[11] involve protective coating of the AuNPs (15 nm) with a single chain of pyridyldithio-functionalized dextran (MW ∼ 2000 kDa)[11a] and free radical polymerization of 4-vinylthiophenol monomers anchored at the surface of AuNPs.[11b] In comparison with AuNPs functionalized with a single homopolymer chain, AuNPs functionalized with a single block copolymer chain would be more intriguing in view of the robust self-assembly properties of block copolymers in both solution and bulk states,[4b−d,12] which would certainly further broaden the field of directed NP self-assembly. However, efficient fabrication of the latter has not been accomplished to date.

We herein propose a new strategy for the highly efficient, template-free, size-selective fabrication of ultrasmall anisotropic AuNPs (<4 nm) anchored with a single amphiphilic triblock copolymer chain (Scheme 1). The triblock copolymer consists of poly(ethylene oxide) (PEO) and polystyrene (PS) outer blocks and a 1,2-dithiolane-functionalized AuNP-binding middle block, poly(lipoic acid 2-hydroxy-3-(methacryloyloxy)-propyl ester-*co*-glycidyl methacrylate) [P(LAMP-*co*-GMA)]. We speculated that when AuNP size is smaller than or comparable to the hydrodynamic dimension of the middle

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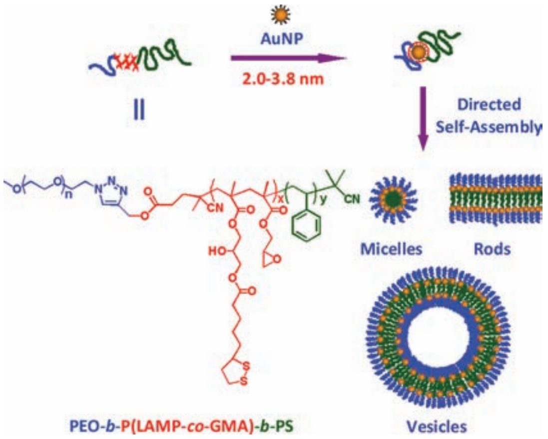
Scheme 1. Schematic Illustration of the Template-Free, Size-Selective Fabrication of Ultrasmall AuNPs (2.0−3.8 nm) Anchored with a Single Triblock Copolymer Chain and the Hierarchical Self-Assembly of the Resulting AuNP Hybrid Amphiphilic Triblock Copolymers PEO−AuNP−PS in Aqueous Media



block, monofunctionalization of AuNPs by a single triblock chain should proceed in a stoichiometric manner because the middle block could wrap around the periphery of the AuNP; moreover, the presence of the PEO and PS outer blocks would provide additional steric hindrance that would effectively prevent further AuNP or polymer chain conjugation. The as-synthesized monofunctionalized AuNPs could also be viewed as polymer−metal−polymer analogues of conventional amphiphilic triblock copolymers[3c] (Scheme 1). They would be expected to exhibit rich self-assembly morphologies in aqueous solution, thus allowing directed AuNP self-assembly to be achieved.

PEO-*b*-P(LAMP-*co*-GMA)-*b*-PS amphiphilic triblock copolymers with varying degrees of polymerization (DPs) were synthesized via sequential reversible addition-fragmentation chain transfer (RAFT) polymerization utilizing a PEO macroRAFT agent followed by reaction with an excess of DL-lipoic acid [Scheme S1 in the Supporting Information (SI)]. Triblock copolymers were characterized by ^{1}H NMR spectroscopy (Figure S1) and gel-permeation chromatography (GPC) (Figure S2), and their structural parameters are summarized in Table S1. Monodisperse *n*-butanethiol-stabilized AuNPs with varying average diameters (∼2.0, 2.9, 3.8, and 4.9 nm; Figure S3 and Table S2) were synthesized according to literature procedures.[13] Triblock-copolymer-functionalized AuNPs (denoted as PEO_m−AuNP_x−PS_n, where m and n are the DPs of the PEO and PS blocks, respectively, and x is the average diameter of the AuNPs in nm) were prepared via a facile ligand exchange reaction between the *n*-butanethiol-stabilized AuNPs and the PEO-*b*-P(LAMP-*co*-GMA)-*b*-PS triblock polymer in a common solvent. The number concentration of AuNPs was in slight excess relative to that of triblock chains (5:3). Typically, a PEO_{45}-*b*-$\mathrm{P(LAMP}_{0.78}$-*co*-$\mathrm{GMA}_{0.22})_{16}$-*b*-$\mathrm{PS}_{260}$ solution was slowly added into a THF dispersion of *n*-butanethiol-stabilized AuNPs at a mole ratio of 3:5. The excess AuNPs were then facilely removed by precipitation into petroleum ether, as the triblock copolymer−AuNP hybrid conjugates are insoluble in nonpolar solvents (see the SI for details).

Detailed characterizations were then conducted to investigate the binding stoichiometry and structural properties of the hybrid conjugates. High-resolution transmission electron microscopy (HRTEM) characterization revealed that triblock-copolymer-functionalized AuNPs can be well-dispersed in THF, exhibiting negligible changes in size and size distribution after the ligand exchange process (Figure S4). Though the presence of the PEO and PS chain segments at the periphery of the AuNPs could not be discerned from the HRTEM image (Figure S4b) because of their much lower electron contrast relative to that of AuNPs and the limit of TEM resolution, XPS analysis confirmed the presence of both the AuNPs and the triblock copolymers, as evidenced by the appearance of the O 1s peak and the prominently enhanced C 1s peak after the ligand exchange reaction (Figure S5).

Next, we investigated the average number of triblock copolymer chains conjugated per AuNP (2.0 ± 0.2 nm). As shown in Figure 1a, the GPC trace of PEO_{45}−$\mathrm{AuNP}_{2.0}$−PS_{260} was shifted to lower MW relative to the triblock precursor (Figure 1a). The binding between the AuNP and the 1,2-dithiolane-functionalized middle block (∼12 moieties) actually occurs in a cooperative and multidentate manner through the formation of multiple dative covalent bonds at the AuNP surface;[14] this leads to collapse of the middle block and concomitant conformational changes of the two outer blocks upon anchoring on the AuNP surface (Scheme 1). Thus the shift to lower MW for the hybrid conjugates can be reasonably interpreted. Most importantly, no higher-MW shoulders or additional peaks could be discerned in the GPC elution profile, partially confirming the monofunctionalization of the AuNPs. This fact was further corroborated by thermogravimetric analysis (TGA) results (Figure 1b). The number of triblock copolymer chains anchored per AuNP was calculated to be ∼1.1 (Table S3). Thus, we could safely conclude that monofunctionalized ultrasmall AuNPs (2.0 ± 0.2 nm) were successfully fabricated. With similar protocols, the monofunctionalization of AuNPs (2.0 ± 0.2 nm) with other PEO-*b*-P(LAMP-*co*-GMA)-*b*-PS triblock copolymers possessing varying block lengths was also successfully conducted (see Tables S1 and S3), as confirmed by additional GPC and TGA characterization data (Figures S6 and S7).

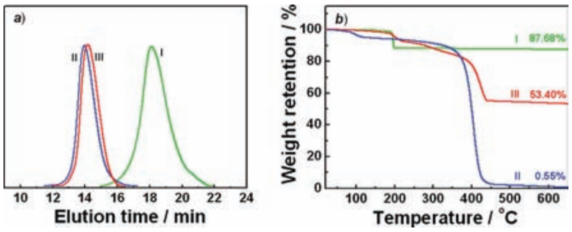


Figure 1. (a) THF GPC traces and (b) TGA profiles recorded for (I) *n*-butanethiol-stabilized AuNPs (2.0 ± 0.2 nm), (II) the PEO_{45}-*b*-$\mathrm{P(LAMP}_{0.78}$-*co*-$\mathrm{GMA}_{0.22})_{16}$-*b*-$\mathrm{PS}_{260}$ triblock copolymer, and (III) the AuNP hybrid amphiphilic triblock copolymer PEO_{45}−$\mathrm{AuNP}_{2.0}$−PS_{260} consisting of a hydrophobic AuNP middle block and PEO and PS outer blocks. TGA was performed in air at a heating rate of 10 °C/min.

To explore further the underlying mechanism of the successful AuNP monofunctionalization, a series of control experiments were then conducted. Upon treatment of PEO_{45}−$\mathrm{AuNP}_{2.0}$−PS_{260} with an excess of triblock copolymer precursor in THF, negligible changes in the GPC elution profile could be discerned (Figure S8). This suggests that these hybrid conjugates are very stable because of the nature of the cooperative multidentate binding between the AuNP and the 1,2-dithiolane-functionalized middle block as well as the additional steric hindrance exerted by the two outer blocks, which prevents further triblock chain conjugation onto the AuNP.[14] Intriguingly, we further found that monofunctionalized AuNPs could even be facilely fabricated in high efficiency by directly mixing the THF solution of PEO_{45}-*b*-P($LAMP_{0.78}$-*co*-$GMA_{0.22}$)$_{16}$-*b*-PS_{260} with the THF dispersion of *n*-butanethiol-stabilized AuNPs (2.0 ± 0.2 nm) rather than the time-consuming slow addition procedure. We also checked the effect of the block copolymer topology on the AuNP monofunctionalization. When the PEO_{45}-*b*-P(LAMP-*co*-GMA)$_{16}$ diblock copolymer was used, the much broadened GPC elution trace strongly suggested that AuNPs were surface-functionalized with multiple chains (Figure S9). Therefore, the steric hindrance exerted by the two outer blocks anchored on the surface of the AuNP is quite necessary to ensure successful monofunctionalization during the ligand exchange process.

We also examined the effect of the AuNP size on the fabrication of monofunctionalized AuNPs from the PEO_{45}-*b*-P($LAMP_{0.78}$-*co*-$GMA_{0.22}$)$_{16}$-*b*-PS_{260} triblock precursor. GPC results revealed that monofunctionalization of AuNPs with an average diameter of ~4.9 nm could not be achieved, as revealed by the presence of a higher-MW shoulder (Figure S10), whereas monofunctionalization of AuNPs with average diameters of ~2.0, ~2.9, and ~3.8 nm could be accomplished. These results strongly imply that the synthesis of triblock-chain-monofunctionalized AuNPs follows a size-selective rule. For larger AuNPs (~4.9 nm), the size mismatch with the hydrodynamic dimension of the P($LAMP_{0.78}$-*co*-$GMA_{0.22}$)$_{16}$ middle block (~3 nm) results in incomplete wrapping of the AuNP surface, allowing further polymer conjugation to occur. We speculate that larger AuNPs could be monofunctionalized by increasing the chain length of the AuNP-binding middle block in combination with those of the two outer blocks.

Amphiphilic block copolymers are well-known to self-assemble in aqueous media into robust nanostructures, including spherical micelles, rods, vesicles, and other more complex morphologies.[12] The AuNPs functionalized with a single triblock chain, PEO−AuNP−PS, can be considered as a polymer−metal−polymer analogue of conventional amphiphilic triblock copolymers.[3c] Since the hydrophobic AuNP hybrid middle block is sandwiched between PEO and PS outer blocks, the AuNPs would be expected to locate at the interface between the hydrophilic PEO and hydrophobic PS domains within self-assembled nanostructures. Figure 2 shows typical HRTEM images for NP assemblies of PEO−$AuNP_{2.0}$−PS with varying DPs of PEO and PS. We can tell that only PEO_{45}−$AuNP_{2.0}$−PS_{260} with the highest PS molar content (Table S1) can self-assemble into hybrid vesicles with diameters of 300−500 nm, and this was also confirmed by the observation of hollow nanostructures using atomic force microscopy (AFM) (Figure 2d). PEO_{45}−$AuNP_{2.0}$−PS_{45}, PEO_{45}−$AuNP_{2.0}$−PS_{135}, and PEO_{113}−$AuNP_{2.0}$−PS_{60} hybrid triblocks self-assemble into morphologically irregular but relatively monodisperse hybrid nanoclusters with average diameters of ~13, 17, and 32 nm, respectively. It is quite interesting to observe that PEO_{113}−$AuNP_{2.0}$−PS_{300} self-assembles into quite uniform and spherical hybrid supermicelles with an average diameter of ~34 nm.

Higher-magnification HRTEM images, additional AFM images, and dynamic light scattering (DLS) characterization results for hybrid AuNP assemblies are shown in Figures S11−S13, respectively. The relatively high NP packing density, relatively narrowly dispersed size distribution, and nanosized dimension ranges provide strong support that the self-assembly of anisotropic AuNPs monofunctionalized with a single triblock chain resembles those of conventional amphiphilic block copolymers.[12] From Figures S11c and S12c, we can clearly tell that the AuNPs are mainly located at the interior and outer interface of hybrid vesicle bilayers.

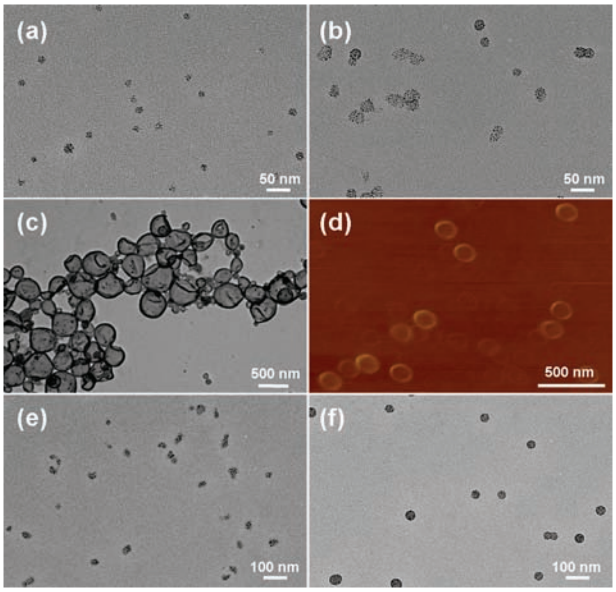


Figure 2. (a−c, e, f) HRTEM images and (d) AFM height image recorded for hierarchical NP assemblies fabricated from AuNP (2.0 ± 0.2 nm) hybrid amphiphilic triblock copolymers in aqueous solution: (a) PEO_{45}−$AuNP_{2.0}$−PS_{45}; (b) PEO_{45}−$AuNP_{2.0}$−PS_{135}; (c, d) PEO_{45}−$AuNP_{2.0}$−PS_{260}; (e) PEO_{113}−$AuNP_{2.0}$−PS_{60}; (f) PEO_{113}−$AuNP_{2.0}$−PS_{300}. During the self-assembly process, 0.4 mL of water (16.7% v/v) was added at a rate of 1.0 mL/h into 2.0 mL of AuNP hybrid triblock copolymer solution in 1,4-dioxane (1.0 g/L); after further stirring for 2 h at room temperature, 18.0 mL of water was injected in one shot followed by dialysis.

Figure S14 compares HRTEM images recorded for aqueous assemblies fabricated from PEO_{45}−$AuNP_{2.0}$−PS_{260} and the triblock precursor PEO_{45}-*b*-P($LAMP_{0.78}$-*co*-$GMA_{0.22}$)$_{16}$-*b*-PS_{260}. To our surprise, although PEO_{45}−$AuNP_{2.0}$−PS_{260} self-assembles into large hybrid vesicles, the triblock precursor primarily self-assembles into spherical micelles coexisting with a few fused vesicles. This can be ascribed to the introduction of the hydrophobic AuNP into the middle block, which increases the volume of the hydrophobic region (v); on the other hand, the interfacial area (a) remains unchanged, and the hydrophobic chain length (l) tends to decrease slightly because of AuNP-binding-induced wrapping of the middle block (Figure 1a). Thus, the packing parameter ($p = v/al$) of PEO_{45}−$AuNP_{2.0}$−PS_{260} is considerably larger than that of the triblock precursor, favoring the formation of hybrid vesicles ($^1/_2 \leq p \leq 1$) for the former and micelles ($p \leq {}^1/_3$) for the latter.[12,15] As a further confirmation that the same morphological transformation can occur for hybrid triblock copolymers with varying AuNP sizes, we also checked the self-assembly behavior of PEO_{45}−$AuNP_{3.8}$−PS_{135} and PEO_{45}−$AuNP_{3.8}$−PS_{260} (Figure S15) and observed the formation of robust vesicles in both cases. On the other hand, the PEO_{45}−$AuNP_{2.0}$−PS_{135} triblock copolymer self-assembled only into spherical hybrid micelles (Figure 1b).

When THF instead of 1,4-dioxane was used as the cosolvent during self-assembly, spherical supermicelles encapsulating multilamellar layered internal nanostructures were observed for the PEO_{45}−$AuNP_{2.0}$−PS_{260} hybrid triblock copolymer (Figure S16), whereas for PEO_{113}−$AuNP_{2.0}$−PS_{300}, large compound micelles (LCMs) with multicompartment internal spherical nanostructures were obtained. These morphologically different hybrid nanostructures self-assembled from AuNP hybrid triblocks via the variation of the cosolvent are quite comparable to those of conventional amphiphilic block copolymers.[12a,b,j]

We also investigated the microstructural evolution of PEO_{45}−$AuNP_{2.0}$−PS_{260} assemblies in 1,4-dioxane at varying stages of water addition (Figure S17) and time-dependent evolution of self-assembled hybrid nanostructures at fixed water contents (Figure S18−S20). Please refer to the Supporting Information for detailed discussions (pages S9−S10).

In summary, we have developed a highly efficient, size-selective, template-free strategy for the fabrication of ultrasmall anisotropic AuNPs (<4 nm) monofunctionalized with a single triblock copolymer chain that exploits the cooperative, multidentate AuNP-binding nature exhibited by the middle block and the additional steric hindrance exerted by the two outer blocks. The as-synthesized AuNP hybrid amphiphilic triblock copolymers can spontaneously self-assemble into various morphologies, including hybrid micelles, (branching) rods, vesicles, and LCMs, in aqueous media. The emerging strategy in this work represents a general methodology for the highly efficient preparation of monofunctionalized ultrasmall anisotropic NPs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, NMR and XPS spectra, GPC and TGA traces, HRTEM and AFM images, and DLS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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