

Amphiphilic Janus Gold Nanoparticles via Combining “Solid-State Grafting-to” and “Grafting-from” Methods

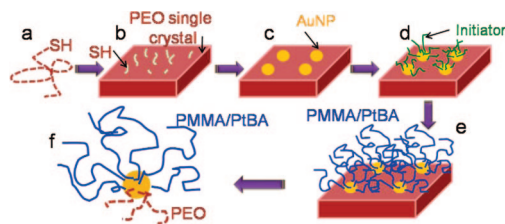
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Nanoparticles (NPs), both in solution and in solid state ensembles, show fascinating optic, electronic, and magnetic properties.¹ In particular, Janus NPs, which possess a noncentrosymmetric structure with a single core surrounded by compartmentalized corona, are of great interest because of their unique surface pattern. Since de Gennes coined the Janus concept,² a number of Janus “architectures” have been reported, including dendrimers, block copolymer micelles, etc.³ While a Janus NP possesses *two* types of surface structures, the Janus concept can be extended to “patchy particles” where multiple “patches” (functional groups) are introduced to the NP surface.⁴ Judicious selection of patches could lead to directed assembly of NPs into complex structures for targeted applications. Most of the reported works on Janus NPs have been focused on relatively large size particles (with diameters greater than 20 nm) and small molar mass ligands. Polymers brushes have also been attached to a NP surface.⁵ Despite the extensive efforts in polymer-modified NP research, because of the difficulty of controlling polymer phase separation on a NP surface, synthesizing sub-10 nanometer, polymer-modified Janus NPs is challenging. We recently demonstrated a synthesis using the single crystal of thiol-terminated polyethylene oxide (HS-PEO) as the solid substrate to immobilize gold NPs (AuNPs); polyethylene oxide (PEO) was attached to the selected area of the AuNP surface.⁶ This approach was referred to as a “solid-state grafting-to” method where polymer single crystals were used as the substrates.

Herein, we report synthesizing Janus AuNPs that are functionalized with two different types of polymer chains on the opposite sides of the AuNP by combining “solid-state grafting-to” and “grafting-from” methods. Detailed experimental procedure can be found in the Supporting Information. Scheme 1 shows the synthesis strategy. HS-PEO was solution crystallized into lamellar single crystals with a typical thickness of ~12 nm and the thiol groups were excluded on the crystal surface (Scheme 1b).^{6a} AuNPs were then immobilized on the crystal surface by mixing ammonium-ligand-protected AuNPs (average diameter ~6 nm estimated using ImageJ software) solution and HS-PEO single crystal suspension. This step is critical both to prohibiting AuNP agglomeration and to achieving preferred AuNP areal density on the HS-PEO single crystals.⁶ Thiol-terminated initiator 11-mercaptopentadecyl 2-bromo-2-methylpropionate (**1** in Figure 1) was used to replace ammonium ligands on the “free” surface of AuNPs (top part in Scheme 1d), affording asymmetric PEO/AuNP/initiator complexes (PEO–Au–I) with PEO and initiators on the opposite sides of the AuNPs (Scheme 1d). We anticipate that the place exchange reaction between initiators and the HS-PEO chains in the single crystals is less likely to occur because of the multiple Au–S bonds between each AuNP and the underneath PEO single crystal.⁶ Free initiators and the protection ligands were removed by centrifugation and repeated washing. Transmission electron microscopy (TEM) experiments

Scheme 1. Schematic Illustration of Polymer-Functionalized Janus AuNPs by Combining “Solid-State Grafting-to” and “Grafting-from” Methods



showed that AuNPs were retained on the crystal surface after the ligand exchange process (Supporting Information, Figure S1). PEO–Au–I was then dissolved in CDCl_3 for ^1H NMR study (Figure 1). Spectrum I is from the pure initiator (**1**) while spectrum II shows the characteristic peaks of both PEO (d in the spectrum) and **1** in PEO–Au–I. Because the initiators are covalently bound to the Au surface, all of the initiator peaks in spectrum II (e.g., $-\text{CH}_2-$ (b) next to the ester group ($\delta = 4.15$ ppm)) were significantly broadened.⁷

Atom transfer radical polymerization (ATRP) was performed from the initiator-coated side of PEO–Au–I (Scheme 1e). To prevent desorption of thiol ligands, the reaction was performed at room temperature using the catalyst system of $\text{CuBr}/\text{Me}_6\text{TREN}$.⁸ Furthermore, pentyl acetate was used as the solvent for the polymerization process in order to avoid the dissolution of HS-PEO single crystals. Poly(methyl methacrylate) (PMMA) was successfully synthesized on the AuNP surface. After dissolving the single crystal substrates, Janus AuNPs were obtained (Scheme 1f). The grafted polymers were cleaved from NPs by reacting with iodine and were subjected to gel permeation chromatography (GPC) study. Two peaks were obtained from the GPC elution curve (Figure S2). The first peak was ascribed to PMMA on the Janus NPs with the number average molecular weight (M_n) ≈ 30100 g/mol. Note that because the polymerization was performed from the NP surface without the addition of free sacrificial initiators, the polydispersity index (PDI) of PMMA (1.47) is slightly greater than that of the polymers synthesized without AuNPs.⁹ The second peak was ascribed to HS-PEO with a M_n of 2900 g/mol and a PDI of 1.03. Figure 2a shows a TEM image of these NPs after drop casting NP/chloroform solution on a carbon-coated TEM grid; The NPs are separated from each other because of the grafted polymer chains. On the basis of Figure 1–III, the average number ratio of PEO and PMMA chains on each Janus AuNP surface was calculated to be 1:3.54, which is consistent with the results calculated from GPC analysis (Supporting Information). The surface areal chain density was ~ 1.3 to 2.4 chains/ nm^2 (Supporting Information).^{5c,g}

For polymer-functionalized Janus AuNPs, because of their small diameter and high electron density contrast between AuNPs and polymers, direct observation of asymmetrical surface functionalization is challenging. Nevertheless, metal NP decoration has been successfully

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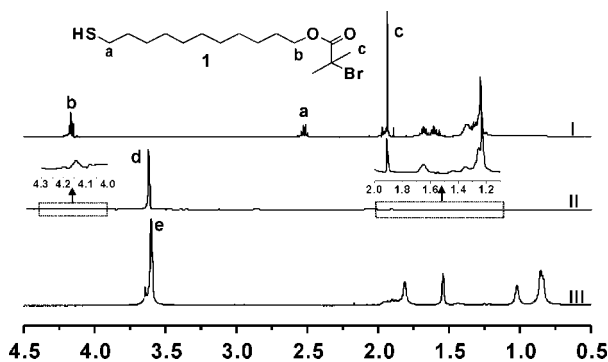


Figure 1. ^1H NMR spectra of the initiator **1** (I), initiator and PEO-coated AuNPs (PEO-Au-I) (II), and PEO and PMMA-modified Janus AuNPs (PEO-Au-PMMA) (III).

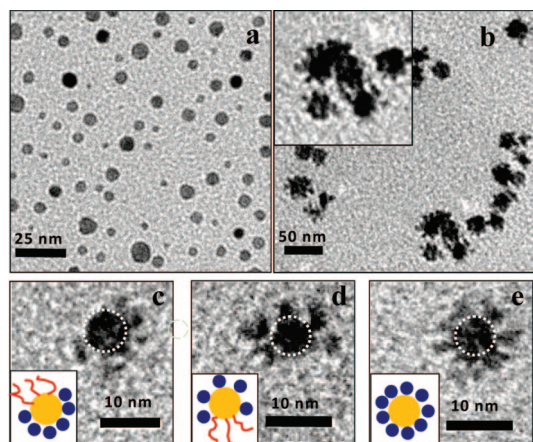


Figure 2. (a) TEM images of Janus AuNPs: PEO-Au-PMMA dispersed in chloroform and (b, c, d, and e) platinum nanoparticle-decorated PEO-Au-PAA (gold, AuNPs; blue, PtNPs; red, PEO).

used to demonstrate ~ 400 nm Janus particles.^{3,10} Furthermore, $-\text{COOH}$ has been used to adsorb metal ions for in situ metal NP synthesis.¹¹ In our preliminary work, to demonstrate the Janus feature of the NP complex, we synthesized Janus AuNPs modified with PEO and poly(*tert*-butyl acrylate) (PtBA) (PEO-Au-PtBA), hydrolysis of which led to PEO/poly(acrylic acid)-functionalized Janus AuNPs (PEO-Au-PAA, Supporting Information). Platinum NPs (PtNPs) were synthesized in situ in the PAA regions of PEO-Au-PAA following the reported procedure.¹² The formation of PtNPs on AuNP surface was supported by UV-vis experiments which showed the disappearance of the surface plasmon resonance peak of AuNPs upon PtNP formation (Figure S4).¹³ Figure 2b shows a TEM micrograph of PtNP-decorated Janus AuNPs, and Figure 2c–e are the enlarged images. The center cores (within the dashed circles in Figure 2c–e) are AuNPs with a diameter of ~ 6 nm and the decorated PtNPs have a diameter of ~ 1 to 2 nm, consistent with the reported data.¹² In most of the NP complexes we observed, PtNPs occupy $\sim 3/4$ of the AuNP surface while the rest of the area appears “empty” (Figure 2c,d). As a control experiment, symmetric PAA-modified AuNPs were synthesized (Figure S5, S6a). A similar PtNP-decoration experiment was conducted and the results showed that all the AuNPs were symmetrically decorated with PtNPs (Figure S6b). These results clearly demonstrate that in PEO-Au-PAA, PEO and PAA (thus PtBA) cover opposite sides of the AuNPs. Therefore, the NPs synthesized by combining grafting-to and grafting-from methods are Janus in nature. Note that very few PEO-Au-PAA NPs appear symmetrically decorated with PtNPs (Figure 2e); this might be due to the different orientations of these NP complexes on TEM grids, that is, the PEO

area might be directly underneath/above the AuNP and therefore cannot be observed because of the transmission image mode used in the TEM experiment.

In summary, by combining polymer single crystal solid-state grafting-to and grafting-from methods, Janus AuNPs with two types of different polymer chains decorated on the opposite sides of the NPs were achieved. Amphiphilic PEO-Au-PMMA and PEO-Au-PtBA and hydrophilic PEO-Au-PAA were synthesized. The Janus nature was clearly demonstrated using the PtNP-decoration method. Using polymer single crystals as the reaction substrates is advantageous because they afford higher throughput compared with self-assembled monolayers. Dissolution of the single crystal also leads to NPs with defined polymer patches. A number of crystalline polymers such as polyethylene, Nylon, or polypeptides could be used as the single crystal templates. We anticipate that our approach could serve as a generic method for synthesizing polymer-functionalized Janus NPs and this unique system holds promises for achieving controlled assembly and tunable optic and electronic properties of NPs.

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Supporting Information Available: Experimental procedures for synthesis and characterization of polymer-modified AuNPs, GPC data, TEM images, FTIR, and UV-vis spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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