



Surface engineered gold nanoparticles through highly stable metal–surfactant complexes



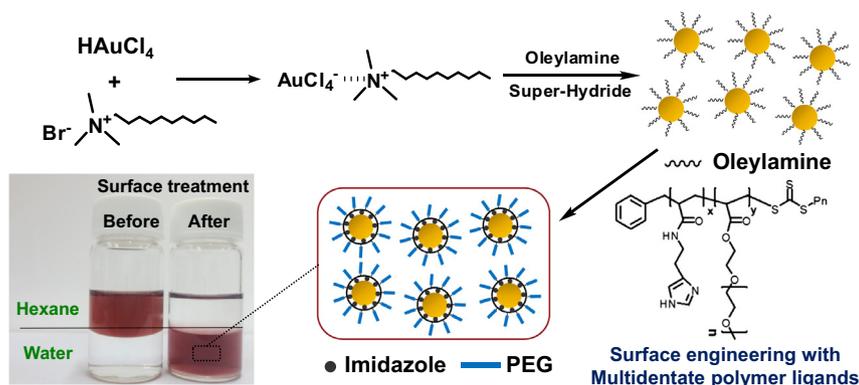
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GRAPHICAL ABSTRACT



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ABSTRACT

Monodispersed Au nanoparticles were synthesized by the reduction of Au-decyltrimethylammonium bromide (Au-DTAB), which was easily prepared via the reaction of HAuCl_4 and DTAB. This Au-DTAB complex is highly stable in air and moisture, and suitable for large-scale synthesis of uniform-sized Au nanoparticles. The nanoparticles were characterized by transmission electron microscopy, optical absorption spectrometry, X-ray diffraction, and Fourier Transform infrared spectroscopy. The size of Au nanoparticles was controlled in the range of 5–10 nm by changing the concentrations of reducing agent and Au precursor. The resulting Au nanoparticles were transferred to the aqueous phase after surface engineering using multidentate polymeric ligands with multiple imidazole functional groups. Polymeric imidazole ligands (PILs) demonstrated enhanced binding stability with the Au surface, and overcame the disadvantage of multidentate thiol ligand systems which have oxidative cross-linking and the formation of disulfide bonding. The colloidal stability of surface engineered Au nanoparticles with PILs was investigated by dynamic light scattering (DLS) characterization.

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1. Introduction

Synthetic chemistry of nanomaterials has developed rapidly over the last two decades, motivated by the unique chemical, physical, optical, magnetic, and mechanical properties of nanoparticles that are never observed in their bulk counterparts [1–4]. Novel properties of nanomaterials are of great importance not only for fundamental scientific interest, but also for many technological applications such as nanoelectronics [5,6], biological application [7–11], and magnetic devices [12,13]. Such properties are strongly correlated with the dimensions of the nanomaterials [14,15]. As a result, the synthesis of monodispersed nanoparticles with controlled size and shape is a key step for their application. Au nanoparticles have been the most intensely studied noble metal nanoparticles throughout the history of nanomaterial synthesis, and many potential applications have been studied to date [16–23]. Due to their plasmonic properties and good biocompatibility, bioconjugated Au nanoparticles have been intensively studied for applications in diagnosis and cancer therapy [20–23].

Since Faraday's report on the synthesis of an Au sol in the 19th century, various synthetic methods for Au nanoparticles have been reported [24–36]. Hydrogen tetrachloroaurate (HAuCl_4) is a popular Au precursor for the synthesis of Au nanoparticles. However, it is unstable in air and deteriorates under ambient conditions, absorbing moisture. Because the instability of the Au precursor is one of the major obstacles for the large-scale synthesis of Au nanoparticles, the preparation of a stable precursor has been strongly desired. In this study, we prepared a highly stable Au–surfactant complex from a simple reaction between an Au salt and a surfactant. Using this precursor, monodispersed Au nanoparticles were prepared by the reduction method. This method is highly reliable and suitable for large-scale synthesis. The synthesized nanoparticles were capped with alkylamine, which has moderate binding affinity to the Au surface compared with alkylthiol. Therefore, the surface of nanoparticles can be easily engineered, depending on their purpose. Here, Au nanoparticles were ligand exchanged with polymeric imidazole ligands (PILs) to impart water solubility, which is essential for biological applications.

Thiol-based coordinating ligands such as mercaptoalkyl carboxylic acid, and lipoic acid, have been widely used for the surface modification of Au nanoparticles. In spite of the high binding affinity of thiol to Au surfaces, Au nanoparticles passivated with monothiol ligands are quite unstable under high temperature conditions [37,38] and in the presence of competing thiols [39–41] or oxidizing agents [42,43]. In order to enhance the dispersibility of Au nanoparticles, there have been several reports of a multidentate approach in which the number of thiols per ligand is increased [44–46]. In fact, it is quite difficult to protect the oxidative cross-linking between neighboring thiol ligands because of the dimerization of the thiol groups, and the reaction process for synthesizing multidentate thiol ligands with a controlled distance between the thiol ligands is quite complicated.

Recently, several groups have introduced imidazole bearing ligands for biomolecule conjugation [47–49] or immobilization [50], demonstrating that imidazole functional groups exhibit high affinity to an Au surface. Here, we report that multidentate PILs with multiple imidazole functional groups can exhibit enhanced binding stability with the Au surface, and overcome the disadvantages of thiol-based bidentate or multidentate ligands systems. We successfully modified the surface of Au nanoparticles using these designed PILs, to transfer into the aqueous phase, demonstrating long term stability of colloidal dispersion over one month. In addition, we studied the influence of PILs on the colloidal stability of Au nanoparticles, by controlling the ratio of imidazole anchor group and the repeating number of PEG moiety under various conditions.

2. Experimental section

2.1. Chemicals

Hydrogen tetrachloroaurate (III) hydrate ($\text{HAuCl}_4 \cdot \text{H}_2\text{O}$) was purchased from Strem. Decyltrimethylammonium bromide (DTAB; $\text{CH}_3(\text{CH}_2)_9\text{N}(\text{CH}_3)_3\text{Br}$) was purchased from Acros. Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) was purchased from TCI. Polyethylene glycol methyl ether acrylate M.W. 1000 (methoxyPEG acrylate) was purchased from Alfa Aesar. α, α -Azobis(isobutyronitrile) (AIBN) was purchased from Junsei. All other chemicals were obtained from Sigma Aldrich. Hexane, tetrahydrofuran (THF), ethanol, N,N-Dimethylformamide (DMF), methanol, and acetone were used without further purification.

2.2. Synthesis of Au-DTAB complex

The Au-DTAB complex was prepared by adding 3.0 g of DTAB to a solution of 1.0 g of $\text{HAuCl}_4 \cdot \text{H}_2\text{O}$ in 20 mL of H_2O at room temperature. The color of the solution turned to deep orange after complete dissolution of the precursor, indicating the formation of the Au-DTAB complex. The resulting metal complex was extracted with 30 mL of hexane, and separated using a separating funnel.

2.3. Synthesis of Au nanoparticles

Au nanoparticles were synthesized via chemical reduction of the Au-DTAB precursor by super-hydride[®] in solution mixtures including ethylene glycol, THF, and oleylamine. For the synthesis of 5 nm Au nanoparticles, a mixture of 0.1 g of Au-DTAB, 2 mL of ethylene glycol, and 3.0 mL of THF was loaded into the three-neck round bottom flask. This reaction mixture was heated to 50 °C in air, and 1.0 mL of oleylamine was added. After injecting 1.0 mL of super-hydride, this solution was aged at 50 °C for 1 h. As the reduction reaction proceeded, the color of the solution turned from red to deep purple. After completion of the reaction, nanoparticles were precipitated by adding excess ethanol, and collected by centrifugation. Dried nanoparticles were easily dispersed in hexane with good colloidal stability. For the synthesis of 6 and 7 nm Au nanoparticles, 2.0 and 3.0 mL of oleylamine were used, respectively, with other steps in the procedure unchanged. For the synthesis of 10 nm Au nanoparticles, a mixture containing 2.0 g of Au-DTAB, 4.0 mL of ethylene glycol, and 7.0 mL of THF was used, with no change to the rest of the procedure.

2.4. Synthesis of PILs, PIL_{40%}-PEG(480)

PILs were denoted as PIL_{x%}-PEG(MW) with respect to the ratio of imidazole monomer(x) and PEG acrylate monomer molecular weight (MW) during the polymerization process. Other types of PIL_{x%}-PEG(MW) were synthesized by controlling the composition of monomers and the chain length of PEG acrylate monomers.

In a typical synthesis, Monomer **1** and PIL_{40%}-PEG480 were synthesized using a previously reported method with slight modification [51]. The prepared monomer was kept as a dilute stock solution at 100 mg/mL in methanol. Stock solution of reversible addition-fragmentation chain transfer-mediated (RAFT) agent was prepared at 271 mg/mL in DMF, and AIBN was prepared at 50 mg/mL in DMF. Monomer **1** (31.8 mg, 0.12 mmol), monomer **2** (86.4 mg, 0.18 mmol), and RAFT agent (2.90 mg, 0.01 mmol) were added to a 5 mL vial. The solvent was removed in vacuo and then 150 μL of dry DMF and AIBN (1.64 mg, 0.01 mmol) were added. The contents were mixed, centrifuged at 4000 rpm for 2 min, and then transferred to a 2 mL ampule. The ampule was subjected to 4 freeze–pump–thaw cycles, and sealed under vacuum using

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