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Tailoring the surface potential of gold nanoparticles with self-assembled monolayers with mixed functional groups

Yu-Chin Lin [a], Bang-Ying Yu [a], Wei-Chun Lin [a], Szu-Hsian Lee [b], Che-Hung Kuo [b], Jing-Jong Shyue [a,b,*]

[a] Research Center for Applied Sciences, Academia Sinica, Taipei 115, Taiwan
[b] Department of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan

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ABSTRACT

Self-assembled monolayer (SAM)-modified gold nanoparticles can be used to immobilize and transport molecules including DNA and proteins. However, these molecules are usually covalently bound to the surface and chemical reactions are required to cleave and release them. Therefore, immobilizing molecules using electrostatic interactions might be beneficial. In this work, Au nanoparticles modified by SAMs with mixed carboxylic acid and amine functional groups are presented. The surface potential and the iso-electric point (IEP) of the nanoparticles can be tailored by the ratio of these functional groups and arbitrary IEPs between 3.2 and 7.3 can be achieved. As a result, based on electrostatic interactions, molecules could be triggered to adsorb/desorb by changing the environmental pH around this tunable IEP. These engineered nanoparticles were synthesized in a single-phase system based on the reduction of $HAuCl_4$ by $NaBH_4$ in ethanol with a mixture of 16-mercaptohexadecanoic acid and 8-amino-1-octanethiol that forms the SAM on the synthesized nanoparticles. Transmission electron microscopy, X-ray photoelectron spectroscopy, and electrophoresis light scattering revealed the particle size, ratio of the functional groups, and zeta-potential of the particles as a function of pH, respectively.

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1. Introduction

Self-assembled monolayers (SAMs) provide a convenient and simple system to tailor the interfacial properties of metals, ceramics, and semiconductors. A major thrust in SAM research is the continual expansion in the substrates used to support SAMs and the types of surface functional groups that are used [1]. Different surface functional groups and different types of SAMs are found to either promote or inhibit the adhesion of materials based on electrostatic interactions. Many studies have focused on the selective growth of inorganic thin-films on SAMs that are controlled by the electrostatic interactions between the precursor and the organic functional group of SAMs [2–6]. Based on the concept of electrostatic interaction, selective immobilization and release of bio-materials on SAMs could be achieved and a molecule transportation system could be developed.

The most extensively studied class of SAMs is derived from the adsorption of alkanethiols on gold [7–11], because gold binds thiols with a high affinity [7]. Moreover, SAMs form on objects of all sizes, are critical components that determine specific properties of the object and stabilize nanomaterials. Brust et al. opened an avenue to the synthesis of gold nanoparticles (AuNPs) stabilized by a variety of functional thiol ligands [12–14]. Subsequently, many publications have described the use of the Brust–Schiffrin procedure for the synthesis of other stable AuNPs that contain functional thiols [15–18]. While the Brust–Schiffrin method yields high-quality and mono-dispersed AuNPs, the use of hazardous organic solvents and phase transfer agents could limit its application in biological systems. Therefore, an environmentally benign process could be advantageous.

Tailoring surface properties with a single functional group is useful for applications in nanotechnology that depend on the chemical composition of the surface [19]. However, for molecule transportation where the pH range is often limited, the ability to control the surface potential is necessary so that the surface charge can flip at a specific pH to trigger the adsorption or desorption of molecules. For a given functional group, the surface potential is controlled by the properties of the functional group, so it is not possible to tailor the iso-electric point (IEP) where the charge flip occurs. For example, gold nanoparticles modified with amine-SAM tend to be positively charged and have high IEPs due to the weak-base nature of amine groups. Similarly, gold nanoparticles modified with carboxylic acid-SAM tend to have a low IEP due to the weak-acid nature of the functional group. Recently, the concept of tailoring the surface potential with mixed functional groups has been reported [20]. In this concept, homogeneously mixed functional groups with opposite surface charge will result in charge cancelation (Fig. 1). Consequently, it is possible to tailor the surface potential by altering the functional groups ratio.

* Corresponding author. Address: Research Center for Applied Sciences, Academia Sinica, 128 Section 2, Academia Road, Taipei 115, Taiwan.
E-mail address: shyue@gate.sinica.edu.tw (J.-J. Shyue).

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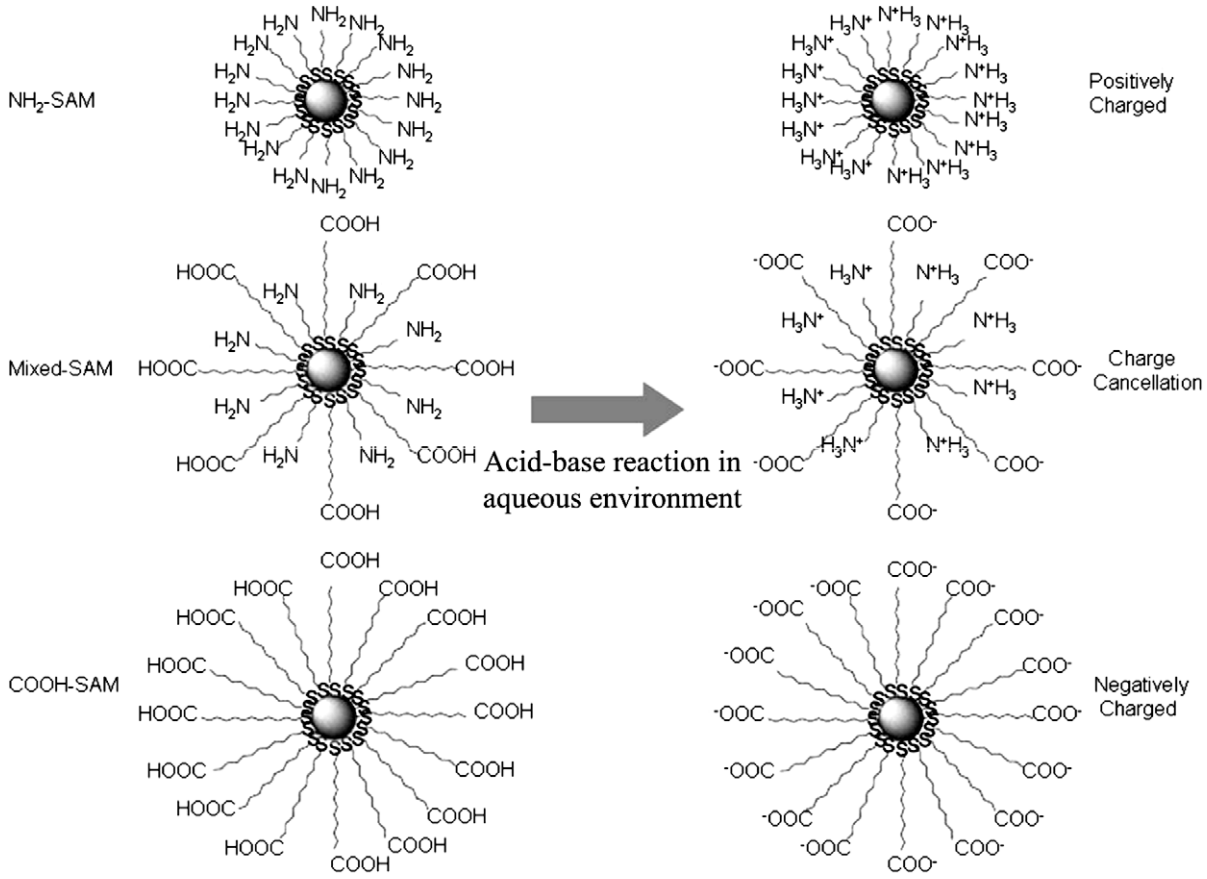

Fig. 1. The structure of gold nanoparticles modified with SAMs and charge formation in an aqueous solution.

In this work, nanoparticles with a size distribution of 2–10 nm were synthesized in a single-phase system based on the reduction of $HAuCl_4$ by $NaBH_4$ in a water–ethanol solution with the presence of 16-mercaptohexadecanoic acid and 8-amino-1-octanethiol that forms the SAM on the synthesized nanoparticle. By avoiding the use of hazardous solvents and phase transfer agents, the process is environmentally benign. Through altering the ratio of thiols, AuNPs with IEPs between 3.2 and 7.3 could be synthesized.

2. Materials and methods

2.1. Particle preparation

Modified gold nanoparticles were synthesized with 16-mercaptohexadecanoic acid (Aldrich, USA), 8-amino-1-octanethiol (Dojindo, Japan) or a combination of both. The synthesis procedure is modified from the procedure of Chen and Kimura [21]. A quantity of 0.05 g of hydrogen tetrachloroaurate (Acros Organics, Germany) was dissolved in 2 mL DI water then mixed with a solution of 16-mercaptohexadecanoic acid and 8-amino-1-octanethiol dissolved in 100 mL ethanol. The proportion of total thiol:Au used in the synthesis was fixed at 1:3 and the ratio between thiols was varied. A freshly prepared 10 mL aqueous solution of sodium borohydride (0.02 g, Acros Organics, USA) was then added dropwise at a rate of 0.01 mL/min with vigorous stirring. The resulting dark brown solution was stirred for an additional hour, after which the gold nanoparticles were collected by decantation and centrifugation. The particles were washed by dispersing them in water and then in ethanol by removing the solvent using centrifuge. The cleaning procedure was repeated three times to remove impurities and byproducts as well as excess layers of surfactant formed on SAMs through acid–base reaction. A drop of 1 M HCl was sometimes added to ensure that Na^+ ions were displaced from the 16-mercaptohexadecanoic acid groups [22].

2.2. Characterization

A transmission electron microscope (TEM, operated at 200 kV; JEOL JEM-2100F, Japan) was used to examine the size distribution of gold nanoparticles. Scanning X-ray photoelectron spectroscopy (XPS/ESCA; PHI 5000 VersaProbe, ULVAC-PHI, Japan) was used to confirm the existence and determine the ratio of functional groups. The spectra were recorded with micro-focused Al Kα X-ray radiation (25 W, 100 μm). The take-off angle of the photoelectron was fixed at 45°. High resolution N(1s), S(2p), Au 4f and C(1s) spectra were collected with an analyzer pass energy of 58.7 eV and a step size of 0.5 eV. Peak positions were referenced to Au 4f at 84 eV. Nanoparticles modified with single functional group are used as referencing standards for quantification analysis of the spectra. The IEP of gold nanoparticles was obtained by using electrophoresis light scattering (90-Plus ZetaPALS, Brookhaven Instruments Corp., USA) in a 1 mM NaCl supporting electrolyte.

3. Results and discussion

3.1. Synthesis

Mixed carboxylic acid-SAM- and amine-SAM-modified gold nanoparticles were synthesized based on the reduction of hydrogen tetrachloroaurate(III) by sodium borohydride in ethanol, rather than extracted into toluene and metathesized to the tetraoctylammonium salt. Because $HAuCl_4$ and $NaBH_4$ do not dissolve in ethanol di-

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