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Synthesis of 16-Mercaptohexadecanoic acid capped gold nanoparticles and their immobilization on a substrate

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ABSTRACT

Controlled assembly of nanoparticles on substrates is a promising path to develop miniaturized electronic and optical devices. Among the important issues to be addressed in this area include immobilization of the nanoparticles on substrates in order to ensure that the system is robust. In this work, 16-mercaptohexadecanoic acid (16-MHDA) capped gold nanoparticles with a narrow size distribution have been synthesized through a single phase synthesis method and subsequently immobilized on to silicon surface through covalent molecular assembly. Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) confirmed the absence of unreacted thiol in the synthesized gold nanoparticles. Presence of gold nanoparticles on Si surface after the immobilization process was confirmed through XPS. Cross-sectional high resolution transmission electron microscopy (HR-TEM) images provide direct evidence that the particles are indeed anchored to the silicon surface. The formation of uniform-sized and separated acid functionalized gold nanoparticles and their immobilization on to Si provide a basis for further nano-structuring.

1. Introduction

Two-dimensional assemblies of monodisperse metal particles with controlled size in nano scale range have potential applications in solid state electronic devices [1,2]. Functionalized gold nanoparticles (AuNPs) are attractive for many of these applications since properties such as solubility [3] and electron density [4] can be tuned with capping ligands. While reduction of auric chloride in aqueous media is well known [5], synthesis of p-mercaptophenol stabilized AuNPs in a single phase by Brust et al. [6, 7] has opened new avenues in creating functionalized thiol capped nanoparticles. Despite continuous progress in this field, there still remain significant limitations for practical applications due to weak interactions that can disrupt the assemblies by dissolution, pH change or heating. Drop cast films of capped nanoparticles have been investigated for electron transfer applications [8]. However, drop cast films lose adhesion to the substrate when exposed to the solvent media. Recently, the Langmuir–Blodgett deposition of organically passivated AuNPs has been reported for flash memory application [9], ester-modified Pd nanoparticles have been immobilized on the substrate through hydrogen bonding [10] and citrate-capped AuNPs have been electrostatically assembled on to carbon surfaces [11]. But these nanoparticle films are not mechanically robust due to weak interlayer bonding. Films with covalent interlayer bonding are more advantageous due to their ability to withstand elevated temperature, polar solvent attack and mechanical wear and abrasion [12].

Covalent immobilization of AuNPs on to gold substrate has been demonstrated through oxime, ester and amide binding between functionalized gold nanoparticles and self-assembled monolayer (SAMs) modified gold surface [13–15]. However, the SAMs on the gold surface degrade structurally and the alkanethiols desorb over a period of days [16]. As opposed to thiol-based SAMs, silane-based SAMs are thermally and chemically robust, and are stable even at temperatures approaching 600 K in an inert nitrogen environment [17]. Various metal nanoparticles capped with inert ligands (such as alkene functionalized Ag nanoparticles [18] and monodisperse $MnFe_2O_4$ nanoparticles [19]) have been immobilized on Si substrates. However, there is no information available about the morphology of the immobilized nanoparticles. A series of inert ω-alkene-1-thiol-protected AuNPs has been covalently immobilized on to hydrogen-terminated silicon surfaces by thermal hydrosilylation reactions [20]. While most of the published work involves capping of nanoparticles with inert species, use of functionalized capping species will enable specific interactions with the substrate and facilitate immobilization. Use of functional species as capping agents can also facilitate formation of multilayers with covalent interlayer links. The challenge in adopting this technique lies in preventing undesirable interactions between the capping agents that may lead to aggregation of the nanoparticles. In this paper, we report synthesis of well-separated 16-MHDA capped AuNPs having a narrow size distribution and their covalent immobilization on to silicon surfaces without causing aggregation of nanoparticles. To our knowledge, this work represents

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the first attempt in providing direct evidence for covalently anchored functionalized AuNPs on a SAM modified Si surface through cross-sectional HR-TEM.

2. Experimental

2.1. Synthesis of thiol-stabilized gold nanoparticles

16-MHDA capped AuNPs were synthesized by employing two methods: one carried out at room temperature (method A) and the other at 0 °C (method B). Nanoparticles were synthesized at room temperature by a procedure similar to reported previously [6]. For the nanoparticles synthesis at 0 °C, 5 mL of 0.05 M 16-MHDA solution in methanol was added to 20 mL of 5 mM $HAuCl_4.3H_2O$ in methanol with vigorous stirring, in a flask surrounded by an ice–water mixture at 0 °C. After 10 min, 40 mL of freshly prepared 0.39 M aqueous sodium borohydride was added to the mixture with stirring. After reaction, the precipitate was washed twice with a 20% (v/v) water/methanol solution to remove excess surfactants, centrifuged to remove solvents and finally vacuum dried at room temperature.

2.2. Immobilization on silicon surface

3-cyanopropyltrichlorosilane (CPS) (98%, Lancaster) functionalized silicon surface was prepared as described elsewhere [21]. The cyano functional group at the free end of the immobilized silane was hydrolyzed to carboxylic acid. Acid to acid chloride conversion was performed in a gaseous phase of $SOCl_2$ [22]. Acid terminated nanoparticles were covalently bound to the acid chloride-derivatized surface through anhydride formation [23]. The acid chloride-containing surfaces were immersed in a 100 μg/mL solution of 16-MHDA capped AuNPs in DMAc at 75 °C for 2 h after the addition of 50 μL of pyridine which acted as catalyst and proton scavenger. Subsequently, the substrates were rinsed with DMAc followed by sonication for 10 min in DMAc to remove any physically bound nanoparticles and rinsed again with DMAc as well as acetone, and were finally blown dry with nitrogen. Details of various deposition steps are shown in Fig. 1a.

2.3. Characterization

FTIR was carried out using a Bio-Rad FTIR 3500 system in the transmission mode. Samples for TEM (JEM-2010 TEM (JEOL)) were

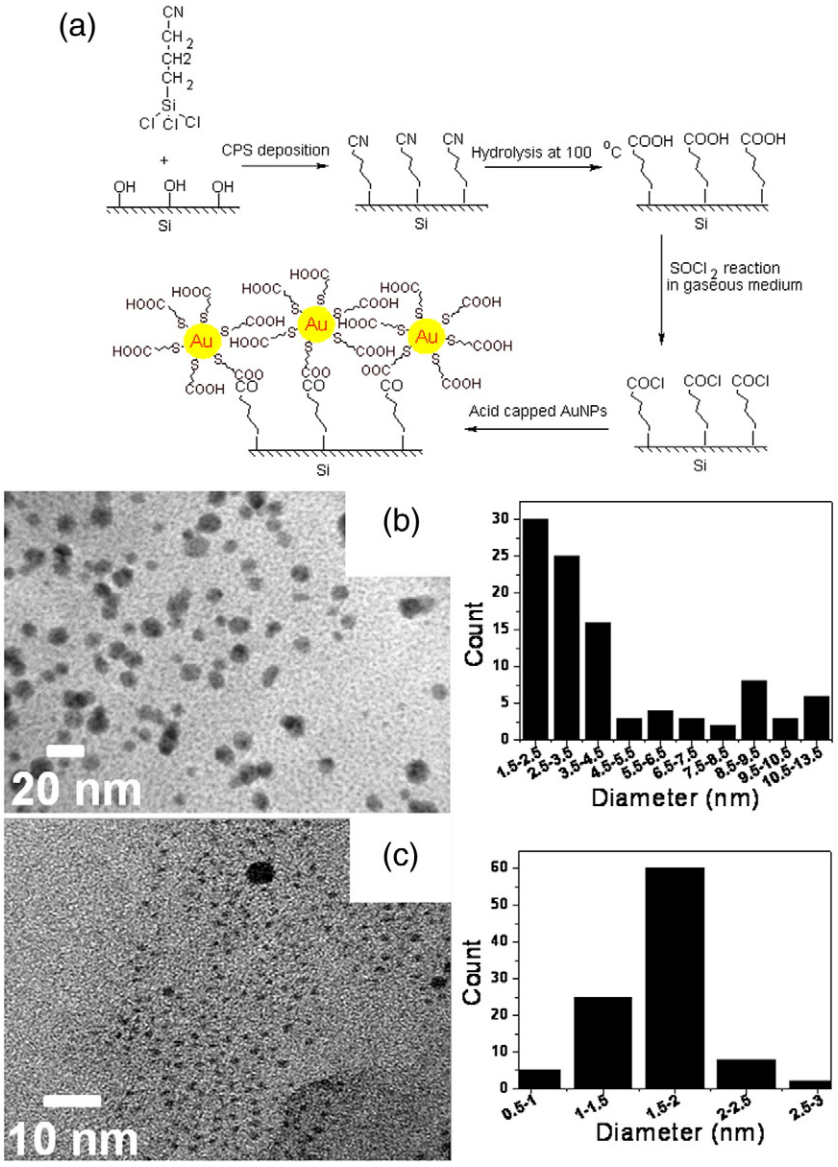

Fig. 1. (a) Schematic for immobilization of acid terminated gold nanoparticles on to a hydroxyl-terminated silicon surface, TEM images and size histograms for 16-MHDA capped gold nanoparticles synthesized by (b) Method A — carried out at room temperature and (c) Method B — carried out at 0 °C.