Immobilization and Assembly of Mixed Monolayer-Protected Au Nanoparticles on Glass substrate via Covalent Bond Interconnection

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The fabrication of two-dimensional, covalent bond-mediated assembly of gold nanoparticles on glass substrates is reported herein. Highly monodispersed gold nanoparticles protected by mixed monolayers comprising of decanethiol (DT) and 11-mercapto-1-undecanol (MUO) are covalently immobilized on isocyanate-bearing layers on glass substrates through carbamate-forming reaction. Specifically, two-dimensional structures of these immobilized gold nanoparticles depend on the surface monolayer coverage of MUO molecules attached on the nanoparticles. The lower coverage allows formation of ordered two-dimensional superlattice, whereas increase in the MUO coverage induces disordered assembly and sometimes domain structures, as indicated by atomic force microscopy (AFM) and transmission electron microscopy (TEM). The reason for this can be due to a steric effect and a significant change in the hydrophobicity of protective monolayers associated with interaction between immobilized gold nanoparticles.
Key words: Au nanoparticles, Surface functionalization, Immobilization, Carbamate bond

1. INTRODUCTION

Composite nanostructures consisting of metal nanoparticles and organic surroundings have attracted recently for both fundamental and practical reasons.[1] In particular, much effort has been devoted to directing monolayer-protected metal nanoparticles into organized structures onto solid state substrates by a variety of fabrication techniques.[2-6] The nanostructures of these immobilized nanoparticles have been recognized as promising candidates for future generations of optical and nanoelectronics devices. One of the emerging techniques for immobilization is to use organic monolayers attached on the nanoparticles and substrate of interest to guide the assembly of the nanoparticles through predesigned chemical and physical interactions. Self-assembly,[7-9] electrostatic interaction,[10,11] hydrogen bonding,[12] molecular linking,[13] and covalent bonding[14,15] has been used in a directed-immobilization process for the nanoparticles. Most notably, monolayer-protected gold (Au) nanoparticles are widely used to create two- or three-dimensional assembly that involve organized artificial nanostructures, which has been carried out onto a specific layers including self-assembled monolayers and functional polymers initially deposited on supports of interest. The selectivity and resulted relative stability of covalent bond-forming reactions make it particularly attractive for immobilizing the nanoparticles, especially for fabrication of the optical and electronic devices that can operate under ambient conditions.

In practice, covalent bond-forming reaction between functional groups bearing on nanoparticles and those on supports are generally limited by factors such as structure of monolayers, reactivity of functional groups, and stability of nanoparticles at desired reaction temperature. Thus, the selection of stable coupling partners that can be reactive in mild conditions is critical to covalent bond-mediated immobilization of nanoparticles. Thus far, the reactions used for immobilization of monolayer-protected Au nanoparticles include oxime-coupling between ketones and aminooxy groups for gold substrates,[16] and amide-coupling between carboxylic anhydride and amine groups for silica substrates and colloids.[17] However, the former process requires the synthesis of organic ligands, and the later process involves the transformation into interchain carboxylic anhydride after the synthesis of Au nanoparticles functionalized with carboxylic acid groups. Herein, we report a simple and general method for immobilizing the highly monodispersed, mixed monolayer-protected gold nanoparticles on glass substrate through covalent bond-forming reaction that occurs at room temperature. The use of highly monodispersed nanoparticles is a key concept not only for fabricating perfect ordered structures of nanoparticles but also for investigating their size-dependent physical and chemical properties. In addition, chemical properties of monolayers protecting the nanoparticles plays a key role in determining

two-demensional structures of immobilized nanoparticles, of which are associated with particle-support and particle-particle interactions.

2. EXPERIMENTAL

Synthesis of DT-stabilized Au Nanoparticles

Au nanoparticles were prepared by Brust method.[18] Briefly, a solution of tetraoctylammonium bromide (328 mg, 0.60 mmol) in toluene (40 mL) was added to an aqueous solution of HAuCl$_4$ · 4H$_2$O (15 mM, 20 mL, 0.30 mmol). A solution of 1-decanethiol (DT) (65.5 mg, 0.3 mmol) in toluene (10 mL) was then gradually added to the resulting mixture while stirring vigorously, followed by dropwise addition of a freshly prepared aqueous solution of NaBH$_4$ (0.30 M, 10 mL, 3.0 mmol). After stirring the mixture for 3 h, the organic layer was separated, and concentrated to dryness under reduced pressure. The black solid thus obtained was heated at 170 °C for 20 min to grow Au nanoparticles.[19]

Surface Modification Using Place-Exchange Reaction.

After the purification with ethanol, Au nanoparticles were dispersed in THF, and 11-mercapto-1-undecanol (MUO) molecules in THF were then added into nanoparticles solution. The resulting products were characterized by TEM, FT-IR and NMR.

Immobilization of Au Nanaoparticles Through Carbamate Bond-Forming Reaction.

The quartz substrate was cleaned by irradiation of vacuum ultraviolet (VUV) light (wavelength: 172 nm) for 20 min and then immersed in toluene containing hexamethylene diisocyanate (1M, 5 mL) at room temperature for 4 h, followed by rinsing with toluene under ultrasonication. The isocyanate-functionalized quartz substrate was immersed in THF containing hydroxyl group-functionalized Au nanoparticles for 2 h. The resulting substrates were characterized by XPS, AFM and TEM.

3. RESULTS AND DISCUSSION

Surface Modification of Au Nanoparticles by Partial Introduction of MUO Molecules.

Figure 1 schematically describes the procedure for the preparation of size-controlled, DT-protected Au nanoparticles (DT-Au) and DT/MUO-protected Au nanoparticles (DT/MUO-Au). The mean size of DT-Au was determined to be 4.3 nm (standard deviation = 0.26 nm) by TEM observation. The surface modification process and reactivity of introduced hydroxyl groups on Au nanoparticles were characterized by FT-IR, as shown in Figure 2. The FT-IR spectrum of products after heat treatment clearly shows the C-H stretching bands around 2900 cm^{-1}, which are assigned to alkyl chains of DT molecules. After place exchange with MUO, the spectrum of the resulting nanocrystals show that C-H
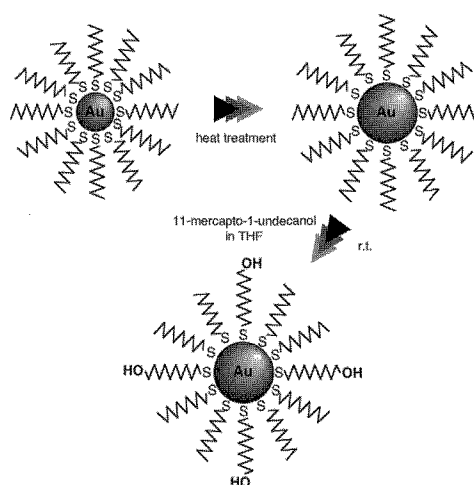

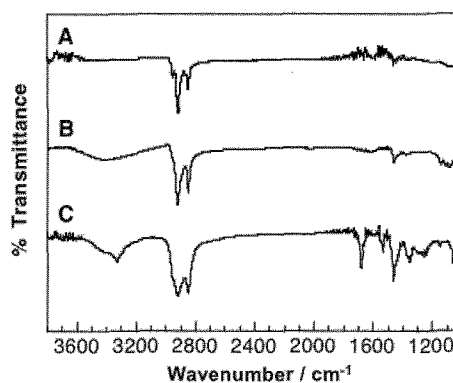**Figure 1.** Schematic illustration for preparation of DT/MUO-stabilized Au nanoparticles.

Figure 2. FT-IR spectra of the nanocrystals obtained after heat treatment (A), place-exchange reaction (B), and reaction with isocyanic acid *n*-octadecyl ester (C).

stretching bands remain unchanged, whereas weak absorption bands are observed around 3400 cm^{-1} and at 1150 cm^{-1} which are associated with the O-H stretching and C-O stretching bands. In addition, The nanoparticles obtained after place-exchange reaction were soluble in THF but were found to be insoluble in non-polar solvents such as toluene and chloroform. These results indicate that partial introduction of MUO molecules was achieved by a place-exchange reaction. No change in mean size of Au nanoparticles was observed after place exchange reaction.

We used isocyanic acid *n*-octadecyl ester to characterize the reactivity of introduced hydroxyl groups on Au nanoparticles. The carbamate bond forming reaction between hydroxyl and isocyanate groups has been reported to proceed cleanly in ambient conditions
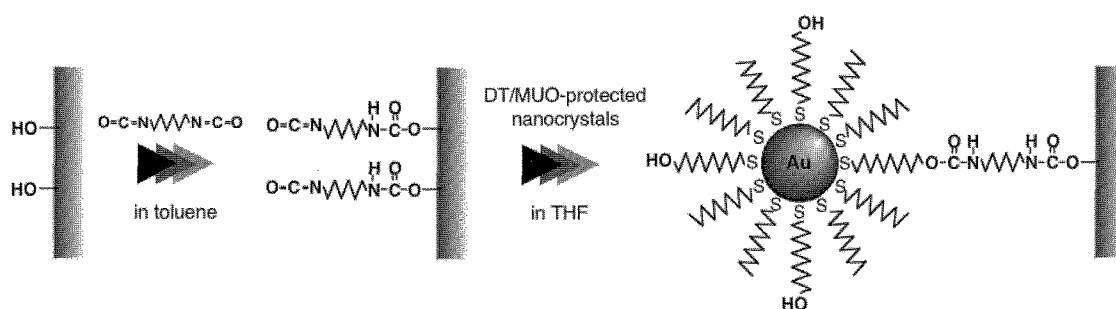
Figure 3. Schematic illustration for immobilization of Au nanoparticles on the isocyanate-bearing substrate through carbamate bond-forming reaction.
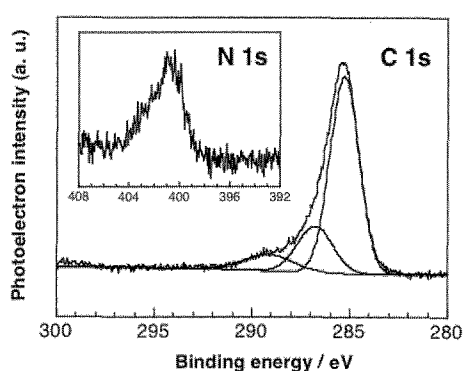

Figure 4. X-ray photoelectron spectra for C1s and N1s (inset) of Si wafer substrate obtained after surface modification with hexamethylene diisocyanate.

Figure 5. AFM images of immobilized Au nanoparticles on the Si wafer substrate. MUO coverage of Au nanopartcles is 18.7 %.

Figure 6. TEM images of immobilized Au nanoparticles with MUO coverage of 18.7 (A), 37.0 (B), and 56.3 % (C) in protective monolayers on glass substrate.

[20]. Figure 2C shows FT-IR spectra of the Au nanoparticles obtained after reaction with isocyanic acid *n*-octadecyl ester in THF solution for 3h. The spectrum of Au nanoparticles after the reaction (Figure 2C) is well-characterized by a band attributed to the characteristic vibration mode for carbamate groups formed by the reaction of hydroxyl with isocyanate groups, with primarily associated bands at 1690, 1550 and 1250 cm^{-1} arising from amid I (asymmetric C=O stretching), amide II and amide III (C-N stretching and N-H bending), respectively. The spectrum is similar in form to that of those observed for self-assembled monolayers of MUO on a Au substrate after reaction with 1,4-phenylene diisocyanate,[20] showing that the surface-bound hydroxyl groups could undergo covalent-forming reaction to form the corresponding carbamate groups in high yield.

Immobilization of Au Nanoparticles Through Carbamate Bond-Forming Reaction.

The hydroxyl group onto the nanoparticle surface can be used to immobilize the nanparticles on the
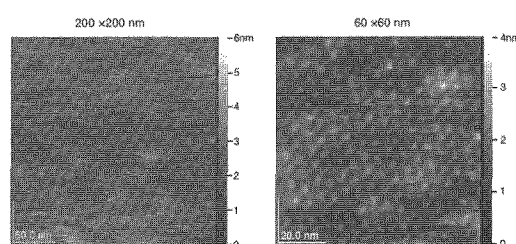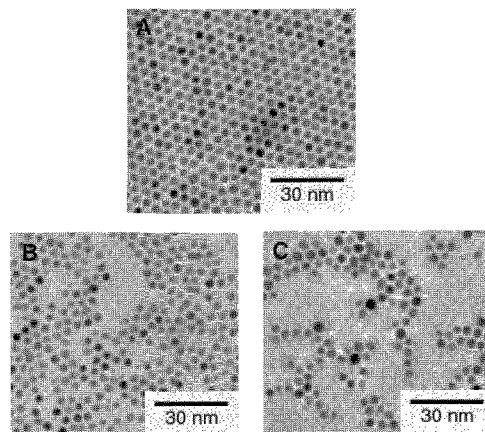
isocyanate-bearing quartz glass substrate through carbamate bond-forming reaction (Figure 3). To introduce the isocyanate groups, hexamethylene diisocyanate molecules were used as linker between the Au nanoparticles and the glass substrate. As shown in Figure 4, XPS measurements of the C (1S) and N (1S) on the substrate after immersion of hexamethylene

diisocyanate reveals that the substrate is functionalized with isocyanate groups.

Immobilization of Au nanoparticles was characterizaed by AFM in order to assess the surface topography of the layer. The AFM image in Figure 5 confirms that the Au nanoparticles are successfully immobilized on the glass substrate after immersion in THF containing DT/MUO-Au nanoparticles. Most of the nanoparticles are isolated individually to form an ordered two-dimensional hexagonal arrangement of the nanoparticle monolayer. To confirm that the observed morphology resulted from the immobilized Au nanoparticles, TEM observation was performed for the substrate after immobilization. This was achieved by removing the layer from the glass substrate using HF vapor. A typical TEM image is shown in Figure 6. The nanoparticles clearly have a mean diameter of 4.3 nm. This diameter is consistent with the starting DT/MUO-Au. The image further demonstrates that the immobilized Au nanoparticles form well-ordered two-dimensional superlattices.

It is well known that the degree of ordered arrangement is related to the monodispersity of nanoparticle diameter. For the present process, it is also strongly affected by the coverage of MUO on the Au nanoparticles. The immobilization does not proceed using the Au nanoparticles with lower degree of MUO surface coverage (< 10 %). For the surface coverage of MUO on Au nanoparticles below 15 %, Au nanoparticles were immobilized on the substrate. However, well-ordered arrangement was not observed in the images, which may be due to the poor reactivity of Au nanoparticles functionalized with MUO molecules. On the other hand, a higher degree of coverage above 30 %, which might induce the formation of multipoint carbamate bond, leads to disordered two-dimensional structure based on Au nanoparticles. The well-ordered hexagonal packing arrangement of nanoparticles was obtained as the immobilization process was conducted using Au nanoparticles with ca. 20 % surface coverage of MUO.

4. CONCLUSION

We have demonstrated the functionalization of Au nanoparticles with hydroxyl groups through place-exchange reaction and the formation of well-ordered two-dimensional structures through carbamate bond-forming reaction. The hydoroxyl groups onto the nanocrystal surface can readily react with the isocyanate groups onto the quartz substrate, resulting in the immobilization of Au nanoparticles onto the substrate through carbamate bond-forming reaction. The results reported herein have significant advantages in electronic devices based on Au nanoparticle building blocks.

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