

Covalent Bond-Mediated Network Fabrication of Carboxylic Anhydride-Protected Gold Nanoparticles

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The reactivity and network formation of Au nanoparticles protected by interchain carboxylic anhydride has been studied, which relies on a covalent bond formation that utilizes an amide-forming coupling reaction between carboxylic anhydride introduced on the surface of Au nanoparticles and amine-terminated molecules. The procedure involves the synthesis of Au nanoparticles protected by a carboxylic acid monolayer, followed by transformation of these protective molecules into interchain carboxylic anhydride by treatment with trifluoroacetic anhydride and triethylamine, as applied for self-assembled monolayers on gold substrates. The anhydride-protected Au nanoparticles are then reacted with amine-terminated molecules for facile surface modification and with diamine-terminated molecules providing Au nanoparticle-based networks connected through amide bond.

Keywords: Au nanoparticles, interchain carboxylic anhydride, network formation

1. INTRODUCTION

During the past decade, nanostructured composite materials of organically encapsulated metal nanoparticles have gained considerable attention due to their unique electrical and optical properties, which arise from the size-dependent physical properties of the nanoparticles [1-4]. Nanoparticle-based composites have potential applications in nanoelectronics and photonics devices [5,6], chemical sensors [7-9], and catalysis [10]. In particular, monolayer-protected gold nanoparticles have become an attractive materials as nanoscale building blocks for these nanocomposites [11-16].

The formation of two- and/or three-dimensional nanostructures based on monolayer-protected gold nanoparticles have been studied extensively, most of which have focused on the interconnection of individual Au nanoparticles through a variety of chemical and physical interaction. Among these, the process using non-covalent bond-mediated interconnection, e.g., self-assembly, electrostatic force, and molecular linking, has been the subject of intense study for the development of nanoparticle-based structures. It is, however, considered to be stable only under specific conditions, which limits their range of applications. To our knowledge, there are few studies related to the fabrication of the composites through interconnection of the particles mediated by covalent bond-forming reaction [17,18], although it may be suitable for the development of nanoelectronic devices due to their stability. In the previous work, we have reported the immobilization of Au nanoparticles on silica support through covalent bond formation [19]. The immobilization was achieved via amide-forming coupling reaction be-

tween carboxylic anhydride introduced on Au nanoparticle surface and amine end group attached on silica. The advantage of this approach is that an active site for amide-forming coupling (interchain carboxylic anhydride) is located at entire surface of the Au nanoparticles, which provides rapid and high yield formation of amide bonds. Since the conventionally used activation and ligand coupling strategy to form amide bond between carboxylic acid and amine groups using carbodiimide derivatives provides less reactivity in these hetero-phase systems due to steric hindrance of the ligands attached on Au nanoparticles [20], it may not be suitable for covalent bond-forming interconnection in these system. In this study, we extended previously developed facile process for stable covalent bond-forming reaction to fabricate macroscopic networks based on Au nanoparticles, which depends on the reaction and mixing conditions of these coupling partners (carboxylic anhydride and amine end group).

2. EXPERIMENTAL PROCEDURE

Nanometer-sized gold nanoparticles functionalized with 11-mercaptopundecanoic acid (MUA) were prepared by two phase solution method outlined by Brust et al. [21]. Transformation of carboxylic acid moieties to interchain carboxylic anhydride was performed according to our previous study [19]. Briefly, to a freshly prepared solution of trifluoroacetic anhydride (10 mmol) and triethylamine (20 mmol) in DMF was added a solution containing 30 mg of MUA-functionalized Au nanoparticles in DMF under dry argon. After stirring for 1 h, solvent and remaining triethylamine were removed by distillation at 45 °C under reduced pressure. The crude product was washed by distilled water

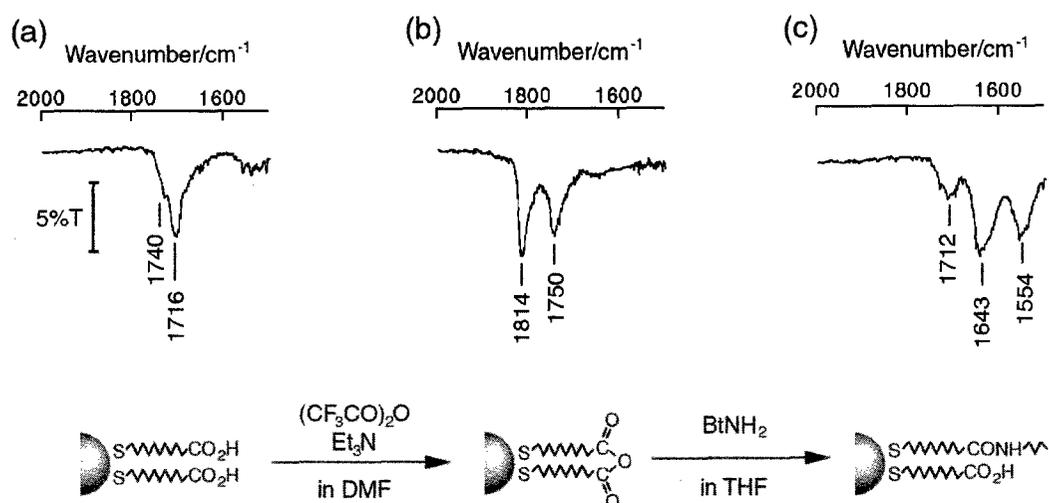


Fig. 1 Schematic diagram of present reactions for monolayers attached on Au nanoparticles and corresponding FT-IR spectra of MUA-functionalized Au nanoparticles (a), interchain carboxylic anhydride-functionalized Au nanoparticles (b) and Au nanoparticles functionalized with MUA and alkylamide (c).

and collected using 1.0 μm membrane filter, and then dried under vacuum.

Reactivity of interchain carboxylic anhydride-functionalized Au nanoparticles for amide-forming coupling was studied as follows: *n*-butylamine was dropped into the THF solution containing the anhydride-functionalized Au nanoparticles at room temperature. After stirring the mixture for 30 min, the solvent and remaining *n*-butylamine were evaporated under vacuum. For the preparation of network aggregates consisting of Au nanoparticles covalently linked through amide bond, ethylenediamine was added into THF solution containing the anhydride-functionalized Au nanoparticles in an appropriate proportions.

FT-IR spectra of the products were measured with infrared spectrometer (Magna-IR550, ThermoNicolet) in the range 400 - 4000 cm^{-1} . Mean size and morphology of the Au nanoparticles and their networks were observed using JEOL JEM-2000EX transmission electron microscope operating at 200 kV.

3. RESULTS AND DISCUSSION

Figure 1 shows schematic representation of the present transformation process of MUA into the anhydrides and corresponding FT-IR spectra in the region of carbonyl vibration modes. In Fig. 1a, the FT-IR spectrum for MUA-functionalized Au nanoparticles is well characterized by a band attributable to hydrogen-bonded (1716 cm^{-1}) and free carboxylic acids (1740 cm^{-1}) [22]. These terminal carboxylic acid groups of MUA attached on the surface of Au nanoparticles were successfully transformed into its anhydrides by treatment with trifluoroacetic anhydride and triethylamine under dry conditions. This is confirmed by FT-IR spectra shown in Fig 1b. After the treatment, two C=O stretching bands of carboxylic acids disappeared completely. Instead, two new bands assigned to C=O

asymmetric (1814 cm^{-1}) and symmetric (1750 cm^{-1}) stretching modes of carboxylic anhydride appeared, both of which arise from intra-molecular coupling in in-phase and out-of-phase modes, respectively, between the carbonyl vibrations [23]. The detailed analysis of the peak position and relative intensity of these stretching bands revealed that a unconjugated aliphatic carboxylic anhydrides were formed from carboxylic acids on adjacent chains attached on one Au core. These changes in FT-IR spectra suggest that the these anhydrides are similar to acyclic-type anhydride observed for self-assembled monolayers of 16-mercapthexanoic acids and their anhydrides on gold substrate [24].

The reaction of the surface anhydrides with *n*-butylamine proceeded cleanly, the FT-IR spectra of which is shown in Fig. 1c. After the reaction of the anhydride-protected Au nanoparticles and *n*-butylamine, the two C=O stretching bands characteristic of the interchain anhydride disappeared completely and some new bands appeared. The bands observed at 1643 cm^{-1} and 1554 cm^{-1} are assigned to C=O stretching (amide I) and N-H bending (amide II) modes of the amide bond [25], and the band at 1712 cm^{-1} arises from C=O stretching vibration of the carboxylic acid. In the C-H stretching region, the band at 2960 cm^{-1} appeared corresponding to the asymmetric C-H stretching vibration of the terminal methyl groups in addition to the bands of symmetric C-H stretching vibration of the methyl group of the *n*-butyl and undecane groups (results not shown). These results demonstrate that monolayers on Au nanoparticles formed after the reaction with *n*-butylamine consist of a mixture of carboxylic acids and alkylamides on the Au core. This reaction is rapid and occurs in high yield, which takes place at room temperature within few minutes, indicating that the extremely high reactivity of the surface anhydrides with respect to the amide-forming coupling reaction.

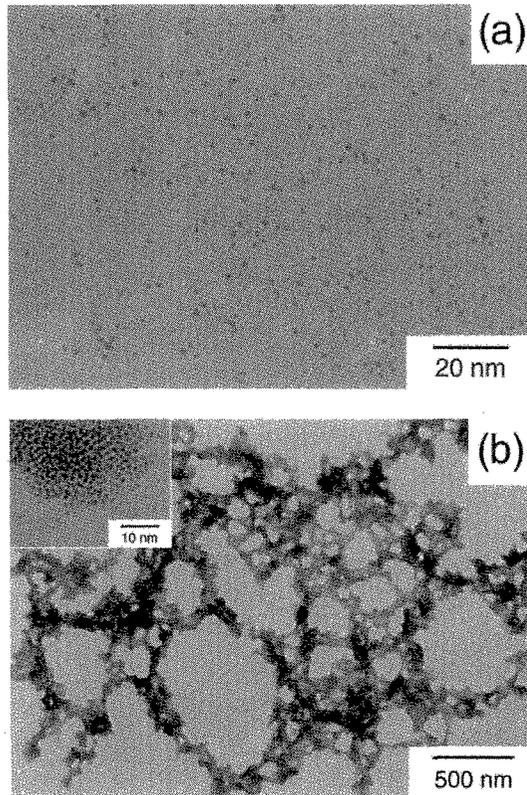


Fig.2 TEM images of the anhydride-functionalized Au nanoparticles after reaction with ethylenediamine under conditions where the excess amount (a) and the trace amount (b) of ethylenediamine were added into the solution.

In our strategy for network fabrication, diamine-terminated molecule was used as linkers to interconnect the anhydride-functionalized Au nanoparticles. In the present study, ethylenediamine was used for this purpose as a model system. By mixing the two components, intermolecular coupling to form amid bond would result in the network formation of Au nanoparticles linked by covalent (amide) bonds. The dimension of these networks can be controlled by changing initial concentration of these

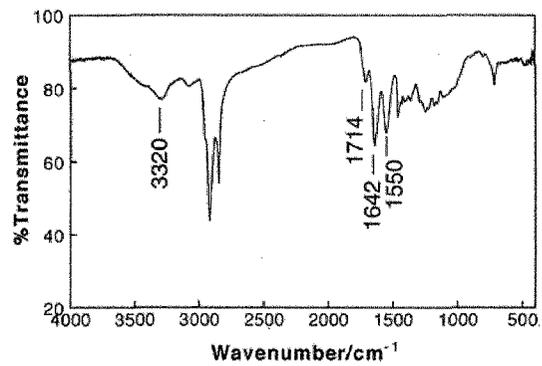
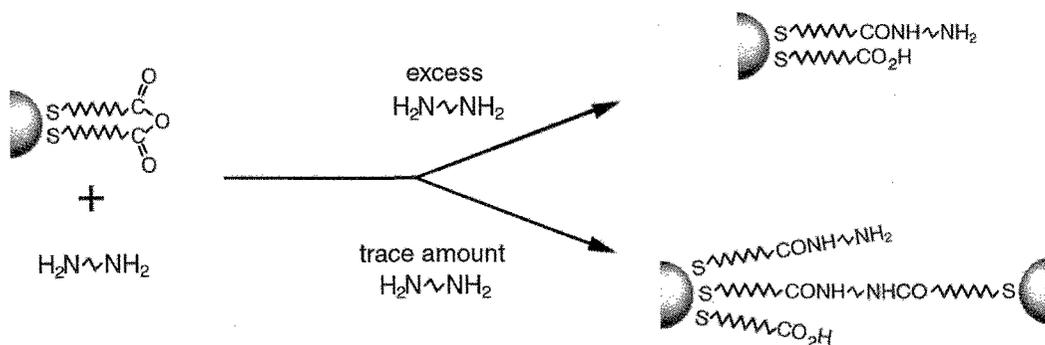


Fig.3 FT-IR spectrum of aggregates formed after reaction of the anhydride-protected Au nanoparticles with ethylenediamine. The spectrum was taken from the aggregates shown in Fig. 2b.

components. In a typical experiment, two THF solutions containing the anhydride-functionalized Au nanoparticles and ethylenediamine were mixed in dry argon while stirring. By mixing them under the condition where excess amount of ethylenediamine relative to that of the anhydride-functionalized Au nanoparticles was added, no distinct change was observed (no precipitation). In Fig. 2a, TEM image confirms that the Au nanoparticles with mean size of 2.1 nm are well dispersed and isolated individually on carbon thin film supported on copper mesh grid. In this case, almost entire surface of the Au nanoparticles can be covered by amine terminal groups though amide-forming coupling between one terminal amine end group and the carboxylic anhydride attached on Au nanoparticles (Scheme 1). Therefore, interconnection of neighboring Au nanoparticles would not occur in this condition. On the other hand, rapid precipitation took place after adding the trace amount of ethylenediamine into solution containing Au nanoparticles. TEM image of this precipitation shows the presence of fractal-like aggregates with dimensions ranging between 1 and 2 μm (Fig. 2b). Enlarged image (inset in Fig. 2b) reveals that the Au nanoparticles are attached each other to form large network aggregates. Regular spacing



Scheme 1 Schematic representation for proposed formation of amide bond after the reaction of the anhydride-functionalized Au nanoparticles and ethylenediamine in THF under different conditions.

for separations between neighboring Au nanoparticles was also observed. FT-IR spectrum of these network aggregates is shown in Fig. 3. Some characteristic peaks are observed, corresponding amide I (1642 cm^{-1}), amide II (1550 cm^{-1}) and C=O stretching vibration of carboxylic acid (1714 cm^{-1}). No bands assigned to carboxylic anhydride are observed while the band at 3320 cm^{-1} is assigned to N-H stretching vibration of terminal amine groups. The results demonstrates that the network formation observed here arises from amide-forming coupling reaction, in which the individual Au nanoparticles are connected by diamine-terminated linkers. Thus, mixing of highly reactive intermediate-functionalized Au nanoparticles and molecules bearing amine terminal ends under controlled conditions allows facile formation of a nano-networks having a three-dimensional structure.

4. SUMMARY

In this study we have described here the surface modification of carboxylic acid-functionalized Au nanoparticles and formation of macroscopic network aggregates through amide-forming coupling between interchain carboxylic anhydride-functionalized Au nanoparticles as a building blocks and diamine-terminated molecules as a linkers. The introduction of highly reactive intermediate into entire surface of the Au nanoparticles provides a facile surface modification of Au nanoparticles and a controllable fabrication of Au nanoparticles-based composites. The network structure can be controlled by concentration of two components, particle size, and kinds of linker molecules. For instance, interparticle spacing can be readily tuned through the appropriate choice of linker molecules with various lengths. The present covalent bond-mediated methodology can be suitable for fabrication of functionally diverse nanocomposite materials with controlled structures and functions. Potential applications for this approach is now underway.

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