Articles

The Characteristic Self-assembly of Gold Nanoparticles over Indium Tin Oxide (ITO) Substrate

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Ordered array of gold nanoparticles (Au NPs) over ITO glass was investigated in terms of ITO pretreatment, particle size, and diamines with different chain length. Owing to the indium-tin-oxide (ITO) layer coated on the glass, the substrate surface has a limited number of hydroxyl groups which can produce functionalized amine groups for Au binding, which resulted in the loosely-packed array of Au NPs on the ITO surface. Diamine ligand as a molecular linker was introduced to enhance the lateral binding of adjacent Au NPs immobilized on the amine-functionalized ITO glass, consequently leading to the densely-packed array of Au NPs over the ITO substrate. The molecular bridging effect was strengthened with the increase of chain length of diamines: C-12 > C-8. The packing density of small Au NPs (< 40 nm) was significantly increased with the increase of C-8 diamine, but large Au NPs (> 60 nm) did not produce densely-packed array on the ITO glass even for the dosage of C-12 diamine.

Key Words : ITO Glass, Gold nanoparticles, Diamine ligand, Chain length

Introduction

The synthesis and application of gold nanoparticles (Au NPs) are one of the major nanomaterial researches owing to the new discoveries by interdisciplinary works related to self-assembly, nano-catalysis, bio-imaging, and molecular electronics.¹⁻⁵ Gold nanoparticles can play as a core material for the development of novel-type biomedical devices including diagnosis and bio-sensing agents.⁶⁻¹¹ In particular, the organization of Au NPs onto monolayer-modified substrates (or electrodes) has established means to develop amperometric biosensors and reversible amperometric immunosensors.^{12,13}

Ordered structure of nanoparticles can be obtained either by the self-organization of particles capped with alkyl chains or assembly on modified substrates.¹⁴⁻¹⁸ In either case, an intermediating ligand plays an important role for the ordered packing density. Several research groups have evaluated the effect of mono-functional ligands (such as alkyl (or aromatic),¹⁹⁻²¹ thiols (or dithiols), alkylamines,²² ammonium salts,²³ and alkyl silanes²⁴) on the self-assembly of nanoparticles. The primary amine groups in alkyl chains, which is well known to interact with gold ions and the corresponding reduced metal, is expected to exhibit a significant effect on the self-assembly of Au NPs.²⁵⁻²⁷ William *et al.* reported an incomplete coverage of gold colloids (ranged in 25-120 nm) on indium tin oxide (ITO) surface, i.e., Au NPs were deposited as a discontinuous layer with a large gap among the adjacent particles.²⁸ Sugimura *et al.* showed the pro-

gressive growth of small ensembles of Au NPs (ca. 20 nm) onto the amine-functionalized ITO surface through the neutralization of these particles using dodecanethiol as a surfactant.²⁹ Even though inter-particle distance between small Au NPs was successfully adjusted, the cyclic immobilization and neutralization process was very cumbersome.

In this study, small (30 ± 8 nm) and large Au NPs ($D = 70 \pm 14$ nm) were immobilized onto the ITO surface using a one-step dipping method. The inter-particle distance between Au NPs and the size of ensembles are tuned with the assistance of bi-functional diamines. The characteristic self-assemblies of Au NPs on the ITO glass were investigated in terms of ITO pretreatment, particle size, diamines with different chain length and dosage amounts. Bi-functional diamines with different chain lengths (C-8 and C-12) were used as a molecular linker to enhance the lateral assembly of adjacent Au NPs on the ITO glass. The surface morphology and characteristic properties of Au NPs were analyzed by scanning electronic microscopy (SEM), atomic force microscope (AFM), contact angle measurements, and UV-vis spectroscopy.

Experimental Section

Chemicals. All chemicals were obtained from Aldrich and used as received: Hydrogen Tetra-chloroaurate (III) Hydrate (HAuCl_4 , 99.99%), 3-Aminopropyl Trimethoxysilane (APTMS, 97%), Hydrochloric Acid (conc. HCl), Sodium Citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$), Absolute Ethanol ($\text{C}_2\text{H}_5\text{OH}$,

99.5%), HPLC grade water (H_2O), Hydrogen Peroxide (H_2O_2 , 35%), 1,8-Diaminooctane ($\text{C}_8\text{H}_{20}\text{N}_2$, 98%), 1,12-Diaminododecane ($\text{C}_{12}\text{H}_{28}\text{N}_2$, 98%), and Indium-tin-oxide (ITO) glass.

Gold Nanoparticles. Gold nanoparticles (Au NPs) were prepared by the citrate boiling method, in which 90 mL of HPLC water containing 1.0 mL of 1.0 wt % HAuCl_4 was heated to boiling temperature and then an aliquot volume of 38.8 mM sodium citrate was injected into the boiling water. After 2 minutes while the color changed from black (deep blue) into red, the reaction flask was immediately removed from the hot plate and kept stirring in ambient condition until the reaction flask was cooled down to room temperature. Gold nanoparticles ranged in 30 nm-80 nm were simply prepared by adjusting the molar ratio of sodium citrate to chloroauric acid.³⁰

Gold Nanoparticle Array. ITO glass was first cleaned in ethanol sonication and then put into a Plasma Cleaner for 2 min at RF power of 16.8 W and vacuum pressure of 120-180 millitorr. The plasma-treated ITO glass was immediately dipped into the ethanol solution containing APTMS (4 g of APTMS in 36 g of ethanol) in order to induce the chemisorption of APTMS molecules onto the ITO surface, in which activated hydroxyl groups on the ITO glass interacted with Si-OR groups in APTMS molecules *via* the formation of Si-O-Si bonds by losing water molecules. The resulting amine-functionalized ITO glass was immersed into the gold colloidal solution containing various amounts of C-8 and C-12 diamines for 12 hrs, and the ITO glass was rinsed with copious D.I. water. Then, C-8 and C-12 diamine solutions were prepared by adding 0.2 g of 1,8-diaminooctane ($\text{C}_8\text{H}_{20}\text{N}_2$, 98%) and 0.28 g of 1,12-diaminododecane ($\text{C}_{12}\text{H}_{28}\text{N}_2$, 98%) into 40 g of $\text{H}_2\text{O}/\text{EtOH}$ solution, respectively.

Figure 1. Air/water contact angles on the pretreated ITO glass by various methods: (a) short time-evolution, (b) long time-evolution.

Figure 2. SEM and AFM images of pretreated ITO glass by (a) plasma treatment, and (b) piranha soaking method.

Results and Discussion

Figure 1(a) shows the air/water contact angles on the ITO glass pretreated by various cleaning methods. ITO glass (black curve) pretreated by ethanol sonication exhibited the highest contact angles of ca. 33° in average. Plasma-treated (red curve) and piranha-soaked (blue curve) ITO glasses showed contact angles less than 10° , i.e., the hydrophilicity of the ITO surface was significantly enhanced. ITO glass pretreated by both plasma and heat treatment (green curve) showed slightly higher contact angles than those obtained from plasma treatment only, but exhibited more stable contact angles during the measurement times. Figure 1(b) shows the time-evolution of air/water contact angles on the activated ITO glass when exposed to the ambient condition. Pristine ITO glass almost kept the initial contact angles of ca. 35° , while other three ITO samples exhibited a distinct increase of contact angles by more than 15° within 20 minutes. This clearly shows that the activated ITO glass should be used immediately to prevent the aging of activated hydroxyl groups on the ITO surface.

Figure 2 shows the SEM and AFM images of ITO glasses pretreated by plasma treatment and piranha soaking method, respectively. Figure 2(a) represents the ITO glass treated by the ambient air plasma treatment, and Figure 2(b) shows the ITO glass treated by the piranha soaking method. Although piranha solution is more effective for ITO activation than plasma treatment (i.e., ITO glass pretreated by piranha solution exhibited the lowest contact angles), piranha soaking method apparently damaged the indium-tin-oxide layer on the glass substrate as seen from Figure 2(b). The conductivity of ITO glass was significantly reduced probably due to the removal of ITO materials with the consequent exposure of non-conductive glass substrate. On the contrary, ITO glass activated by the plasma treatment kept the almost same surface morphology and electrical conductivity as those of the pristine ITO glass.

Figure 3 shows the UV-vis spectra of Au NPs in the presence of diamine ligands with different chain length. To avoid the precipitation caused by heavy aggregation of Au NPs, small amounts of diamine (5 μ L) were added into 3 mL of gold colloids. Also, UV-vis spectra of gold colloids shown in Figure 3(b) were only displayed within short times of 30 minutes because of the fast precipitation of Au NPs in the presence of C-12 diamines. With the increase of elapsed time, the primary absorption peak of Au at ca. 520 nm was gradually decreased and the secondary absorption peak of aggregated Au appeared at longer wavelength (700–800 nm). The decrease of the primary peak and the simultaneous increase of the secondary peak clearly indicated that the aggregation of Au NPs was caused by molecular bridging effect of diamines. In addition, the maximal position of secondary peak was gradually shifted to longer wavelength owing to more aggregation of Au NPs.

The secondary peak was compared to estimate the bridging force of diamines with different chain length. According to Figure 3(a)–(b), the maximal peak position at 30

Figure 3. UV-vis spectra of gold colloids by the addition of diamine ligands: (a) C-8, (b) C-12.

minutes after diamine addition was quite different depending on the chain length of added diamines: C-8 diamine at ca. 800 nm, and C-12 diamine at ca. 860 nm. The red-shift of maximal peak position is closely related to the aggregation degree of Au NPs, i.e., more aggregation of Au NPs induced more red-shift of secondary absorption peak. In summary, C-12 diamine induced the largest aggregation of Au NPs, consequently leading to the more red-shift of secondary peak than the other diamine with shorter chain length. The longer chain length is more effective for molecular bridging of Au NPs, probably due to the enhanced flexibility of longer chain length which can freely approach to adjacent nanoparticles.²⁶

Diamine ligand was also introduced into the arraying process, in order to increase the packing density of Au NPs on the ITO glass. Figure 4 shows the dosage effect of diamine ligand on the self-assembly of small Au NPs (30 ± 8 nm) over the ITO substrate. Without the addition of diamine ligand as shown in Figure 4(a), loosely-packed array of Au NPs was observed on the ITO glass, probably due to the limited amine-functionalized sites for Au binding.^{31,32} However, another reason might not be negligible for the loosely-packed array of Au NPs, caused by the roughness of pristine ITO glass and/or the chemical defects on the ITO surface.²⁸

Figure 4. SEM images of small Au NPs ($D = 30 \pm 8$ nm) arrayed on the ITO glass with the increase of C-8 diamines (in 6 mL of Au colloids): (a) 0 μ L, (b) 2 μ L, (c) 4 μ L, (d) 6 μ L, (e) 8 μ L, (f) 12 μ L.

With the increase of C-8 diamine dosages, the packing density of Au NPs on the ITO glass was gradually increased as shown in Figure 4(b)-(d), finally leading to a densely-packed array of small Au NPs (see Figure 4(d)). Excessive dosage of C-8 diamines resulted in the multi-layer films of Au NPs on the ITO glass as shown in Figure 4(e)-(f).

Large Au NPs more than 60 nm were also tested for the self-assembly on the ITO glass with the increase of C-8 diamine dosages. Figure 5 shows the SEM images of Au-arrayed samples for large Au NPs (70 ± 14 nm). Without the addition of C-8 diamine, isolated Au NPs were observed on the ITO glass as shown in Figure 5(a). According to Figure 5(b)-(f), the progressive increase of packing density was not observed for large Au NPs with the increase of C-8 diamine, but rather showed the increase of Au cluster size. That is, the addition of C-8 diamine produced loosely-packed array of large Au NPs. The reason may be that negatively-charged Au NPs with large size exhibit stronger repulsive forces, and/or singular amine group on the ITO surface is not strong enough to immobilize large Au NPs.

To elucidate the chain length effect on the Au array, small and large Au NPs were employed in the presence of C-8 and C-12 diamines. Here, C-8 and C-12 diamines possess eight alkyl and twelve alkyl groups, respectively. For the array of small Au NPs on the ITO glass, C-12 diamine exhibited stronger aggregation effect on Au NPs as compared to C-8 diamine. As shown in Figure 6(a) for small Au NPs, C-12 diamine produced heterogeneous deposition of Au NPs on the ITO glass while C-8 diamine induced the relatively

Figure 5. SEM images of large Au NPs ($D = 70 \pm 14$ nm) arrayed on the ITO glass with the increase of C-8 diamines (in 6 mL of Au colloids): (a) 0 μ L, (b) 2 μ L, (c) 4 μ L, (d) 6 μ L, (e) 8 μ L, (f) 12 μ L.

Figure 6. Comparative SEM images of Au array on the ITO glass by the addition of C-8 and C-12 diamines (6 μ L of diamines in 6 mL of Au colloids): (a) small Au NPs ($D = 30 \pm 8$ nm), (b) large Au NPs ($D = 70 \pm 14$ nm).

homogeneous array of Au NPs on the ITO glass. Furthermore, the heterogeneous deposition of small Au NPs shown in Figure 6(a) implicated the fast precipitation of heavily-aggregated Au NPs in the presence of C-12 diamines. As shown in Figure 6(b) for large Au NPs, C-8 diamine produced loosely-packed array on the ITO glass, and C-12 diamine produced multilayered structures of Au NPs on the ITO glass. These results clearly indicated that longer chain length of diamines possessed stronger molecular bridging force for Au.²⁶

In summary, the diamine ligand as a bridging linker provides the equivalent bridging force toward lateral directions, resulting in densely-packed array of Au NPs. For small Au NPs, the packing density of Au NPs on the ITO glass was

easily adjusted by the variation of C-8 diamine dosages. For large Au NPs (> 60 nm), the addition of C-8 diamines produced loosely-packed array of Au NPs on the ITO glass, probably due to the increased repulsive forces of large Au NPs and a limited number of binding sites for Au. Also, C-12 diamine with longer chain length produced multiple-layered films of Au NPs on the ITO glass.

Conclusions

The characteristic self-assemblies of Au NPs on the ITO glass were investigated in terms of ITO pretreatment, particle size, dosage amounts, and chain length of diamine ligands. The plasma treatment did not change surface morphology of the ITO glass, in contrast with the significant damages on the indium-tin-oxide layer by piranha soaking method. The packing density of small Au NPs (< 40 nm) on the ITO glass was facilely adjusted simply by the variation of C-8 diamine dosages, while for large Au NPs C-8 diamines induced loosely-packed array on the ITO glass. C-12 diamines with longer chain length generally produced multiple-layered films of Au NPs on the ITO glass. Bi-functional diamines successfully played as the molecular linker for the lateral growth of Au assembly, consequently increasing the packing density Au NPs on the ITO glass. This chemical strategy offers a simple and controllable method to provide mono and/or multi-layered films of Au NPs to the prospective biomedical devices for diagnostic and bio-sensing analysis.

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