

Competitive Attachment of Gold Nanoparticles on an Indium Tin Oxide Electrode

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Fundamental aspects of the attachment of gold nanoparticles (AuNPs) onto a 3-aminopropyltrimethoxysilane (APTMS) modified indium tin oxide (ITO) electrode were explored using commercially available Au colloid solutions of 5, 10 and 20 nm. In particular, competitive attachments of AuNPs were observed using mixed solutions of two Au colloids. Consequently, it was found that smaller AuNPs are easily attached on an APTMS modified ITO. On the other hand, the result of the stepwise attachments showed that after the surface was modified by the first AuNPs, the second AuNPs have difficulty attaching. This means, if surface connecting $-NH_2$ terminals of APTMS are once occupied, further modification or exchange of the attached AuNPs would not be easy. From the present results, a contaminant amount of smaller AuNPs is considered to be a practical problem in modifying ITO surfaces by AuNPs.

Keywords Gold nanoparticles, indium tin oxide, competitive attachment, electrode modification

(Received February 25, 2015; Accepted March 18, 2015; Published July 10, 2015)

Introduction

Metal nanoparticles (NPs) have been attracting intensive attention for the past two decades because of their unique optical, electronic, magnetic, and catalytic properties. In the field of electroanalysis, metal NPs have been actively utilized as a functional unit to modify electrode surfaces.¹⁻⁵ While some advanced applications have been of focus in recent years, *e.g.*, the combination of metal NPs with carbon-based nanomaterials such as graphene,⁶ now metal NPs are being regarded as indispensable functional nanomaterials for designing new electrode surfaces and electrochemical devices.

Among metal NPs, gold NPs (AuNPs) are of particular interest because of their stability, optical properties and biocompatibility. In the previous reviews,^{1-5,7} the utilization of AuNPs in electroanalysis has been summarized well. For modifying AuNPs on electrode surfaces, there are two typical preparation methods of AuNPs, *i.e.*, electrochemical and chemical preparations. Since the size-controlled chemical synthesis of AuNPs has been established well,⁸ the use of uniform-sized AuNPs might be a straightforward way to utilize AuNPs as a functional unit or building block of modified electrodes or electrochemical devices. In this case, a bridging reagent or cross-linker molecules are normally used to achieve sufficient contact to both the electrode surface and AuNPs. We described the situation of modifying AuNPs in the case of carbon surfaces in a previous paper.⁹ Also, since bridging reagents, such as 3-mercaptopropyltrimethoxysilane (MPTMS) and 3-aminopropyltrimethoxysilane (APTMS), are useful for linking indium tin oxide (ITO) surfaces and AuNPs,^{10,11} their effects for

modifying ITO electrodes was studied previously.¹² In addition, methodological development of the preparation for monodispersed AuNPs would be important.¹³

Although certain sized AuNPs have been successfully modified on electrode surfaces in general, we are interested in fundamental aspects of the attachment of AuNPs whose sizes are different. Actually, we are interested in determining what happens if two different sized AuNPs are present in a solution in which AuNPs are linked with the bridging reagent and attached competitively. In our experience, the density of the attachment seems to depend on the size of AuNPs. However, to the best of our knowledge, there is no experimental report on the competitive attachment of two different sized AuNPs.

Thus, in the present work, we observed the changes in the attachment of AuNPs depending on the size onto an APTMS modified ITO electrode. Since the size dispersion of AuNPs contained in commercially available Au colloid solutions has been guaranteed, we used Au colloid solutions of 5, 10 and 20 nm from Sigma-Aldrich Co., Ltd. for treating an APTMS modified ITO. In addition to the single solutions, we used mixed solutions of the two Au colloids. The surface images observed using field-emission scanning electron microscopy (FE-SEM) after the modification of AuNPs show a general tendency in the attachment of AuNPs depending on the size.

Experimental

Apparatus and materials

Scanning electron microscopic (SEM) images were obtained with a field emission SEM instrument (JSM-7400F, JEOL, Japan). ITO film coated glass plates were purchased from CBC Optics Ltd. and used after cutting into the size of approximately 10 mm × 7 mm.

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Au colloidal solutions of 5, 10 and 20 nm were purchased from Sigma-Aldrich Co., Ltd. (G1402, G1527 and G1652, respectively). The size distribution of AuNPs is guaranteed as 3.5 – 6.5, 8 – 12 and 17 – 23 nm, respectively. All three Au colloid solutions were noted as having been produced by a modified tannic acid/citrate method.⁸ The content was mentioned as approximately 0.01% HAuCl₄ suspended, so that the number of AuNPs was assumed based on the spheres' volume ratio of 1:8:64 for the diameters of 1:2:4. As an example, for equi-volume mixed solutions of 5- and 20-nm Au colloids, the ratio of the number of AuNPs would be 64:1 assuming that the amount of Au was the same and that the sizes of AuNPs are uniform (though they are dispersed actually as mentioned above).

HAuCl₄·3H₂O, APTMS and cetyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich Co., Ltd. Other reagents were obtained from Wako Pure Chemicals Ltd. All solutions were prepared with ultra-pure water obtained from a water purification system (Millipore WR600A, Yamato Co., Japan).

Attachment of AuNPs on an APTMS modified ITO

The preparation of an APTMS modified ITO electrode and the surface modification with AuNPs were carried out following a manner described previously.¹² Briefly, a piece of ITO plate was washed in acetone, ethanol and pure water with sonication, then dried with N₂ gas. Then, the ITO substrate was immersed in 5 mL of the ethanol solution containing APTMS (5 vol. %) for 24 h at 28.0°C, washed well with pure water, dried with N₂ gas, and then dried at 40°C for 1 h to remove residual APTMS. The thus-prepared APTMS modified ITO (APTMS/ITO) was immersed in an Au colloid solution for 24 h, washed with pure water, and dried and used for the surface evaluation. The immersion time of 24 h was fixed because no change in the attached density of AuNPs was observed after 24 h.

A seed-mediated growth treatment was performed when necessary using a growth solution, which was prepared by mixing 20 mL of 0.1 M CTAB, 0.5 mL of 0.01 M HAuCl₄, 0.1 mL of 0.1 M ascorbic acid and 0.1 mL of 0.1 M NaOH solutions. An ITO substrate was immersed in the growth solution for 24 h, and the changes in the surface images were observed.

Results and Discussion

Attachment of AuNPs on APTMS/ITO surfaces using single Au colloid solutions

Figure 1 shows typical FE-SEM images of ITO substrates on which 20-, 10- and 5-nm AuNPs were modified *via* APTMS using single Au colloid solutions. For 20-nm AuNPs, white images of AuNPs were well-recorded with the exact size judging from the scale of the FE-SEM image (Fig. 1A). In contrast, as a practical problem in our FE-SEM measurements, the recognition of AuNPs whose size is smaller than 10 nm became worse or difficult. Actually, the size of 10-nm AuNPs recorded in the FE-SEM image (Fig. 1B) was apparently smaller than 10 nm judging from the scale, and recognized also as smaller in comparison with the size of 20-nm AuNPs in Fig. 1A. Furthermore, after 5-nm AuNPs were modified on the APTMS/ITO, no AuNPs could be recognized except unclear ones in the FE-SEM image (Fig. 1C).

To explain these results, we need to consider an actual or practical resolution of the FE-SEM apparatus. For the FE-SEM we used, the minimum resolution has been mentioned as

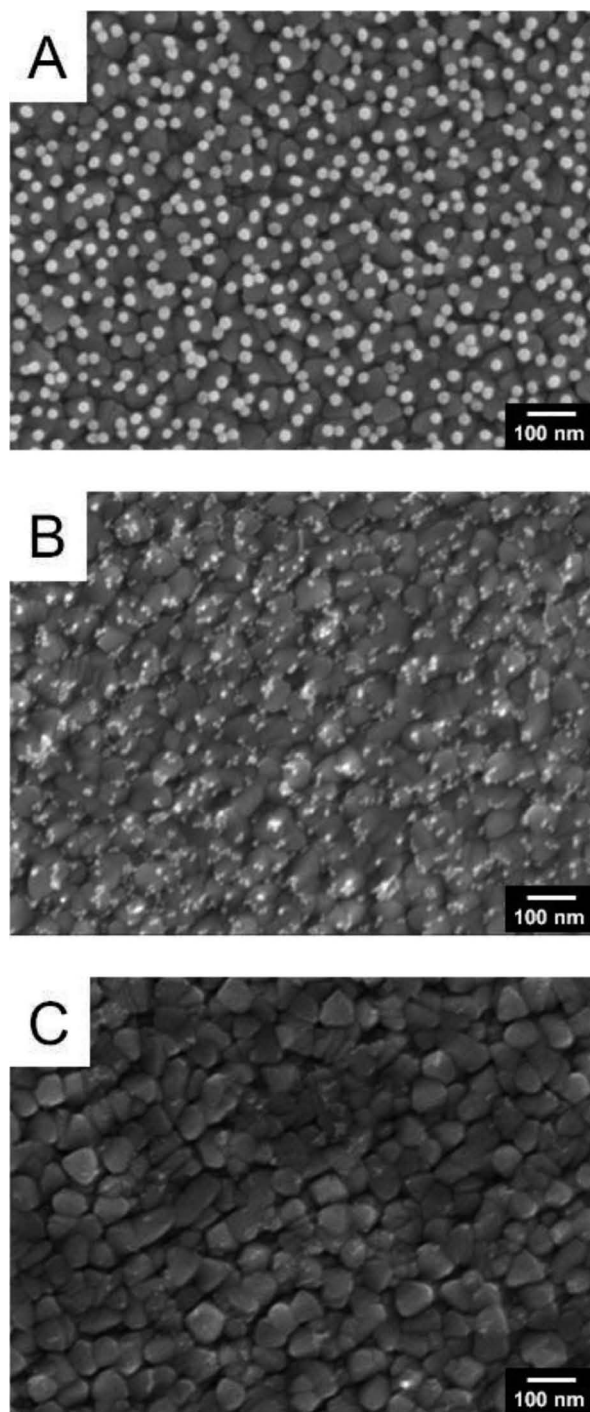


Fig. 1 Typical FE-SEM images of ITO substrates on which (A) 20-nm, (B) 10-nm and (C) 5-nm AuNPs were modified *via* APTMS using Au colloid solutions of 20, 10 and 5 nm.

1 – 2 nm. However, for the present samples, the recognition should depend on the combination of the background material and the attached ones. Also, the focusing has become very difficult for lesser conducting materials, so that the best performance cannot be expected for all the cases. Hence, for the present results of Fig. 1, we assume that the size of 10-nm AuNPs would be observed as smaller compared with the case of 20-nm AuNPs, and that the AuNPs of 5 nm could not be recognized in the measurement conditions of Fig. 1C. We reported the same difficulty to recognize 3.5 nm AuNPs on ITO

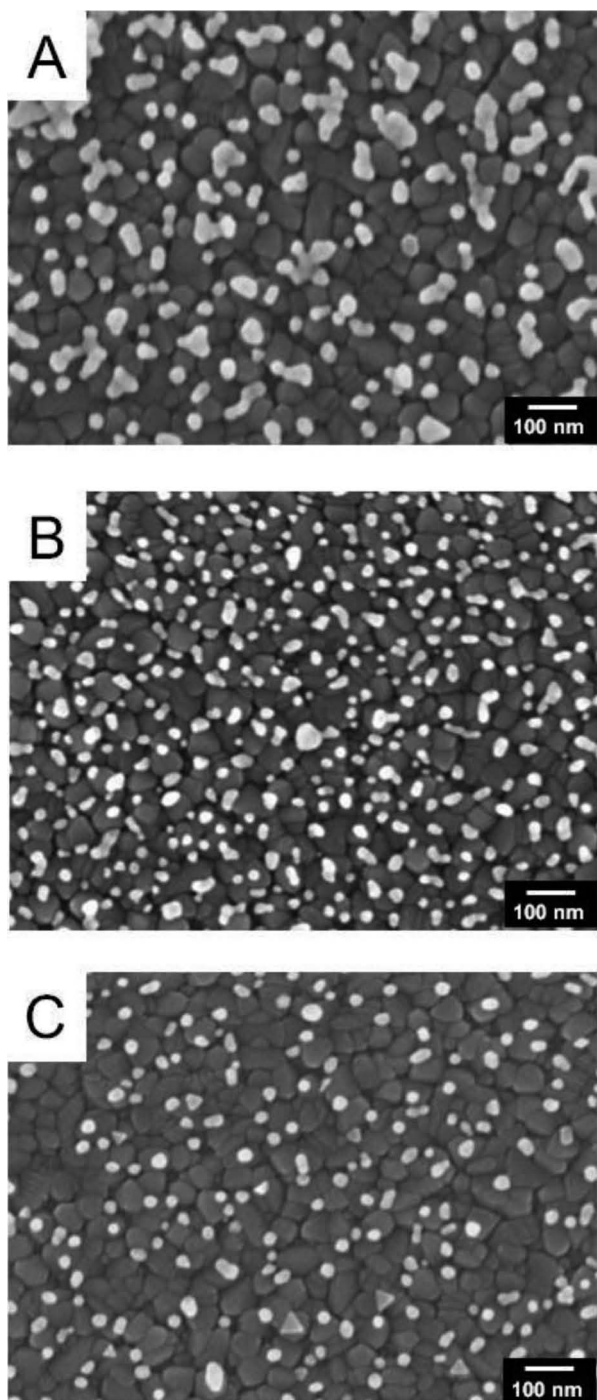


Fig. 2 Typical FE-SEM images of ITO substrates on which (A) 20-nm, (B) 10-nm and (C) 5-nm AuNPs were modified *via* APTMS using Au colloid solutions of 20, 10 and 5 nm, and then a seed-mediated growth treatment was performed.

in a previous paper.¹⁴

To imagine the actual attachment of 5- and 10-nm AuNPs on the ITO surfaces, we performed a seed-mediated growth treatment for the surfaces whose FE-SEM images are those in Fig. 1. The FE-SEM images after the growth treatment are shown in Fig. 2. As shown in Fig. 2C, well-dispersed and grown AuNPs could be shown from the 5-nm AuNPs modified AMPMS/ITO. Since a growth treatment of a bare ITO never shows such a dispersion of AuNPs, it is reasonably considered

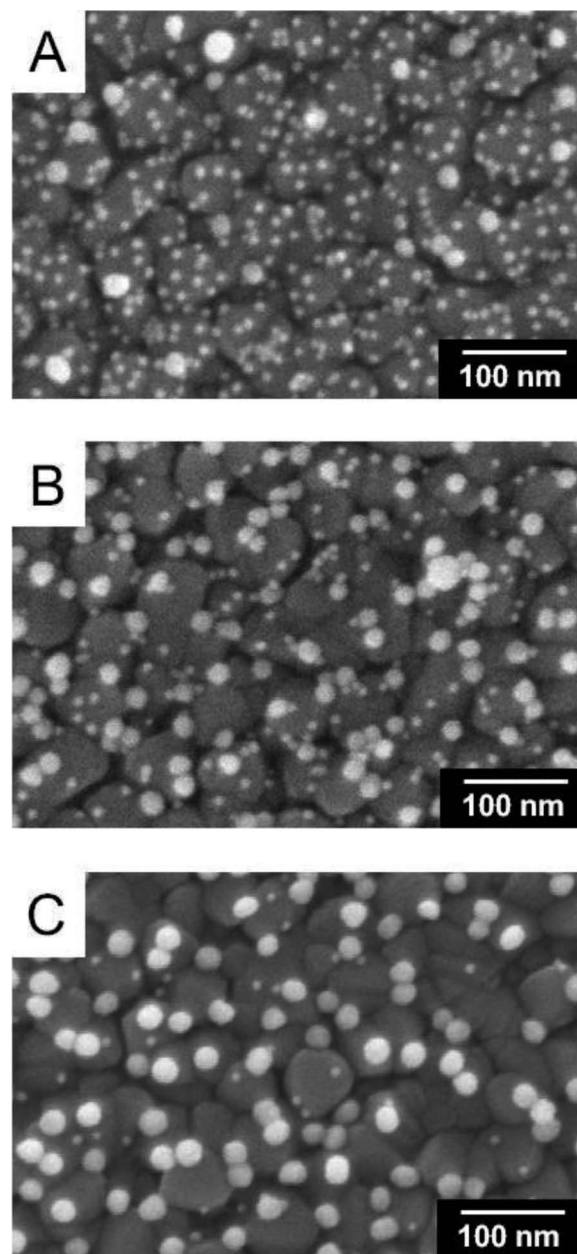


Fig. 3 Typical FE-SEM images of APTMS modified ITO substrates after treatment in mixed solutions composed of (A) 1:1, (B) 10:1 and (C) 100:1 (in volume) of Au colloid solutions of 20 and 10 nm. The ratios of the numbers of 20-nm:10-nm AuNPs in the mixed solutions are approximately (A)1:8, (B) 10:8 and (C) 100:8.

that the attached 5-nm AuNPs were just invisible in the FE-SEM image in Fig. 1C. The FE-SEM image obtained after the growth of 10-nm AuNPs (Fig. 2B) showed the grown AuNPs were observable and kept a similar density of the attached AuNPs recorded in Fig. 1B. Therefore, in the case of 10-nm AuNPs, it is expected that almost all the 10-nm AuNPs were visible in Fig. 1B, though the size recorded as the FE-SEM image was smaller than 10 nm. The result of the growth of 20-nm AuNPs (Fig. 2A) showed some decrease in the attached density compared with the result of Fig. 1A, for which some dissociations are considered to have occurred as the result of the structural growth.

Thus, in the following sections, we assume that: 1) 20-nm

AuNPs are visible with the exact size in the FE-SEM images; 2) 10-nm AuNPs are visible, but the size is actually smaller; and 3) 5-nm AuNPs are not visible even if they attached except some ones recognized accidentally.

Attachment of AuNPs on APTMS/ITO surfaces using mixed Au colloid solutions

To compare the attachment of different sized AuNPs directly, we observed the surface FE-SEM images after an APTMS/ITO was treated in a mixed solution containing both 10- and 20-nm Au colloid solutions. Figure 3A shows a typical FE-SEM image observed after treatment in an equi-volume (1:1) mixed solution of 20- and 10-nm Au colloids. In this case, the ratio of the numbers of AuNPs can be assumed as 1:8 for 20-nm:10-nm as estimated in the Experimental section. Figures 3B and 3C show the results observed after treatment in 10:1 and 100:1 mixed solutions of 20- and 10-nm Au colloids in volume, respectively. The ratio of the numbers of AuNPs would be 10:8 and 100:8 in these cases.

From Figs. 3A – 3C, it is recognized that the attachment of 10-nm AuNPs would be slightly dominant assuming the number ratios in the solutions. For estimations, we counted the numbers of 20- and 10-nm AuNPs in typical FE-SEM images. As the result, the ratio of the attached numbers of 20- and 10-nm AuNPs was 21:230, 112:135, and 113:42 for those in mixed solutions 1:8, 10:8 and 100:8, respectively. Therefore, the attachment of 10-nm AuNPs is expected to be slightly easier compared with that of 20-nm AuNPs.

Next, similarly, competitive attachments were observed using mixed solutions of 20- and 5-nm AuNPs. We observed FE-SEM images after APTMS/ITOs were treated in mixed solutions of 20- and 5-nm Au colloids, whose volume ratios were 1:1, 10:1, 100:1 and 500:1. The number ratios of 20-nm:5-nm AuNPs in the mixed solution can be assumed as 1:64, 10:64, 100:64 and 500:64, respectively. In the former two cases, no or scarce attachment of 20-nm AuNPs was observed in the FE-SEM images (the data are not shown). Thus, it is expected that the attachment of 20-nm AuNPs was significantly hindered by the attachment of 5-nm AuNPs, whose numbers in the mixed solutions are greater than that of 20-nm AuNPs (64:1 and 64:10). Although 5-nm AuNPs were invisible in the FE-SEM images, the attachment was actually confirmed by a seed-mediate growth treatment from the substrates.

In the mixed solutions for preparing the samples of Fig. 4, the number of 20-nm AuNPs was larger than those of 5-nm AuNPs. However, the attachment of 20-nm was apparently smaller than those expected from the simple number ratio of 100:64 and 500:64 of 20-nm:5-nm AuNPs, which was recognized in comparison with the FE-SEM image of the full attachment of 20-nm AuNPs (Fig. 1A). Thus, invisible 5-nm AuNPs attached on the surfaces in Fig. 4 should be expected to hinder the attachment of 20-nm AuNPs. The degree of the hindrance of 5-nm AuNPs would be greater than that of 10-nm AuNPs judging from the results of Figs. 3 and 4.

To observe the competitive attachment of 5-, 10- and 20-nm AuNPs directly, we prepared two mixed solutions in which the number ratio was 1:1. Actually, for preparing a mixed solution of 20- and 10-nm AuNPs with a number ratio of 1:1, we mixed 20- and 10-nm Au colloid solutions at a volume ratio of 8:1. In the case of 20- and 5-nm AuNPs, we mixed the solutions at a volume ratio of 64:1. Figure 5 shows the typical FE-SEM images after treatment in the mixed solutions with number ratio of 1:1. From the results, the dominant attachments of smaller AuNPs could be observed in both Figs. 5A and 5B. In addition, we could recognize the change in the degree of the hindrance

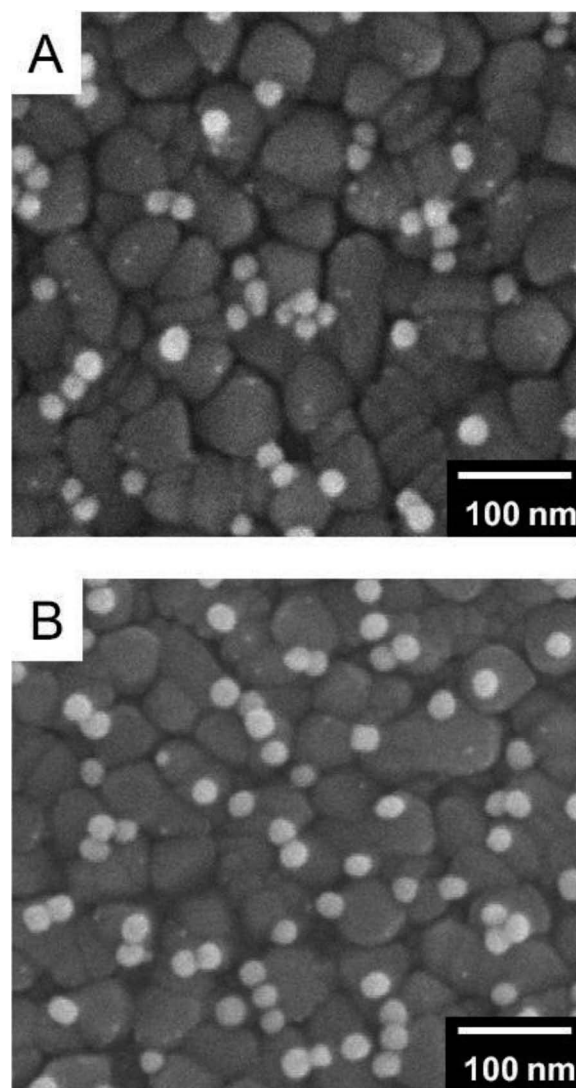


Fig. 4 Typical FE-SEM images of APTMS modified ITO substrates after treatment in mixed solutions composed of (A) 100:1 and (B) 500:1 (in volume) of Au colloid solutions of 20 and 5 nm. The ratios of the numbers of 20-nm:5-nm AuNPs in the mixed solutions are approximately (A)100:64 and (B) 500:64.

between the cases of 5- and 10-nm AuNPs toward the attachment of 20-nm AuNPs.

As a reason for the dominant attachment of smaller AuNPs, it is expected that the approach of smaller AuNPs toward NH_2 -terminals of APTMS in solution becomes easier. Also, the reactivity of smaller AuNPs would be generally higher. While the dominant attachment of smaller AuNPs might be naturally imaginable, the present work has verified it experimentally by observing the competitive reactions of AuNPs of 5, 10 and 20 nm.

Stepwise attachment of AuNPs on ITO surfaces

Finally, we observed FE-SEM images after stepwise treatments. Figure 6A shows a typical FE-SEM image observed after an APTMS/ITO was first treated in 5-nm Au colloid solution, and then re-treated in 20-nm Au colloid solution. The result clearly shows that the attachment of 20-nm AuNPs are very scarce, indicating that the attachment of the second AuNPs is very difficult after the first AuNPs are once attached, or

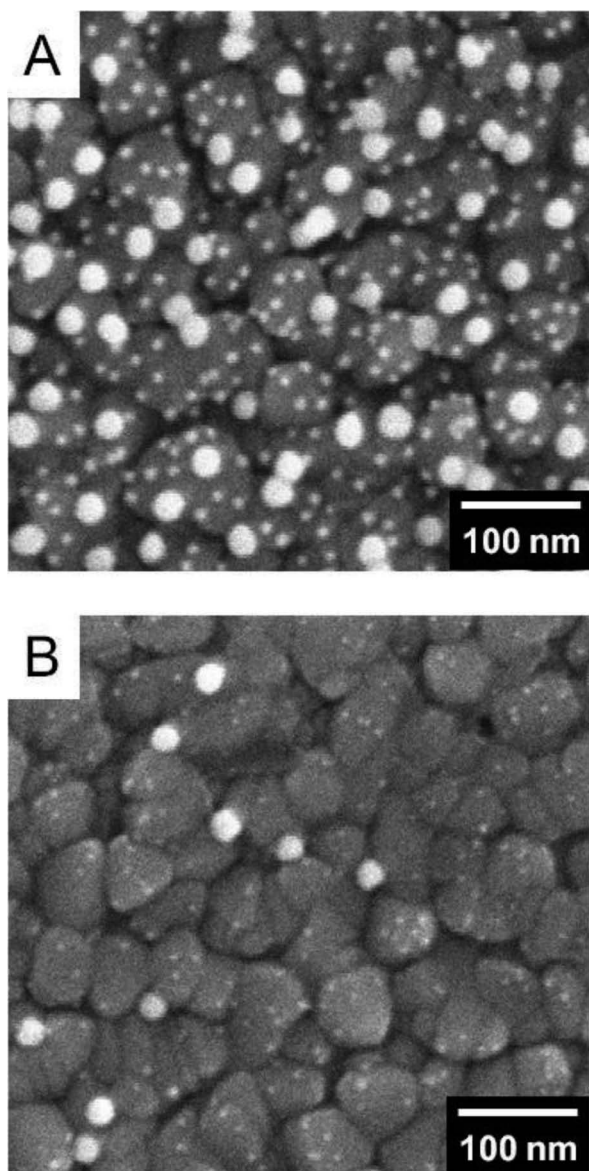


Fig. 5 Typical FE-SEM images of APTMS modified ITO substrates after treatment in mixed solutions containing 1:1 (in number) of (A) 20- and 10-nm AuNPs and (B) 20- and 5-nm AuNPs. For the preparation, (A) Au colloid solutions of 20 and 10 nm were mixed 8:1 (in volume) and (B) Au colloid solutions of 20 and 5 nm were mixed 64:1 (in volume).

occupy NH_2 -terminals, on the ITO surface. The result obtained after the first treatment in 20-nm Au colloid solution followed by the re-treatment in 5-nm Au colloid solution showed a remarkable contrast as shown in Fig. 6B. Because the attached density of 20-nm AuNPs in Fig. 6B was almost identical to that of Fig. 1A, it is considered that the replacement of 20-nm AuNPs with 5-nm AuNPs would not be really difficult. Thus, for the attachment of AuNPs *via* NH_2 -terminals of APTMS, it should be concluded that, once the contacts were formed to attach AuNPs, the dissociation would not be easy.

Conclusions

In the present work, we could experimentally verify that smaller

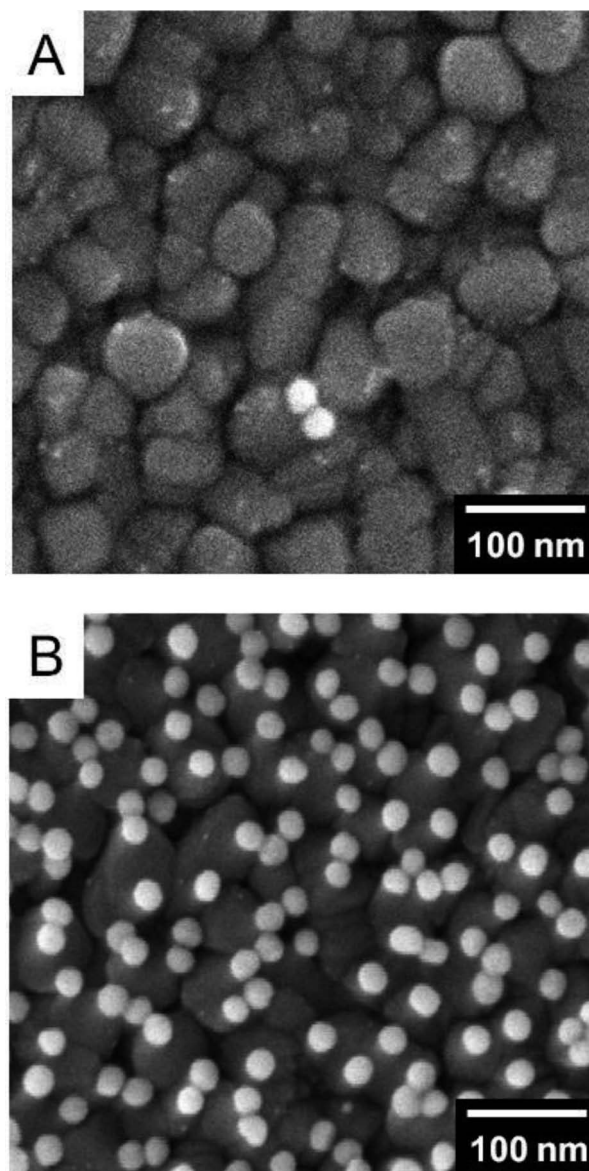


Fig. 6 Typical FE-SEM images of APTMS modified ITO substrates after treatment (A) first in 5-nm Au colloid solution and then in 20-nm Au colloid solution, and (B) first in 20-nm Au colloid solution and then in 5-nm Au colloid solution.

AuNPs easily attached on an APTMS modified ITO electrode by observing the competitive attachments of 10-nm AuNPs *vs.* 20-nm AuNPs and 5-nm AuNPs *vs.* 20-nm AuNPs. While the dominant attachment of smaller AuNPs could be observed in both the cases, it was quite remarkable in the latter case where there was a bigger size gap (*i.e.*, 20 nm *vs.* 5 nm). Therefore, we could recognize a general tendency of the attachment depending on the size (5-nm AuNPs > 10-nm AuNPs > 20-nm AuNPs).

On the other hand, the result of the stepwise attachments showed that after the surface was modified by the first AuNPs, the second AuNPs have difficulty attaching. So, if surface connecting -NH_2 terminals of APTMS are once occupied, further modification or exchange of the attached AuNPs would not be easy.

As a practical caution from the present results, if certain sized AuNPs are to be modified, the contamination of smaller AuNPs

in the solution should be carefully avoided or separated. As inferred from the result of Fig. 4B, a contaminant amount (1/500 in volume) of the smaller AuNPs significantly hindered the attachment of larger AuNPs. Although such contamination might be unusual, wider size distribution of synthesized AuNPs, a formation of smaller AuNPs as by-products, or remaining small seed AuNPs may bring about similar situations. So, it is concluded that smaller AuNPs should be carefully removed from the solution with which certain sized AuNPs would be modified dominantly on electrodes *via* bridging reagents. Furthermore, the smaller AuNPs might be invisible in FE-SEM observations even when they actually occupied the terminals of the bridging reagents.

Acknowledgements

This work was supported in part by the Japan Society for the Promotion of Science (JSPS) KAKENHI Grant Nos. 20550074 and 24550100.

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