

Attachment and Growth of Metal Nanoparticles on Indium Tin Oxide Surfaces

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In recent years, our group is studying on the seed-mediated growth method as a new strategy to attach and grow metal nanoparticles on conducting substrates, such as indium tin oxide (ITO). In this method, metal nanoparticles can be fixed via simple two-step immersion of a substrate into two different solutions at room temperature. The first step includes the physisorption of seed-nanoparticles on the substrate surface in the metal colloid solution (seed solution), and the second step is the gradual nanocrystal growth from the seed particles attached on the substrate by the chemical reduction of metal ions in the solution containing surfactants (growth solution). In this paper, some details of our approach and successful applications obtained up to now are described.

Key words: metal nanoparticles, surface attachment, nanocrystal growth, chemical reduction, electrode materials.

1. INTRODUCTION

Metal nanoparticles (NPs) have been attracting active attention in recent years because of their unique optical, electronic, magnetic, and catalytic properties. For example concerning gold NPs (AuNPs), the assembly, super-molecular chemistry, quantum-size related property, and applications toward biology, catalysis and nanotechnology have been summarized in a review by Daniel and Astuc [1]

Bottom-up type synthetic methods of metal NPs in solution are well-known and established in the field of chemistry, e.g., as reported for AuNPs [2,3]. However, if we would like to use the formed metal NPs as functional materials for some devices with solid support, the metal NPs formed in solution have to be fixed on or into the substrates. Because interesting characteristics of NPs might diminish when they gather to form larger clusters, it is necessary to fix or attach the NPs keeping some dispersed states. Thus, the development of such attachment methods with appropriate dispersion seems to be very important to make the best use of the characteristic features of metal NPs for nano-devices, such as electronic, sensing and optical devices.

As a method to attach AuNPs on the surfaces, peculiar binding molecules suitable for connecting AuNPs with substrates have been normally used. For the case of AuNPs on the glass surfaces, 3-mercaptopropyl-trimethoxysilane (MPTMS) or 3-aminopropyl-trimethoxysilane were adopted utilizing the bonding ability of the silanol group to the glass surfaces and the affinity of $-SH$ or $-NH_2$ group toward the AuNPs [4].

At present, to use peculiar binder molecules seems to have become a standard strategy to attach AuNPs onto the substrate surfaces. However, it is expected that the characteristics of metal NPs such as conductivity and catalytic ability are strongly affected by the chemical reagents surrounding or binding to them. Thus, although the use of bridging reagents is undoubtedly effective in some respects, such as size-control and fictionalizations, the reagents might become interferences to use the peculiar characters of metal NPs.

If we can attach metal NPs on the conducting substrates without using peculiar binder molecules, e.g.,

in the uses as the electrode materials, it is expected that we can fabricate novel conducting mono-dispersed materials with unique electrochemical properties involving both the metal NPs and the conducting substrates.

Thus, we developed the seed-mediated growth method for the surface modification of metal NPs, in particular, on the surfaces of indium tin oxide (ITO).

2. SEED-MEDIATED GROWTH METHOD FOR MODIFYING GOLD NANOPARTICLES

2.1 Attachment and growth of gold nanoparticles on ITO

As the start of our trials, we apply a seed-mediated growth method, which was originally developed by Murphy and coworkers for synthesizing Au nanorods in aqueous solution by the chemical reduction of $HAuCl_4$ [5,6], to the formation of AuNPs on the ITO surfaces [7].

As the actual procedures, a piece of ITO film coated glass was washed with sonication in acetone and then pure water. The washed ITO glass was dried in the air, and ready for the immersion in the seed solution. The seed solution was prepared typically by adding 0.5 mL of cooled pure water solution of 0.1 M $NaBH_4$ into 19.5 mL of pure water solution containing 0.25 mM $HAuCl_4$ and 0.25 mM trisodium citrate with stirring. With this preparation procedure, it has been reported that the gold seed particles of 4 nm were formed in the seed solution [5].

Next, we immersed the ITO glass into this seed solution to attach the seed particles on the surface; actually the glass sample was just left in the seed solution without particular treatments for typically 2 hours. Then, the ITO glass was taken out from the seed solution, and the surface was washed carefully by flushing pure water over the surface for several times. The water remained on the surface was removed using tissue paper by just touching the edges of the glass.

After blowing the surface of the ITO with N_2 gas until dry, it was immersed next in the growth solution, which was prepared typically by addition of 2.5 mL of pure water solution of 0.01 M $HAuCl_4$, 0.5 mL of pure water solution of 0.1 M ascorbic acid, and 0.5 mL of pure

water solution of 0.1 M NaOH into 90 mL pure water solution of 0.1 M cetyltrimethylammonium bromide (CTAB). Again, the ITO glass was just kept or left in the growth solution for typically 24 hours to promote the growth of AuNPs from the attached seeds. Finally, the sample was washed by flushing pure water again similarly.

From the images recorded using a field emission scanning electron microscopy (FE-SEM) after the step-wise immersion into both the seed and growth solutions, it was observed that AuNPs grew up to ca. 80 nm on the ITO surface and were present on the ITO crystals keeping a moderate dispersion [7].

Figure 1 shows the FE-SEM images observed after the step-wise immersion, in particular, to exhibit the effects of the immersion time into the growth solution. By changing the growth time, we could observe the crystal growth of AuNPs on ITO as the increase sizes of white dots in the images. The background crystals are those of ITO. From this figure, it was clarified that AuNPs were grown on the ITO surfaces from the Au nano-seed particles attached on ITO by immersing into the growth solution, i.e., by applying the seed-mediated growth procedure.

The first attachment of nano-seed particles are expected to promote via physisorption of ultra-small NPs dispersed in the seed solution by just dipping action of the substrates [8]. The second process should be the crystal growth via chemical reductions of metal ions in the growth solution, which is inferred to proceed gradually around the nano-seed particles on the substrates.

The observations of the changes in the grown structure of AuNPs on the ITO surfaces in the presence and absence of MPTMS revealed the significant differences in the crystal growth of AuNPs [7]. Because the nanocrystal growth was observed in the absence MPTMS, we would like to propose the validity of the seed-mediated growth approach as a new method to attach Au nanocrystals on the ITO surfaces without using the binder molecules.

2.2 Electrochemical applications of gold nanoparticle-attached ITO electrodes

We applied the AuNPs directly attached ITO (AuNP/ITO) electrodes to some measurements of the redox reactions.

As inferred from the fact that the as-deposited AuNP on the ITO surface displayed a different morphology from a MPTMS-linked AuNPs modified on ITO [7], it provided attractive electrochemical and electrocatalytic properties to promote the heterogeneous electron transfer kinetics. In particular, the electrochemical impedance measurements performed to evaluate the effects of AuNPs on the interfacial electron transfer property revealed that the presence of the MPTMS layer increases the charge transfer resistance value significantly. The quite low charge transfer resistances of the AuNP/ITO electrodes were clarified from the results of the electrochemical impedance measurements [9,10]. The charge transfer resistance of the AuNP/ITO electrode is ca. 1/3 of that of the AuNP/MPTMS/ITO electrode.

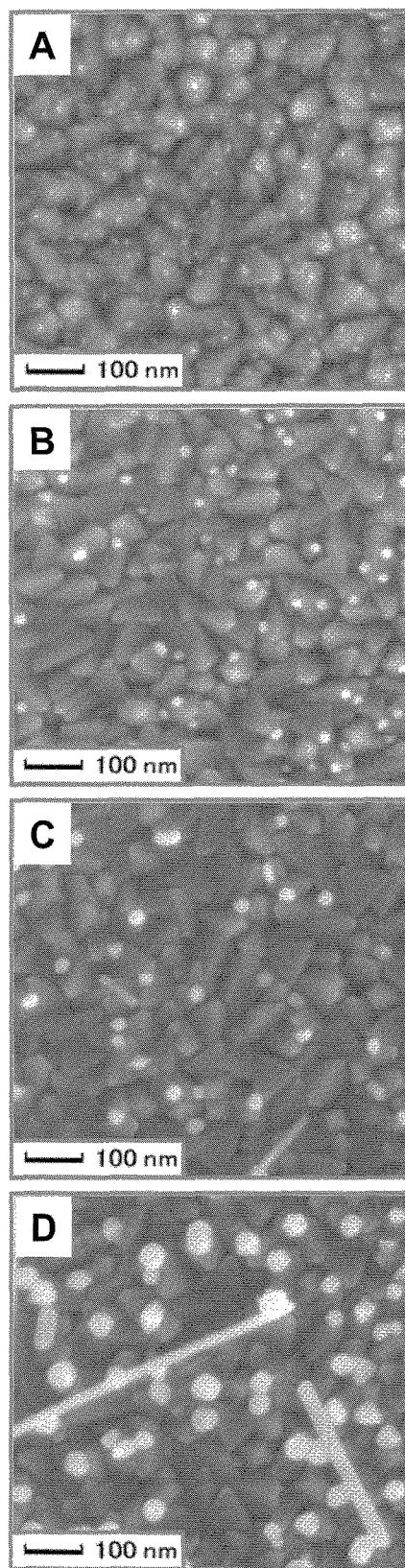


Fig. 1. FE-SEM images of AuNPs attached ITO. After immersing into the seed solution for 2 hrs., the ITO substrates were immersed into the growth solution for (A) 1 min., (B) 5 mins., (C) 1 hr. and (D) 24 hrs.

The AuNP/ITO electrodes were utilized in the observation of the electrooxidation of uric acid, ascorbic acid, dopamine, norepinephrine and epinephrine [10]. While the AuNP/MPTMS/ITO electrodes depressed the selectivity for the determination of epinephrine in the presence of ascorbic acid due to the existence of the thiol monolayer, the AuNP/ITO electrodes could improve the detection sensitivity and retain the selectivity [10].

The AuNP/ITO electrodes provided a biocompatible matrix for the immobilization of hemoglobin (Hb). By electrochemical impedance measurements, AuNPs modification and Hb immobilization on the electrode surfaces were characterized using $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox probe [11]. Owing to the promoted electron transfer of Hb by AuNPs, the Hb immobilized gold nanoparticles-modified ITO (Hb/AuNP/ITO) electrode exhibited an effective catalytic response to the reduction of H_2O_2 with good reproducibility and stability. The linear relationship existed between the catalytic current and the H_2O_2 concentration in the range of 1×10^{-5} - 7×10^{-3} M. The detection limit (S/N = 3) was 4.5×10^{-6} M [11].

Similarly, as the applications of the AuNP/ITO electrodes to the immobilization of myoglobin (Mb), a mediator-free H_2O_2 sensor was developed. The Mb modified AuNP/ITO electrodes showed good reproducibility and stability in pH 7.0 buffer, which was based on the catalytic activity of Mb immobilized on AuNP/ITO toward the reduction of H_2O_2 . The linear relationship existed between the catalytic current and the H_2O_2 concentration in the range of 2.5×10^{-6} - 5×10^{-4} M with a detection limit (S/N = 3) of 4.8×10^{-7} M [12]. In this case, the direct electron transfer of Mb was shown by the stable and well-behaved voltammetric responses with the Mb immobilized AuNP/ITO electrodes in buffer solutions [12].

Furthermore, utilizing the soft capping of CTAB on the grown AuNPs, our group studied the electrocatalytic activity of three-dimensional monolayer of 3-mercaptopropionic acid assembled on AuNPs on ITO [13].

In addition, the effects of capping reagents on the electron transfer reactions on AuNPs attached ITO electrodes were revealed by observing the cyclic voltammograms before and after the replacements of the capping reagents [14].

2.3 Revised methods for attachment and growth of gold nanoparticles on ITO

Some revised methods to improve or perturb the seeding processes have been proposed from our group for the purposes to recognize the significance of the seeding treatment.

The first approach is an in situ reduction method in the seeding process. It was demonstrated that when the seeding procedure of our seed-mediated growth process on ITO surfaces was modified to be the reduction of AuCl_4^- proceed in the presence of an ITO substrate, the density of AuNPs directly grown on surface could be highly improved [15]. By FE-SEM and cyclic voltammetry, the growth of AuNPs with increasing of

growth time on the defect sites of nanostructured ITO surface was monitored. Using the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox probe, the increasingly facile heterogeneous electron transfer kinetics resulting from the deposition and growth of Au NP-arrays was observed. The AuNP/ITO electrodes thus prepared exhibited high catalytic activity toward the electro-oxidation of nitric oxide, which could provide electroanalytical application for nitric oxide sensing [15].

The second approach is an attempt to grow high-density AuNPs on ITO surfaces using a "touch" seeding technique instead of the "normal" seeding in the seed-mediated growth procedure [16]. This approach provided a simple and useful strategy to promote the growth of AuNPs on ITO surfaces by simply touching the surface that has already been covered with a drop of gold nano-seed solution with a tissue paper. The FE-SEM characterization of the growth of AuNPs on two different surface structures of ITO, i.e., rough and smooth structures, has confirmed that this approach is very effective and prospective in fostering the growth of high-density AuNPs with a relatively small size (ca. 10-30 nm) of spherical structure [16]. An optical properties study confirmed that the modified ITO system could be used for photo-electrochemical applications, such as a functionalized optically transparent electrode.

The dense attached AuNP/ITO electrodes thus fabricated was applied to observe the electrochemical responses of hydroquinone and *p*-aminophenol in phosphate buffer solutions [17]. Although the electron transfer reactions of these compounds were sluggish on the bare ITO electrode, improved electrochemical responses could be observed on the AuNP/ITO electrodes fabricated with the "touch" seed-mediated growth method.

The dense attachment of AuNPs also could be performed using a cast seed-mediated growth method [18]. The cast seeding with 3-cycle of the drop of the seed solution containing Au nano-seed particles and the evaporation at 30 °C followed by the treatment in the growth solution containing HAuCl_4 , CTAB and ascorbic acid was found to be suitable to prepare the AuNPs attached ITO surfaces having higher density and narrower size distribution. The 10-cycle cast seeding formed the connected or networked nanostructures of AuNPs, though the optical properties were different from those of the dispersed AuNP-attached ITO [18]. The cast seeding approach provided a facile and useful strategy to attach AuNPs on the surface without the use of certain organic binder molecules.

Furthermore, adjusting the concentration of citrate ions in the seed solution from 1 mM to 50 mM by adding the trisodium citrate after the preparation of the Au seed solution, we could observe the dramatic changes in the SEM images and actual color indicating the changes in nanostructures of AuNPs formed on the ITO surfaces [19]. Whereas the attachment of smaller AuNPs with higher density were observed when 25 mM citrate ions were added in the seed solution, larger AuNPs were observed to attach at 50 mM. On the basis of this difference and the surface SEM images observed just after seeding, it was inferred that the citrate ions affected the growth process as well as the seeding

process. The repulsive power expected from the increased negative charges of citrate ions were not significant, but rather the dense attachment was promoted as the peculiar effect of citrate ions. Such control of the AuNPs attachment on ITO would be practically effective because the dense attachment can be performed by just changing the composition of the seed solution.

2.4 Attachment and growth of gold nanoparticles on different surfaces

The seed-mediated growth method for the attachment and growth of AuNPs was applied to the modification of the surfaces of the different substrates. As the result, it was found that the modification was possible for various materials, such as glassy carbon (GC), mica, stainless, epoxy rosin, phenol rosin and simple glass etc., though the attached density and the grown size of AuNPs were varied depending on the substrates.

In addition, the attachment method of AuNPs on ITO surfaces was applied to a slight different fabrication of the functional electrode. It was utilized to attach AuNPs on the mesoporous TiO₂ film on GC substrate prepared with the liquid phase deposition process [20].

The TiO₂ film showed a strong inhibition to the electron transfer process of [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ redox couple, while the electrochemical measurements indicated that the overpotential for the reduction of maleic acid on bare GC was significantly decreased after the electrode surface was covered with electroactive film, demonstrating the electrocatalytic activity of the TiO₂ film. However, by attaching AuNPs, the sluggish heterogeneous electron transfer kinetics at TiO₂ film was effectively improved while the catalytic activity of TiO₂ film was retained [20]. This is an example that the AuNPs affect the less conducting electrode material.

2.5 Attachment and growth of gold nanoplates on ITO

Although the approaches mentioned in 2.3 were mainly focused on the seeding process, the modification of the growth process should have a potential to alter the grown nanostructures of AuNPs on ITO.

As a new strategy to attach Au nanoplates on ITO surfaces, we permitted the two-dimensional crystal growth of Au through the liquid phase reduction from Au nano-seed particles attached on the ITO surface by using poly(vinylpyrrolidone) (PVP) as a capping reagent in the growth solution instead of CTAB [21].

By controlling the concentration of PVP, the formation of Au nanoplates was possible with surface coverage as high as 30%, though various shaped Au nanocrystals were concurrently formed on the ITO. The Au nanoplates were single crystalline in nature with (111) basal plane, and the edge-length up to ca. ~ 2 μm, growing parallel to the surface of ITO [21]. The concentration of PVP in the growth solution was a key factor for the formation of Au nanoplates, because at higher or lower concentrations of PVP the purely spherical or irregular shaped nanoparticles were formed [21]. The absorption spectra implied anisotropic and specific optical characteristics of the Au nanoplate-attached ITO.

3. ATTACHMENT OF OTHER METAL NANOPARTICLES

3.1 Attachment and growth of silver nanoparticles on ITO

By applying the same seed-mediated growth method, we successfully attached Ag nanosphere and nanorod particles on ITO surfaces [22]. Similar to the cases of AuNPs, the attachment of silver NPs (AgNPs) could be performed without using bridging reagents, such as 3-mercaptopropyl-trimethoxysilane, just through a two-step immersion into the seed solution first, and then into the growth solution that contained AgNO₃, CTAB and ascorbic acid [22].

It was found that the formed nano-structures were very sensitive to the amount of the ascorbic acid in the growth solution. While AgNPs grew on the ITO with keeping a moderate dispersion when the concentration of ascorbic acid in the growth solution was 0.64 mM, the formation of nanorods and nanowires was observed when it was increased to 0.86 mM.

The attachment of Ag nanoparticles onto the ITO surfaces was strong enough for further use, e.g., as the working electrode. From the electrochemical measurement, it was confirmed that the outer-spheres of the Ag nanoparticles involved in the redox reaction show the typical oxidation and reduction waves of Ag [22].

In addition, the redox behavior of [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ was improved on the AgNP/ITO electrode reflecting the low electron transfer resistivity [22]. This result indicated the AgNPs promoted the electron transfer reactions by presenting on the conducting ITO surface. The AgNP/ITO electrode was examined for the reduction of the methyl viologen dication in order to discuss some features of the fabricated electrodes [22].

3.2 Attachment and growth of palladium nanoparticles on ITO

Palladium NPs (PdNPs) were successfully attached and grown on the ITO surface also using the seed-mediated growth method [23]. After the growth treatment for 24 hrs, PdNPs grew up to 60 - 80 nm exhibiting crystalline appearances with facets and accompanying the formation of short rod-like nanocrystals as a minor product. Thus prepared PdNPs tend to stick each other, so that the dense gathering of PdNPs was observed on the ITO surfaces [23].

Due to the dense attachment, the PdNP/ITO electrodes had a significantly lowered charge transfer resistance compared with that of a bare ITO, and the redox reaction of [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ was observed as reversible in 0.1 M phosphate buffer solution. The electrocatalytic property of PdNPs was confirmed for the reduction of oxygen. In addition, some typical responses were observed in 0.5 M H₂SO₄ with the PdNP/ITO electrode, reflecting both the characteristics of NPs and the thin layer in nano-scale [23].

The proposed preparation method of PdNP-attached surfaces would be promising for the catalytic applications as well as the electrochemical uses.

3.3 Attachment of platinum nanoparticles

We also tried to prepare the platinum NPs (PtNPs) on ITO surfaces using the seed-mediated growth method.

However, in our preliminary trial, it was found that the seed-mediated growth method was difficult to apply to the fabrication of PtNPs attached ITO. It was because brown precipitates were appeared in the growth solution prepared in the same principle, i.e., containing K_2PtCl_4 , CTAB and ascorbic acid, even when the seed-attached ITO was not immersed.

In spite of this difficulty, after several trials, we have found that the attachment of PtNPs on ITO is possible by a rather simple method, i.e., the one-step in situ chemical reduction of $PtCl_4^{2-}$ by ascorbic acid without using CTAB [24].

The attached and grown PtNPs were spherical having an agglomerated nanostructure composed of small nano-clusters. From the morphological changes depending on the growth time, PtNPs were found to be grown via the progressive nucleation mechanism [24].

As the characteristics of the PtNP/ITO as a working electrode, it was found that the charge transfer resistance was significantly lowered due to the grown PtNPs. Hence, for a typical redox system of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$, the PtNP/ITO electrode exhibited the electrochemical responses similar to those of the bulk Pt electrode [24]. Furthermore, it was clarified that the PtNP/ITO electrodes had significant electrocatalytic properties for the oxygen reduction and methanol oxidation. The PtNPs that had the agglomerated nanostructure may be promising for a new type of electrode materials.

The same in situ reductive method for preparing PtNPs was applied to the modification of GC surfaces. As the result, a Pt thin continuous film composed of small nano-clusters which had a further agglomerated nanostructure of small grains could be attached on the GC surface [25]. It was found that the electrocatalytic ability of the Pt nano-cluster film (PtNCF) for the methanol oxidation was apparently higher than those of the Pt nano-clusters dispersedly attached on GC or PtNP/ITO electrodes. In addition, the electrocatalytic performance of PtNCF per Pt amount was superior to that of Pt black on GC [25].

These results indicate that, in spite of the continuous nano-structures, nano-grains of PtNCF worked effectively for the catalytic electrolysis. The present PtNCF can be regarded an interesting thin film material, which can be easily prepared by one-step chemical reduction.

3.4 Other nanoparticles

In addition to the above precious metals, nickel nanoparticles (NiNPs) can be attached on the ITO surfaces through the chemical treatment. In the case, by changing the procedures to treat the ITO surfaces with Ni solutions, Ni nanofilms (NiNFs) can be formed on the ITO surfaces. The electrochemical studies on NiNPs and NiNFs are now in progress.

In addition, Dr. Marken's group, Bath, UK, showed that the preparation method of core-shell TiC-TiO₂ nanoparticle films immobilized at ITO electrode surfaces with the interesting electrochemical properties collaborating with us [26].

4. APPLICATIONS OF METAL NANOPARTICLE-ATTACHED ITO SUBSTRATES

4.1 Optical properties

The metal NPs attached ITO or glass materials exhibit interesting optical characteristics. For investigating these properties, we are now collaborating with Prof. Kityk's group, Czestochowa, Poland, and Prof. Ebothe's group, Reims, France, whose major is non-linear optics.

Up to now, various interesting optical properties of AuNPs [27-31] and AgNPs [32,33] attached ITO or glass have been reported as the results of the collaborations.

Because our seed-mediated growth approach includes the chemical reduction in solution, the doping of the second ions can be easily carried out. Thus, not only for the nanoparticles of pure metals, the luminescence properties of erbium ion doped AgNPs has been reported [34].

Now, the target of the collaboration is expanding to PdNPs and PtNPs [35], together with the trials for NiNPs, which is now in progress.

In addition to the non-linear optical properties of metal NPs, the modification of metal NPs has a potential to be uses as new type of substrate for spectroscopic measurements. As the example, the utilization of AuNPs attached glass for the surface plasmon resonance spectroscopy has been reported [36].

4.2 Electrochemistry

The AuNPs attached ITO electrodes can be utilized in the electrochemical measurements of biomolecules. By shipping the AuNPs electrodes fabricated in our group to India, we are collaborating with Prof. Goyal's group in Rookee, India.

Many successful results have been obtained using the electrodes and mainly with a differential pulse voltammetry technique, e.g., for the electrochemical analysis of uric acid [37], paracetamol [38] and atenolol [39]. In addition, simultaneous determination of guanosine and guanosine-5'-triphosphate [40] and dopamine and serotonin [41] were possible using the AuNPs attached ITO electrodes.

5. CONCLUSIONS

We found the validity of the seed-mediated method for the surface modifications with metal NPs by chance. The origin was a trial as the blank experiment for comparing the attachments of metal NPs with bridging reagents.

However, in the course of the studies, it was revealed that small NPs could attach on the surfaces of the substrates, and that they could be grown via the chemical reductions with keeping the strong attachment.

As shown in this paper, this method can be utilized in the preparation of various kinds of metal NPs attached surfaces, and the metal NPs attached substrates would be interesting materials as functional electrodes and in the field of non-linear optics.

The concept of the strong attachment of metal NPs would be utilized as the functional anchors on the surface modification. Such nano-contact utilizing metal NPs may be interesting in relation with the researches of buried interfaces.

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