

# Thermal-driven attachment of gold nanoparticles prepared with ascorbic acid onto indium tin oxide surfaces

Md. Abdul Aziz · Munetaka Oyama

Received: 26 December 2012 / Accepted: 26 March 2013 / Published online: 6 April 2013  
© Springer Science+Business Media Dordrecht 2013

**Abstract** Thermal-driven attachment of gold nanoparticles (AuNPs), of which size was less than 50 nm, onto the surfaces of indium tin oxide (ITO) is reported as a new phenomenon. This was permitted by preparing AuNPs via the reduction of hydrogen tetrachloroaurate (HAuCl<sub>4</sub>) with ascorbic acid (AA). While the AuNPs prepared via the AA reduction sparsely attached on the surface of ITO even at room temperature, a heat-up treatment at ca. 75 °C caused denser attachment of AuNPs on ITO surfaces. The attached density and the homogeneity after the thermal treatment were better than those of AuNP/ITO prepared using 3-aminopropyl-trimethoxysilane linker molecules. The denser attachment was observed similarly both by the immersion of ITO samples after the preparations of AuNPs by AA and by the in situ preparation of AuNPs with AA together with ITO samples. Thus, it is considered that the thermal-driven attachment of AuNPs would occur after the formation of AuNPs in the aqueous solutions, not via the growth of AuNPs on ITO surfaces. The preparation of AuNPs with AA would be a key for the thermal-driven attachment because the same attachments were not observed for AuNPs prepared with citrate ions or commercially available tannic acid-capped AuNPs.

**Keywords** Gold nanoparticles · Hydrogen tetrachloroaurate · Ascorbic acid · Indium tin oxide · Thermal treatment

## Introduction

For preparing gold nanoparticles (AuNPs) in aqueous solutions, the reduction of AuCl<sub>4</sub><sup>-</sup> with citrate is a well-known method since a report by Turkevich et al. (1951) and the refinement by Frens (1973). On the other hand, reports on the reduction of AuCl<sub>4</sub><sup>-</sup> with ascorbic acid (AA) are very limited though it can also prepare AuNPs in aqueous solutions. For example, Kimling et al. (2006) studied the AA reduction process at room temperature to compare with the citrate reduction initiated with thermal treatments and UV irradiation for preparing AuNPs. Goia and coworkers explored the reduction by iso-ascorbic acid (iso-AA) (Goia and Matijevic 1999; Andreescu et al. 2006), which is equivalent in reducing properties with AA but biologically inactive (Goia and Matijevic 1999). Compared with the citrate reduction, “stabilizer-free” AuNPs were reported to be prepared in aqueous solutions at ambient temperature (Andreescu et al. 2006). Recently, Aslam and coworker reported the pH-dependent synthesis of AuNPs using AA (Tyagi et al. 2011). In addition to these achievements, i.e., the pure reaction of AuCl<sub>4</sub><sup>-</sup> and AA or iso-AA, the reduction by AA was conducted in the presence of

Md. A. Aziz · M. Oyama (✉)  
Department of Material Chemistry, Graduate School  
of Engineering, Kyoto University, Nishikyo-ku,  
Kyoto 615-8520, Japan  
e-mail: oyama.munetaka.4m@kyoto-u.ac.jp

PVP (Wagner and Kohler 2005), in reverse micelles (Sun et al. 2009), and for fibrous assembled structures (Murugadoss et al. 2007).

In these studies, formation processes and formed structures of AuNPs with AA have been explored well. However, there is no report concerning any differences in functional properties of AuNPs, thus prepared with the AA reduction in comparison with those prepared with citrate. Because AA has no special functional groups and because AA should work simply as a stronger reductant in synthesizing AuNPs (Kimling et al. 2006), no attention might have been paid to the specific characteristics of AuNPs prepared with the AA reduction. However, as an interesting phenomenon, we have found that it is possible to attach AuNPs densely onto the surface of indium tin oxides (ITOs) by simply heating up the solution of AuNPs prepared with AA to ca. 75 °C. Thus, in the present article, we would like to report this new functional feature of AuNPs prepared with AA, which would be useful and powerful for preparing AuNP-modified surfaces.

The attachment of AuNPs on ITO surfaces is important in the field of electrochemistry. While the use of suitable linker molecules, such as 3-aminopropyl-trimethoxysilane (APTMS) and 3-mercaptopropyl-trimethoxysilane would be a representative method (Freeman et al. 1995; Cheng et al. 2002a, b; Ballarin et al. 2008; Oyama et al. 2009), our group is proposing a seed-mediated growth method for preparing AuNP/ITO electrode (Kambayashi et al. 2005) and some revisions of this method (Zhang and Oyama 2005; Ali Umar and Oyama 2005, 2006a, b). Since a physisorption of small nanoseed particles is utilized as the initial attachment in this method, the AuNP/ITO electrodes can be prepared without using linker molecules. Therefore, the electrochemical measurements can be carried out with smaller charge transfer resistances (Zhang et al. 2004, 2005) and moreover, the capping reagents were found to have less effect in the electrochemical measurements (Horibe et al. 2007).

However, simpler treatments should be still desirable for fabricating AuNP/ITO nanocomposites. Thus, we would like to show a quite simple preparation of AuNP/ITO using AuNPs prepared with AA reduction and the thermal treatment at ca. 75 °C. This attachment is specific for AuNPs prepared with AA because such attachment of AuNPs was not totally observed in the solution of AuNPs prepared with citrate.

Therefore, the thermal-driven attachment would be worthwhile proposing as a new functional feature of AuNPs prepared with the AA reduction.

## Experimental

ITO-coated glass substrates (10 mm × 20 mm × 1.1 mm), of which sheet resistance was ca. 30 Ω/sq., were purchased from Geomatec Co. Ltd., Japan. Fluorine-doped tin oxide (FTO)-coated glass slides, of which sheet resistance was ca. 15 Ω/sq., were purchased from Flexitec, Brazil. Hydrogen tetrachloroaurate (HAuCl<sub>4</sub>), cetyltrimethylammonium bromide, APTMS, and 20-nm Au colloid were purchased from Sigma-Aldrich. Other reagents were obtained from Wako Chemicals, Japan. All solutions were prepared with ultra-pure water obtained from a water purification system (Millipore WR600A, Yamato Co., Japan).

At first, an ITO substrate were cleaned with trichloroethylene, ethanol, and water successively and dried at 40 °C. Next, it was immersed in the mixture of water:hydrogen peroxide (30 %):ammonium hydroxide (30 %) in a ratio of 5:1:1 (v/v) at 70 °C for 1.5 h. Then, the AuNP/ITO electrodes were prepared via two procedures, i.e., the in situ reduction with the presence of an ITO substrate and the immersion of an ITO substrate after preparing AuNPs. The details of the procedures are mentioned later with the results of surface observation. For comparison, 20-nm AuNP-attached ITO electrodes were prepared using the APTMS linker and 20-nm AuNPs from Sigma-Aldrich. For this preparation, a piece of cleaned ITO was immersed in 2 % alcoholic solution of APTMS, and then in 20-nm Au colloid solution from Sigma-Aldrich for 2 h at room temperature. All the prepared AuNP/ITO electrodes were washed with pure water after the preparations and dried at 40 °C. Scanning electron microscopic (SEM) images were observed using a field-emission SEM (FE-SEM; JSM-7400F, JEOL, Japan).

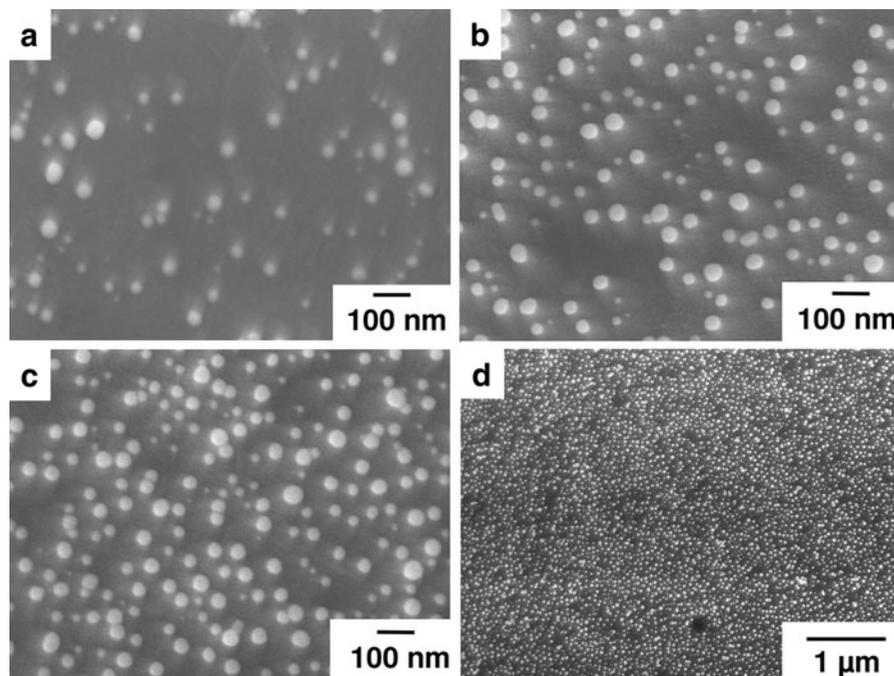
## Results and discussion

As the first example of the thermal-driven attachment of AuNPs prepared with the AA reduction, we show some FE-SEM images of AuNPs attached on ITO

surfaces in Fig. 1. For preparing the sample, first we prepared a solution of AuNP by mixing equivolume 2.5 ml aqueous solutions of 1.34 mM  $\text{HAuCl}_4$  and 10 mM AA at room temperature, and kept it for 15 min. And then, a piece of ITO was immersed in the solution of AuNPs and left at room temperature for further 15 min. A typical FE-SEM image of the thus-prepared AuNP/ITO is shown in Fig. 1a. As shown in this FE-SEM image, the attachment of AuNPs was confirmed after this treatment even after just immersing an ITO sample into the solution of AuNPs at room temperature. In the present study, for all the samples, the surfaces were washed by a copious amount of pure water after immersion, and then dried before the SEM measurement. Thus, the attachment is recognized to be strong enough against such washing.

Next, after preparing the same solution of AuNPs, a piece of ITO was immersed in the solution at room temperature, and then the solution was heated for 15 min at ca. 75 °C using a hot water bath. As apparently recognized from Fig. 1b in comparison

with Fig. 1a, the amount of attached AuNPs was increased by the thermal treatment at 75 °C. Thus, the AuNPs is considered to attach by the thermal treatment when they are prepared by the AA reduction. Figure 1c, d shows the SEM results observed for an ITO sample that was immersed into the solution of AuNPs which was pre-heated for 15 min at 75 °C. In this case, after the immersion, the sample was kept for 15 min. As shown in Fig. 1c, the pre-heating of the solution of AuNPs had some effects to enrich the attachment of AuNPs. Hence, it is concluded that the immersion into the pre-heated solution would be effective for attaching AuNPs compared with the immersion at room temperature followed by a heat-up treatment. However, since the difference in the attached density between Fig. 1b and c was not so significant, it is also mentioned that the thermal-driven treatment would be a key procedure to attach AuNPs rather than the pre-heating of the solution. From Fig. 1d, which is a zoom out SEM image, it is recognized that the AuNPs attached densely on the ITO surface with keeping certain homogeneity.



**Fig. 1** Typical FE-SEM images of AuNP/ITO electrodes prepared via the immersion of ITO after preparing the solution of AuNPs. At first, a solution of AuNPs was prepared by mixing equivolume 2.5 ml aqueous solutions of 1.34 mM  $\text{HAuCl}_4$  and 10 mM AA at room temperature. Then, **a** a piece of ITO was immersed in the solution and kept for 15 min at room

temperature, or, **b** a piece of ITO was immersed in the solution and heated for 15 min at ca. 75 °C using a hot water bath, or **c**, **d** the solution was heated up at ca. 75 °C, kept for 15 min, and then a piece of ITO was immersed and left for 15 min at 75 °C. **d** A zoom out image of **c**

For comparison, we tried to observe the same attachment of AuNPs prepared citrate by heating up at 75 °C. However, we could not observe any images that showed the attachment of AuNPs onto ITO surfaces when AuNPs were prepared via the citrate reduction. Furthermore, this was also true in the cases using a commercially available 20-nm Au colloid solution (Sigma-Aldrich, capped with tannic acid). Therefore, the attachment as summarized in Fig. 1 would be a specific feature of the AuNPs prepared with AA. In particular, though AuNPs do attach at room temperature, the thermal-driven attachment would be regarded as an interesting and useful feature of the AuNPs prepared via the AA reduction.

We compared the attached density of the AuNPs with the conventional method. Actually, we prepared 20-nm AuNP/APTMS/ITO electrodes using commercially available 20-nm Au colloid from Sigma-Aldrich. The FE-SEM images of the prepared surface are shown in Fig. 2. In the high magnification image (Fig. 2a), it is recognized that the size uniformity of the commercial product is much better in comparison with our AuNP/ITO electrodes prepared with AA. However, in the low magnification image (Fig. 2b), some gathered areas and lower density areas are shown even for the 20-nm AuNP/APTMS/ITO. In general, the denser attachment of AuNPs prepared with AA could be recognized as the result of the comparison. For this difference, some physical properties of AuNPs might affect as well as the methodological difference for attaching AuNPs. Whereas size distribution of AuNPs prepared with AA was not good, it is expected that the AA-capped AuNPs can be gathered densely without being suffered by some repulsions. However, as for the details of the integrations of AuNPs, further studies such zeta-potentials measurement would be necessary.

While the results in Fig. 1 were obtained by immersing ITO samples into the solutions of AuNPs prepared with AA, an in situ reduction might change the attachment of AuNPs. Thus, we observed some FE-SEM images after some in situ reduction treatments. As the actual procedure, a piece of cleaned ITO was immersed in 2.5 ml aqueous solution of 1.34 mM  $\text{HAuCl}_4$  at room temperature, and then, 2.5 ml aqueous solution of 10 mM AA was added and left for 15 min. Figure 3a shows a typical FE-SEM image of the sample prepared by this procedure. The attachment of AuNPs was confirmed in this case, but the density

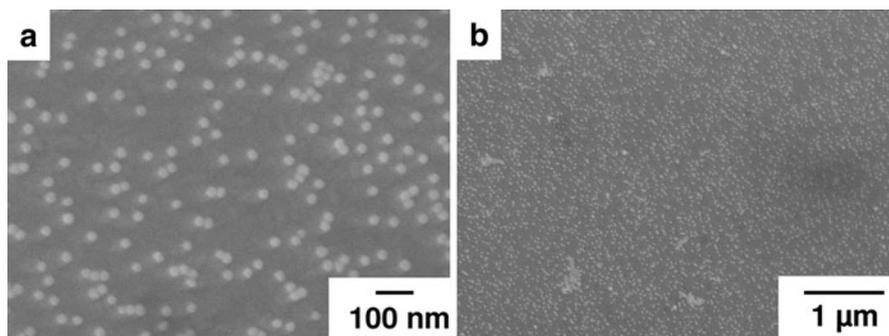
was sparse and the result was not very different from the previous case in that the ITO sample was immersed after the reduction (Fig. 1a).

In this case, to observe the thermal effects on the attachment of AuNPs, we tried to heat-up the solution after the in situ reduction to ca. 75 °C using a hot water bath. As the result, the attachment of AuNPs was promoted as shown in Fig. 3b, so that a significant effect of the thermal treatment on the dense attachment was confirmed. However, the attached density of AuNPs was not higher than the cases of the immersion after the reduction (i.e., Fig. 1). Based on the similarity in the attachments between Figs. 1 and 3, it is inferred that the in situ reduction has less effects on the attachment and growth of AuNPs, but rather, it is reasonable to regard that the AuNPs formed in the solution should attach on the surface of ITO, in particular with the thermal treatment.

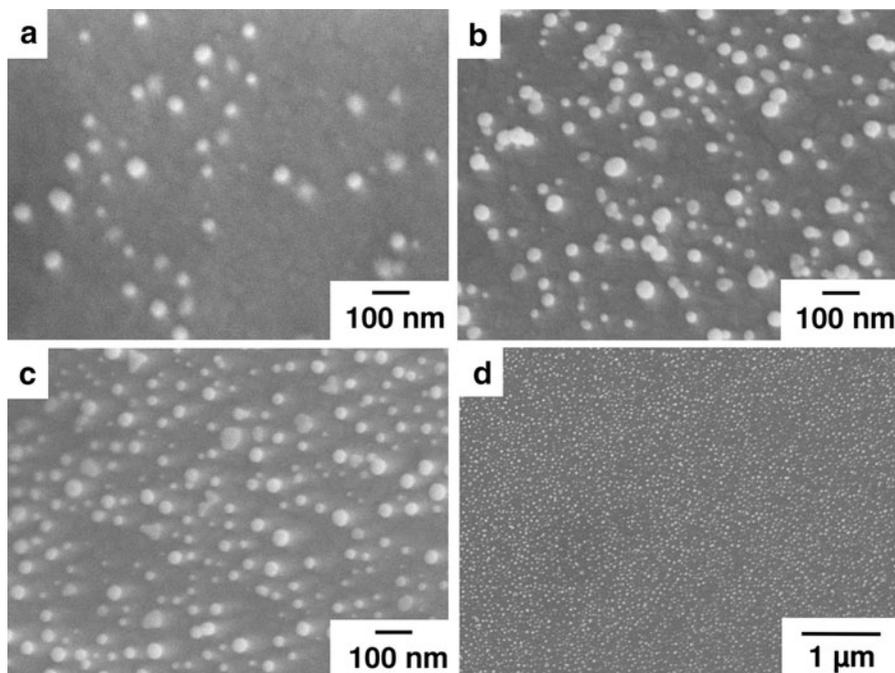
Figure 3c, d shows the FE-SEM results observed when the concentration of  $\text{HAuCl}_4$  was changed 0.68 mM. A slight increase of the attachment of AuNPs was recognized. So, the better attachment was observed in this case with the density and homogeneity recognized in Fig. 3d. However, when the concentration of  $\text{HAuCl}_4$  was changed 0.34 or 2.7 mM, the attached density was decreased apparently. Thus, the optimal concentration for  $\text{HAuCl}_4$  would be 0.5–1.5 versus 10 mM AA for equi-amount mixing to achieve the dense attachment of AuNPs.

Compared with the seed-mediated grown AuNPs on ITO surfaces (Kambayashi et al. 2005), the appearances of AuNPs prepared in the present preparations (Figs. 1, 3) were different. That is, while the crystal-like surfaces and growth were observed in the seed-mediated growth, the round-shaped AuNPs were dominant in the thermal-driven attachment. Thus, special atomic surfaces or facets were not considered to exist on the surfaces of AuNPs in this present case, though further studies such as an XRD analysis would be necessary for details.

The exact attachment mechanism of the thermal-driven attachment is unclear at this moment. However, because the same phenomenon was not observed for citrate-capped AuNPs and the commercially available 20-nm AuNPs capped with tannic acid, the capping of AA on AuNPs would be a key factor. Also, the attachment was apparently promoted at 75 °C, so that the state of capping AA at higher temperature should affect the promotion. As a possibility, less-capped



**Fig. 2** Typical FE-SEM images of a 20-nm AuNP/APTMS/ITO electrode. This electrode was prepared using the APTMS linker and commercially available 20-nm Au colloid (Sigma-Aldrich). **b** A zoom out image of **a**



**Fig. 3** Typical FE-SEM images of AuNP/ITO electrodes prepared via the in situ reduction. **a** A piece of cleaned ITO was immersed in an aqueous solution of 1.34 mM  $\text{HAuCl}_4$  at room temperature, and then, an aqueous solution of 10 mM AA was added, and left for 15 min at room temperature. **b–d** After

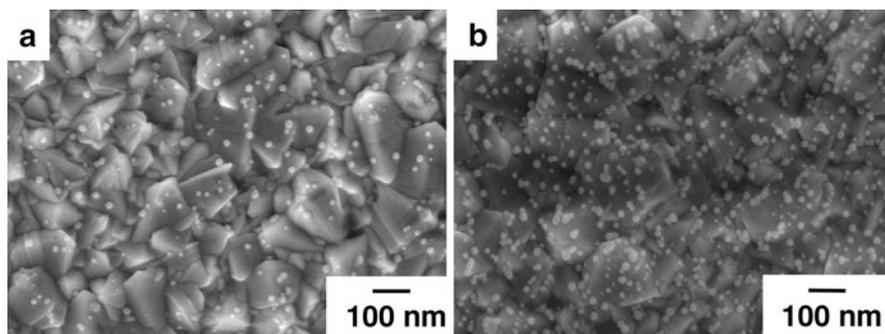
mixing solutions of  $\text{HAuCl}_4$  (in which a piece of ITO was immersed) and 10 mM AA at room temperature, the mixed solution was heated up to ca. 75 °C, and kept for 15 min. The concentration of  $\text{HAuCl}_4$  was **b** 1.34 mM and **c**, **d** 0.68 mM

state of AA with some fluidity at higher temperature might activate the attachment of AuNPs on ITO surfaces.

As for the stability of AuNPs attached on ITO surfaces, all the prepared AuNP/ITO electrodes were washed with a copious amount of pure water before the FE-SEM measurements. In addition, the AuNP/ITO electrodes were actually used as the working electrodes for several systems, and consequently, they

gave stable responses without changing the electrochemical characteristics. Thus, we believe that the prepared AuNP/ITOs are tough enough for electrochemical measurements, similar to the AuNP/ITOs prepared by the seed-mediated growth method.

The thermal-driven attachment was examined also on the surfaces of FTO. The results are shown in Fig. 4. In this case, background images are those of the crystals of FTO, and the formation of AuNPs were



**Fig. 4** Typical FE-SEM images of AuNP/FTO electrodes prepared via the in situ reduction. A piece of cleaned FTO was immersed in an aqueous solution of 1.34 mM HAuCl<sub>4</sub> at

room temperature, and an aqueous solution of 10 mM AA was added. Then, the mixed solution was **a** kept for 15 min at room temperature, or **b** heated up to ca. 75 °C and kept for 15 min

observed on the FTO crystals. The denser attachment of AuNPs was also confirmed on FTO crystals after a thermal treatment at 75 °C (Fig. 4b) in comparison with the result at the immersion at room temperature (Fig. 4a). Thus, it is expected that the proposed method can be applied also on the nanocrystals.

## Conclusions

In the present study, we could propose a new concept of the thermal-driven attachment of AuNPs. While the preparation of AuNPs with AA or iso-AA has been known for those in solutions (Goia and Matijevic 1999; Andreescu et al. 2006; Kimling et al. 2006), it was clarified that the AuNPs prepared via the AA reduction could attach on the ITO surfaces, and furthermore, the thermal treatment significantly promoted the attachment for denser modification. While a hot water bath was used in the heat-up treatment to ca. 75 °C for simplicity, some more control of the density may become possible with the rigid control of temperature.

The present thermal-driven attachment would be a new concept for the surface modification with AuNPs. Actually, while the same attachments were not observed for AuNPs capped with citrate or tannic acid, the present phenomenon would be a specific for the AuNPs prepared with AA. As the appearing point of the proposed attachment of AuNPs, the simplicity of the procedures would be quite beneficial and useful to modify to form AuNP/ITOs. The detailed functions of AA to attach on the surfaces of ITO are not clarified yet. However, practically, such attachment would be

interesting from a view of the fabrications of nanocomposite materials including AuNPs through the nanostructuring on the surfaces.

The prepared AuNPs arrays would be regarded as densely modified nanoelectrode ensembles, so that they could be applied as working electrodes. So, such studies are now in underway.

**Acknowledgments** M. A. A. thanks the Japan Society for the Promotion of Science (JSPS) for the fellowship. This study was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Science, Sports and Technology, Japan, Nos. 20550074 and 21-09245.

## References

- Ali Umar A, Oyama M (2005) Growth of high-density gold nanoparticles on an indium tin oxide surface prepared using a “touch” seed-mediated growth technique. *Cryst Growth Des* 5:599–607
- Ali Umar A, Oyama M (2006a) A cast seed-mediated growth method for preparing gold nanoparticle-attached indium tin oxide surfaces. *Appl Surf Sci* 253:2196–2202
- Ali Umar A, Oyama M (2006b) Attachment of gold nanoparticles onto indium tin oxide surfaces controlled by adding citrate ions in a seed-mediated growth method. *Appl Surf Sci* 253:2933–2940
- Andreescu D, Sau TK, Goia DV (2006) Stabilizer-free nanosized gold sols. *J Colloid Interface Sci* 298:742–751
- Ballarin B, Cassani MC, Scavetta E, Tonelli D (2008) Self-assembled gold nanoparticles modified ITO electrodes: the monolayer binder molecule effect. *Electrochim Acta* 53:8034–8044
- Cheng W, Dong S, Wang E (2002a) Colloid chemical approach to nanoelectrode ensembles with highly controllable active area fraction. *Anal Chem* 74:3599–3604
- Cheng W, Dong S, Wang E (2002b) Gold nanoparticles as fine tuners of electrochemical properties of the electrode/solution interface. *Langmuir* 18:9947–9952

- Freeman RG, Grabar KC, Allison KJ, Bright RM, Davis JA, Guthrie AP, Hommer MB, Jackson MA, Smith PC, Walter DG, Natan MJ (1995) Self-assembled metal colloid monolayers: an approach to SERS substrates. *Science* 267: 1629–1632
- Frens G (1973) Controlled nucleation for the regulation of the particle size in monodisperse gold suspensions. *Nat Phys Sci* 241:20–22
- Goia DV, Matijevic E (1999) Tailoring the particle size of monodispersed colloidal gold. *Colloid Surf A* 146:139–152
- Horibe T, Zhang J, Oyama M (2007) Effects of capping reagents on the electron transfer reactions on gold nanoparticle-attached indium tin oxide electrodes. *Electroanalysis* 19:847–852
- Kambayashi M, Zhang J, Oyama M (2005) Crystal growth of gold nanoparticles on indium tin oxides in the absence and presence of 3-mercaptopropyl-trimethoxysilane. *Cryst Growth Des* 5:81–84
- Kimling J, Maier M, Okenve B, Kotaidis V, Ballot H, Plech A (2006) Turkevich method for gold nanoparticle synthesis revisited. *J Phys Chem B* 110:15700–15707
- Murugadoss A, Pasricha R, Chattopadhyay A (2007) Ascorbic acid as a mediator and template for assembling metallic nanoparticles. *J Colloid Interface Sci* 311:303–310
- Oyama M, Orimo A, Nouneh K (2009) Effects of linker molecules on the attachment and growth of gold nanoparticles on indium tin oxide surfaces. *Electrochim Acta* 54: 5042–5047
- Sun K, Qiu J, Liu J, Miao Y (2009) Preparation and characterization of gold nanoparticles using ascorbic acid as reducing agent in reverse micelles. *J Mater Sci* 44:754–758
- Turkevich J, Stevenson PC, Hillier J (1951) A study of the nucleation and growth processes in the synthesis of colloidal gold. *Discuss Faraday Soc* 11:55–75
- Tyagi H, Kushwaha A, Kumar A, Aslam M (2011) pH-dependent synthesis of stabilized gold nanoparticles using ascorbic acid. *Int J Nanosci* 10:857–860
- Wagner J, Kohler JM (2005) Continuous synthesis of gold nanoparticles in a microreactor. *Nano Lett* 5:685–691
- Zhang J, Oyama M (2005) Gold nanoparticle arrays directly grown on nanostructured indium tin oxide electrodes: characterization and electroanalytical application. *Anal Chim Acta* 540:299–306
- Zhang J, Kambayashi M, Oyama M (2004) A novel electrode surface fabricated by directly attaching gold nanospheres and nanorods onto indium tin oxide substrate with a seed mediated growth process. *Electrochem Commun* 6: 683–688
- Zhang J, Kambayashi M, Oyama M (2005) Seed mediated growth of gold nanoparticles on indium tin oxide electrodes: electrochemical characterization and evaluation. *Electroanalysis* 17:408–416