Deposition of gold nanoparticles upon bare and indium tin oxide film coated glass based on annealing process

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ABSTRACT
We presented a simple and efficient strategy for deposition of gold nanoparticles (AuNPs) upon transparent bare and indium tin oxide (ITO) film coated glass substrate using gold colloids as Au sources. The method involved two steps: embedding in polyvinyl alcohol (PVA) film and annealing at high temperature. The AuNPs deposited on solid substrate because of migration and coalescence of gold at high temperature. The optical and structural properties of the AuNPs were characterised by UV-vis absorption spectra and scanning electron microscopy. The results indicate that the surface of AuNPs upon substrate was clean as annealing at 600°C for 0.5 h. The size of AuNPs deposited on ITO glass increased with annealing time and volume of PVA-AuNPs. Meanwhile, the localised surface plasmon resonance peak of AuNPs deposited on substrate was also gradual red-shift. In addition, the size of AuNPs deposited on ITO substrate was larger than that on bare glass. This work provides a simple, low-cost and large-scale method for fabrication of substrate-based AuNPs, which is benefit for exploiting biosensors, photonic devices and optoelectronic devices.

1. Introduction
Gold nanoparticles (AuNPs) dispersed on solid substrates have attracted great attention during recent years due to many fascinating application in catalysis [1], chemical sensing [2,3] and solar energy device [4]. Supporting of the AuNPs onto solid substrates can avoid coalescence and agglomeration of the particles, as well as stabilise the nanostructures. Different technologies have been employed to produce gold nanostructures on the solid surfaces, such as silica [5], glass substrates [6] and carbon materials [7].

AuNPs are synthesised by wet chemical methods due to its scalability, reproducibility and versatility. A simple method for immobilisation of AuNPs upon solid substrate is self-assembly by linkers [8–12]. Organic polymers, such as 3-mercaptopropyltrimethoxysilane, 3-aminopropyliethoxyxilane, polyethyleneimine and Polyvinylpyridine, are used as
linkers, which is adsorbed on the surface of solid substrate in advance. Then the AuNPs are deposited on the modified substrate by self-assembly. The main disadvantage of this method is that AuNPs coexist with organic stabilisers and linkers, which makes the surface unclean and limits their application [13].

The lithography-based methods are widely employed to directly construct gold nano-structures [14–16]. However, this method is complexity, expensive and poor scalability. In recent years, AuNPs deposited on solid substrate can also be prepared by thermal annealing of thin gold films [17–19]. The metal films are produced by thermal evaporation or sputtering method. AuNPs are formed in the thermal annealing process due to solid state dewetting for the minimisation of surface energy. Since the prepared gold nanostructures are clean, they were widely used in developing localised surface plasmon resonance (LSPR) [20–22] and SERS sensors [23,24].

It is known that thermal treatment is a simple and efficient method to remove organic compounds [25,26]. Indium tin oxide (ITO) thin film coated glass is a widely-used substrate because of its good optical and electrical property. Furthermore, gold nanomaterials modified ITO platform was applied in many fields [27–30]. In this work, we develop an alternative route for depositing clear AuNPs on transparent bare and ITO glass with two steps, which included embedding nanoparticles in polyvinyl alcohol (PVA) film and thermal annealing processes. The AuNPs can distribute in PVA aqueous solution and then form solid film on the substrate. The next stage of annealing can obtain the nanostructures deposited on substrate with aggregation, coalesce and shape change. By controlling the volume of gold colloid and annealing time, the size of AuNPs deposited on substrate can be tunability.

2. Experimental
2.1. Chemicals
The regents of sodium citrate tribasic dihydrate (C₆H₅Na₃O₇•2H₂O), tetrachloroauric acid (HAuCl₄•4H₂O), PVA were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). ITO glass was purchased from Suzhou NSG Electronics Co. Ltd. (Suzhou, China). All chemical regents were of analytical grade and used as received without further purification. Water used in all experiments was purified by a Milli-Q system (resistivity 18.2 MΩ cm).

2.2. Preparation of gold colloid
Gold colloidal solution was synthesised by reduction of HAuCl₄ by sodium citrate [31]. Briefly, the solution containing 35 mL water and 20 mL of 1 mM HAuCl₄ in a 100 mL three-necked flask was stirred with a magnetic stirred. After heated to 100 °C, 4 mL of 10 mM sodium citrate was added and kept reflux for 30 min. While it was cooled down to room temperature, the prepared colloid was centrifuged at 10,000 rpm for 30 min. The deposition was redispersed in water to obtained gold colloid.

2.3. Preparation of PVA-AuNPs film on substrate and annealing process
ITO glass strips (4.0 × 0.5 cm²) were ultrasonically cleaned in dilute ammonium water, water, ethanol and water, respectively. The opposite surface of ITO glass was used as bare glass surface. The PVA-AuNPs film was prepared by drop-casting method. A various
volume (50～200 μL) of the mixed solution (0.9 mL of gold colloid and 100 μL of 5% PVA) was drop-casted on ITO or bare glass surface (about 0.3 cm²). Then, the strips were dried at 130 °C for 2 h in bake oven to form PVA-AuNPs film. Next, the annealing of the strips coated with PVA-AuNPs film were performed in air for 0.5–10 h at different temperature (400–700 °C) in an tubular furnace. Finally, the annealed strips were cooled to room temperature in air.

2.4. Sample characterisation

Transmission electron microscopy (TEM) images were obtained using a FEI TECNAL 20 at an accelerating voltage of 200 kV. The morphology of the annealed samples was characterised by an S-4700 scanning electron microscope (SEM, Hitachi, Japan). The UV-vis absorption spectra of the AuNPs were monitored by a Cary 60 spectrometer (Agilent, Australia) with a bare ITO glass as reference.

3. Results and discussion

3.1. Characterisation of Au colloid

The prepared gold colloid was characterised by UV-vis adsorption spectrum and TEM image (Figure 1). The absorption peak of AuNPs was observed at 528 nm, corresponding to the localised surface plasmon resonance of the nanoparticles. The AuNPs were of quasi-spherical shape with the average size of ~25 nm in the TEM image. These AuNPs were used to investigate the deposition upon the ITO and bare glass substrate.

3.2. Dependence on the annealing temperature

Figure 2A–D shows the SEM images of the Au nanostructures annealed at 400, 500, 600 and 700 °C for 30 min, respectively. It can be observed that the residual of PVA was completely disappeared at an annealing temperature of 600 °C or over. This may be attributed to the rather thickness of PVA film and limit of annealing time. After annealing at 600 °C, the AuNPs exhibited quasi semi-sphere with smooth surface and well dispersed on the ITO substrate (Figure 2C,E). According to the possible mechanism of AuNP annealing at high temperature [7,32,33], as two or more AuNPs are very close,
coalescence begins to form large particles. Moreover, a tendency to shape into spheres (hemisphere) would occur due to minimisation of the surface area. When the sample was annealed at 700 °C, the larger and hexagon shaped nanoparticles was formed (Figure 2D). This phenomenon was also observed in the previous reports [34,35].

Figure 2F shows the UV-vis absorption spectra of the AuNPs before and after annealing at different temperatures. The LSPR peak of AuNPs embedded in a PVA film was located at ~544 nm. The LSPR peak of AuNPs was red-shifted with increasing the annealing temperature. Its peak was located at 568, 573, 582 and 601 nm at an annealing temperature of 400, 500, 600 and 700 °C, respectively. This is ascribed to the dipole LSPR of
the nanoparticles. In addition, a very small peak appeared at \( \sim 515 \text{ nm} \) in the spectra at annealing temperature of 700°C ascribed to the quadrupole resonance \[36\]. The red-shift of the main LSPR peak is mainly due to the fact that the sizes of nanoparticles become larger as increasing the annealing temperature. Since the glass-transition temperature was about 550–600°C \[37,38\], the substrate will distort at high temperature of over 700°C. Therefore, the annealing temperature of 600°C was used for the next experiments.

### 3.3. Dependence on the annealing time

The annealing time for the samples was also investigated. Figure 3 shows the SEM images of AuNPs deposited on ITO surfaces at 600°C for different annealing times. It can be seen that the sizes of AuNPs are gradually increased with increasing the annealing times in the range of 0.5–10 h. The average diameter was 71.6 ± 14 nm after annealing for 0.5 h, while it increased to 95.4 ± 26.2 nm after annealing for 10 h. Moreover, some hexagon-shaped AuNPs were observed for longer annealing time in SEM images. In UV-vis absorption spectra (Figure 4), the dipole resonance of AuNPs (\( \sim 580 \text{ nm} \)) was also gradual red-shift as the annealing time increased due to the increase of nanoparticle size. In comparison with annealing time of 0.5 h, the peak wavelength was red-shift of \( \sim 16 \text{ nm} \) for annealing time of 10 h. Furthermore, a small peak at \( \sim 515 \text{ nm} \) was also observed at the annealing time over 4 h. It has reported that the shape transition to hexagon of Au nanostructures depend largely on the annealing temperature, gold film thickness and substrate \[34,35\]. At high temperature (over 600°C), annealing-induced gold diffusion leads gold
atoms migrate due to minimisation of energy. With a longer annealing process, the 
AuNPs become more flattening, which is favourable for form hexagon-shaped 
nanostructure.

Figure 4. UV-vis absorption spectra of AuNPs deposited on ITO glass after annealing at 600 °C for different annealing time.

Figure 5. UV-vis absorption spectra of AuNPs deposited on ITO glass with different PVA-AuNPs volume before and after annealing at 600 °C for 0.5 h (A), and SEM images of AuNPs deposited on ITO glass with PVA-AuNPs volume of 50 (B), 100 (C) and 200 μL (D) after annealing at 600 °C for 0.5 h. Inset: its size distribution.
3.4. Dependence on the volume of PVA-AuNPs solution

Experiments also exhibit a strong dependence of the size of the AuNPs on the volume of PVA-AuNPs solution. Figure 5A shows the absorption spectra of AuNPs deposited on ITO substrate before and after annealing at 600 °C for 0.5 h. The peak wavelength was red-shifted with increasing the volume of PVA-AuNPs solution. The LSPR peak of AuNPs shifted to 598 nm as 200 μL of PVA-AuNPs solution was casted. Figure 5B–D displays the microscopic characterisation of the gold nanostructures deposited on the ITO surface at different volumes of PVA-AuNPs solution. The diameter of AuNPs deposited on ITO surface was 60.2 ± 11.2, 71.1 ± 16.2 and 126.3 ± 28 nm with addition of 50, 100 and 200 μL PVA-AuNP solution, respectively. This result suggested that size of AuNPs is tunable with controlling the volume of PVA-AuNP solution.

3.5. AuNPs deposited onto bare glass surface

Figure 6 shows the UV-vis absorption spectra and SEM images of AuNPs deposited on bare glass with different volume of PVA-AuNPs solution before and after annealing at 600 °C for 0.5 h. It can be seen the peak wavelength of AuNPs deposited on bare glass was red-shifted less than that on ITO surface. From the SEM images, the diameter of AuNPs was about 39.6 ± 7.6, 68.3 ± 18.9 and 77.6 ± 24.8 nm after addition of 50, 100 and 200 μL PVA-AuNP volume, respectively. At the same conditions, the size of AuNPs deposited on bare glass was lower than that on ITO substrate. This may be ascribed to
the difference of thermal conductivity between ITO thin film and bare glass surface [39].
The ITO surface with high thermal conductivity can transfer heat efficiently to the Au particles, which leads to its high mobility on the ITO surface. However, bare glass surface is thermal insulated, which results in low mobility on the surface. Furthermore, upon high temperature annealing (slightly above glass transition temperature) lead to partial embedding in the glass substrate [38]. Therefore, the AuNPs deposited on bare glass is small size due to the suppression of migration and coalescence process.

4. Conclusions
We developed a simple two-step approach for depositing AuNPs on transparent glass and ITO surfaces. Gold colloid prepared by wet chemistry was used as gold source. Then the gold nanomaterials were embedded in PVA film upon the substrate. After annealing at high temperature, AuNPs were deposited on the bare and ITO glass surface due to migration and coalescence of gold. The prepared gold surface is clean due to annealing process at high temperature of 600°C for 0.5 h. The size of nanoparticles increased with the increasing annealing time or volume of PVA-AuNPs solution. Simultaneously, the LSPR peak of AuNPs was also gradual red-shift with the increasing size of nanoparticles. In addition, type of substrate surface also influenced the gold nanostructures. The size of AuNPs deposited on ITO substrate was larger than that on bare glass at the same experimental conditions. This method provides an alternative simple and efficient method for deposition of AuNPs upon bare and ITO glass surface, which is potential to develop biosensors, photonic devices and optoelectronic devices.

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Disclosure statement
No potential conflict of interest was reported by the authors.

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