

## RAPID COMMUNICATION

# Surface vertical deposition for gold nanoparticle film

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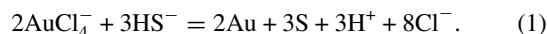
In this rapid communication, we present the surface vertical deposition (SVD) method to synthesize the gold nanoparticle films. Under conditions where the surface of the gold nanoparticle suspension descends slowly by evaporation, the gold nanoparticles in the solid–liquid–gas junction of the suspension aggregate together on the substrate by the force of solid and liquid interface. When the surface properties of the substrate and colloidal nanoparticle suspension define for the SVD, the density of gold nanoparticles in the thin film made by SVD only depends on the descending velocity of the suspension surface and on the concentration of the gold nanoparticle suspension.

Thin films have a number of applications in various fields, including interference filters, polarizers, narrow band filters, solar cells, photoconductors, waveguide coatings, temperature control of satellites, photothermal solar coatings, magnetic film, superconducting films, microelectronics devices, diamond films, and high-temperature wear resistant films. Numerous materials have been prepared in thin-film form because of their potential technical value and scientific curiosity in their properties. Currently, there are many research activities devoted to the development of thin film fabrication methods and functional properties [1–3]. Thus, there are a number of well-known deposition techniques, such as by vacuum evaporation, sputtering and chemical methods such as chemical vapour deposition, spray pyrolysis, electrodeposition, anodization, electroconversion, electroless, dip growth, successive ionic absorption and reaction, chemical bath deposition and suspension–gas interface techniques [4–10].

In this rapid communication, we present a new method to synthesize the gold nanoparticle film, surface vertical deposition (SVD). The gold nanoparticles in the solid–liquid–gas junction of the suspension grow on the substrate by the interface force between the solid substrate and the liquid suspension surface when the suspension surface descends. When the surface properties of the substrate and the solvent of suspension are define the parameters of the SVD, the density

of gold nanoparticles in the thin film is shown to be dominated by the velocity of surface's descent and the concentration of suspension. Single-monolayer gold nanoparticle films are obtained by increasing the descending velocity or decreasing the concentration.

The growth of the gold nanoparticles is initiated in an aqueous mixture of  $\text{HAuCl}_4$  and  $\text{Na}_2\text{S}$ , and the following reaction is the initial reaction process:



Au is liberated for subsequent nucleation and growth, and gold nanoparticles are formed in the mixed solution [11]. The size of the gold nanoparticles depends on the initial concentration and mixed ratio of the solutions of the  $\text{HAuCl}_4$  and  $\text{Na}_2\text{S}$  [12]. The gold nanoparticles from which the thin film forms, are found in the meniscus between the suspension, substrate, and air. This is illustrated in figure 1.

In the figure 1, the solid–liquid–gas junction region A created by the surface tension of the liquid plays a significant role in the SVD because the gold nanoparticles localized here form the thin film. In region A of suspension, the thickness near the solid–liquid–gas junction is thinner than the mean-free path of the nanoparticles, which leaves the attraction to the solid the dominant force in the problem. Therefore, this wetting force, component force  $\vec{n}$ , in region A of figure 1 leads to the

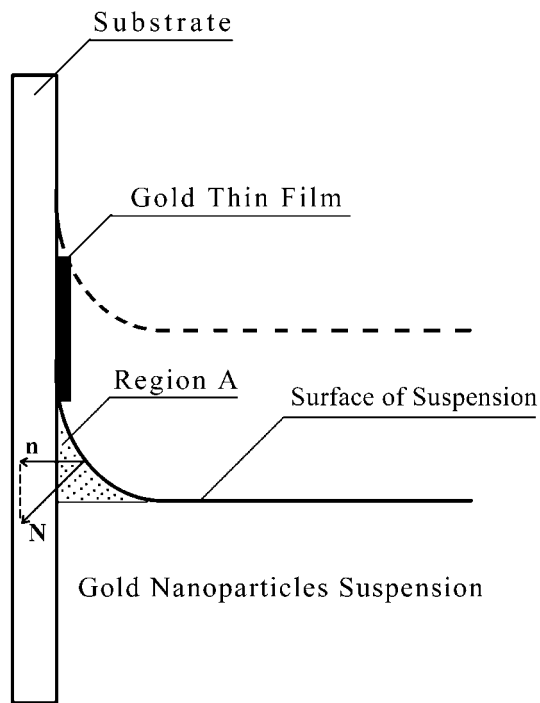


Figure 1. The principle of the SVD.

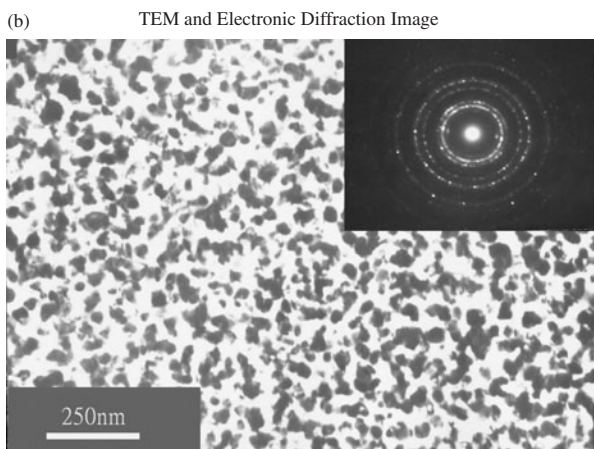
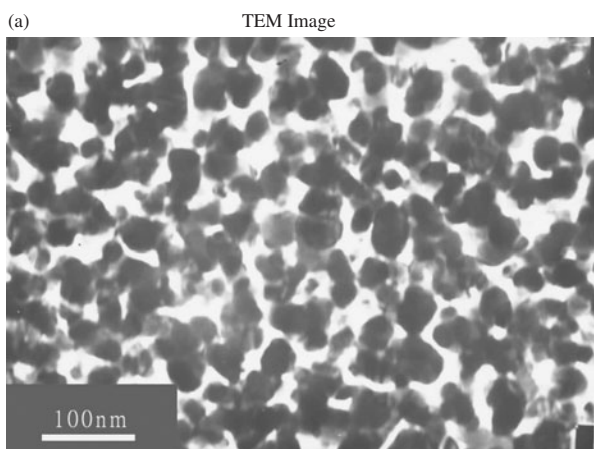


Figure 2. TEM images of the gold nanoparticle film made by the SVD (4 mM  $\text{HAuCl}_4$  was mixed in 2 mM  $\text{Na}_2\text{S}$  with a volume ratio 1 : 2).

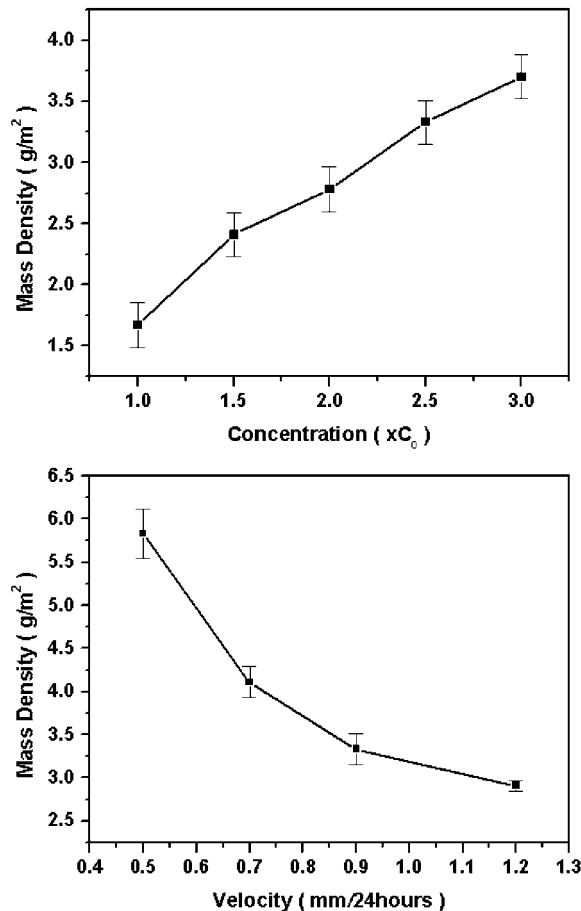


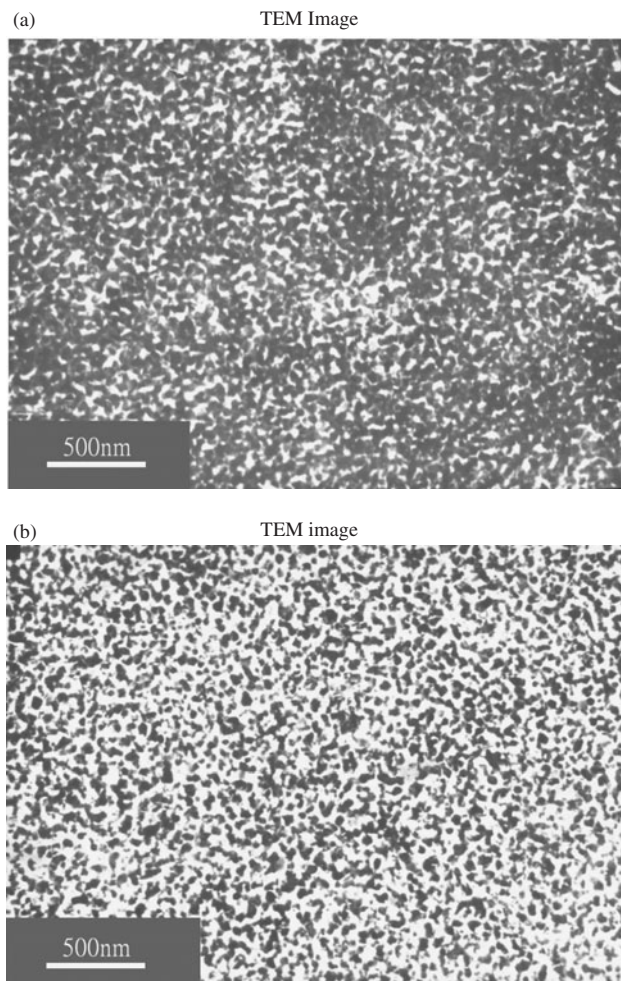
Figure 3. (a) The mass density of gold nanoparticle film vs the concentration of suspension. (b) The mass density of gold nanoparticle film vs the descending velocity of suspension surface.

adsorption of nanoparticles on the substrate. When the surface of the gold nanoparticle suspension goes down from the broken line, the gold nanoparticles in region A will aggregate on the substrate by this normal force. For SVD to succeed, the substrate must be wettable, else the component of force  $\vec{n}$  will point away from the substrate. Thus, in experiments, gold nanoparticle films formed on one side of wettable glass substrate, but did not form on the other side made non-wettable with a wax layer. Transmission electron microscopy (TEM), shown in figure 2 are images of the gold nanoparticle film made by the SVD starting from 4 mM  $\text{HAuCl}_4$  was mixed in 2 mM  $\text{Na}_2\text{S}$ .

The thin film made by the SVD is composed of the gold nanoparticles whose average sizes are approximately 40 nm, and the distribution of the gold nanoparticles in the thin film are homogeneous. The gold nanoparticles tend to order crystallographically in the film as indicated by the electronic diffraction image in figure 2.

The density of nanoparticles in the thin film made by the SVD depends on the surface property of substrate, the solvent of suspension, the concentration of suspension and the descending velocity of the suspension surface. When the substrate and the solvent interface define the SVD process, the density of gold nanoparticle film is related to the concentration and the descending velocity, as shown in figure 3.

The reaction for figure 3 was started when 7.5 mM  $\text{HAuCl}_4$  was mixed in 3.75 mM  $\text{Na}_2\text{S}$  with a volume ratio 1 : 2. When



**Figure 4.** TEM images of the gold nanoparticle film made by the SVD with different descending velocities of the suspension surface ( $V_a = 1.5$  mm/24 h,  $V_b = 2.6$  mm/24 h, the same suspension).

the reaction finished (after 1 h), the suspension was diluted into different concentrations for the SVD with the same descending velocity (0.9 mm/24 h) and diluted into one concentration (dilute ratio: 3:5) for the SVD with different descending velocities.  $C_0$  is the concentration of gold nanoparticle suspension for the dilute ratio: 6:25. The substrate was wettable glass, and the depositions were made at ambient

temperature. Gold nanoparticles in all films were identical in size because of the same initial reaction condition. Figure 3(a) shows that the mass density increases when the concentration of suspension increases. Figure 3(b) shows that the mass density decreases when the descending velocity of suspension surface increases.

The figure 4 shows the TEM images of the gold nanoparticle film made by the SVD from the same suspension with different descending velocities.

In figure 4,  $V_a = 1.5$  mm/24 h,  $V_b = 2.6$  mm/24 h, the number density of the gold nanoparticles in figure 4(a) is higher than the number density in figure 4(b). The density of the gold nanoparticles made by SVD increases both with the concentration of suspension, on with a slowing of the descending velocity of suspension surface. On condition that the concentration is low enough or the descending velocity is fast enough, the density can be so low that the form a single monolayer on the substrate's surface.

In conclusion, the TEM images show that using the SVD makes homogeneous, crystallographic nanoparticle films. Mixed nanoparticle films could also be made by SVD, and it is an easy method for depositing nanometre-scale films. The principle of the SVD is given in this letter. More details about the SVD and the gold nanoparticle films produced by it will be explored in a forthcoming work.

## References

- [1] Mane R S and Lokhande C D 2000 *Mater. Chem. Phys.* **65** 1
- [2] Patil P S 1999 *Mater. Chem. Phys.* **59** 185
- [3] Salditt T, An Q, Plech A, Peisl J, Eschbaumer C, Weidl C H and Schubert U S 1999 *Thin Solid Films* **354** 208
- [4] Ghosh C and Verma B P 1979 *Thin Solid Films* **60** 61
- [5] Nayak B B, Acharya H N, Chaudhari T K and Mitra G B 1982 *Thin Solid Films* **92** 309
- [6] Yale Y Ma and Bube R H 1977 *J. Electrochem. Soc.* **124** 1430
- [7] Pavaskar N R, Menzes C V and Sinha A P B 1977 *J. Electrochem. Soc.* **124** 743
- [8] Pawar S H, Bhosale P N and Tamhankar S P 1983 *Thin Solid Films* **110** 165
- [9] Pawar S H, Tamhankar S P and Bhosale P N 1983 *Indian J. Pure Appl. Phys.* **21** 665
- [10] Pawar S H and Bhosale P N 1984 *Mater. Chem. Phys.* **11** 461
- [11] Turkevich J, Garton G and Stevenson P C 1954 *J. Colloid Sci.* **9** 26
- [12] Leff D V, Ohara P C, Heath J R and Gelbart W M 1995 *J. Phys. Chem.* **99** 7036