Layered Nanocomposite of Close-Packed Gold Nanoparticles and TiO_2 Gel Layers

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Preparation of thin film devices with nanoparticles of semiconductors and metals is one of the hot topics in the field of materials science.[1,2] To prepare nanodevices on the basis of designed architecture of nanoparticles, the preparative technique of two- and three-dimensional regular arrays of nanoparticles is indispensable.[3−13]

Metal nanoparticles embedded in transparent matrixes have been widely studied as resonant-type nonlinear optical materials,[14−17] and metal and semiconductor nanoparticles attract much interest as materials for third harmonic generation (THG).[18,19] Therefore, a wide variety of fabrication techniques including melt quenching, sol−gel process,[18,20] ion implantation,[21] and sputtering[22] were reported for thin films containing small particles of metals and semiconductors. Unfortunately, in most cases, the value of the third nonlinear susceptibility of these films remains very small because of the small content of particles. In cases where particle loading was made high, largely distributed particle size and poor reproducibility were often noted as a consequence of these preparative methods. Quite recently, direct synthesis of gold nanoparticles in silica gel was proposed, leading to relatively high loading.[23]

"Surface sol−gel process" is a simple, reproducible technique to fabricate metal oxide thin films with nanometer-precise control of film thickness.[24,25] This process is composed of four steps: chemisorption of metal alkoxide, rinsing, hydrolysis of adsorbed alkoxide, and drying. Metal alkoxides are adsorbed on a substrate functionalized with hydroxyl groups, and the subsequent hydrolysis of adsorbed alkoxide supplies hydroxy groups again on the surface. Metal oxide films thus prepared have constant thicknesses and the surfaces are flat over a large area. This process can be applied to the preparation of "organic−inorganic" nanocomposites of poly(vinyl alcohol)/TiO_2 and other hydroxyl polymers with TiO_2 layer.[26]

We demonstrate here the preparation of alternate layers of ultrathin TiO_2 films and modified gold nanoparticles. The modified gold nanoparticle possesses surface hydroxyl groups, and they behave as an active component in the surface sol−gel process. Nanocomposites obtained from these components will be composed of high concentrations of nanoparticles in metal oxide thin films.

Bis(11-hydroxyundecyl) disulfide [$HO(CH_2)_{11}SS(CH_2)_{11}OH$ or $(SC_{11}OH)_2$] used as stabilizer was prepared as reported by Wollman and others.[27] Gold nanoparticles were prepared by reduction of $HAuCl_4$ by $NaBH_4$ in methanol/acetic acid in the presence of $(SC_{11}OH)_2$. Each particle had a spherical shape of a uniform size. The average diameter and the standard deviation were 4.7 and 0.64 nm, respectively. The obtained particles were washed with ethanol to remove excess stabilizer molecules which may prevent adsorption of the gold particles onto TiO_2.

Quartz crystal microbalance (QCM) measurement was used for monitoring mass increase due to adsorption. A gold-coated QCM resonator (9 MHz) functionalized with mercaptoethanol was immersed in a 100 mM toluene/ethanol solution of titanium *n*-butoxide [$Ti(O(n\text{-}C_4H_9))_4$] for 3 min. The resonator was then immersed into ethanol for 1 min for the purpose of washing. It was again immersed into water for 1 min for hydrolysis followed by drying with N_2 gas.

In the first stage, 15 cycles of this process were repeated in order to produce a flat TiO_2 surface on a QCM resonator, as illustrated in Figure 1. Preliminary QCM experiments indicated that more than 10 cycles of the process should be repeated for frequency decrease (ΔF) to yield reproducible adsorption of gold nanopar-

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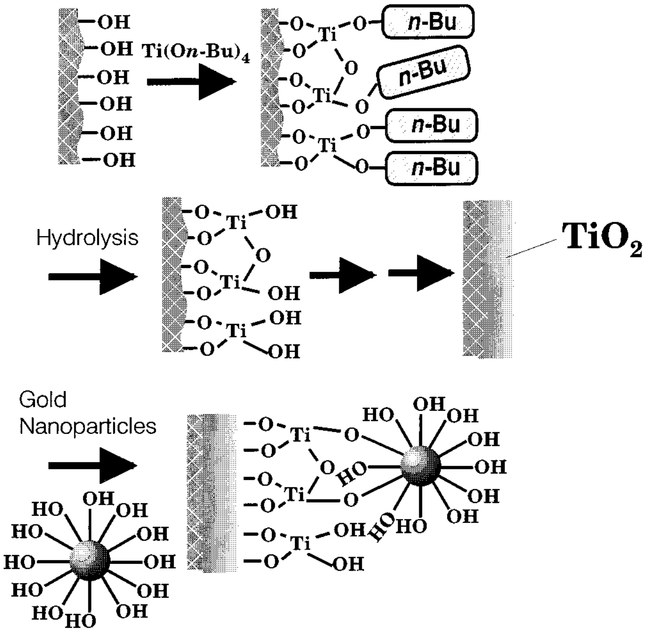

Figure 1. Schematic illustration of sequential of surface sol–gel technique and alternate assembly.

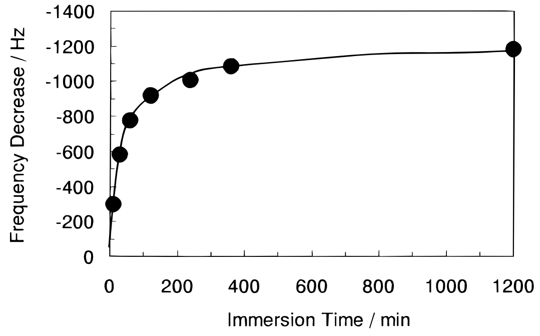

Figure 2. Frequency decrease (ΔF) of QCM upon adsorption of 11-hydroxyundecylsulfide-stabilized gold nanoparticles on the TiO_2 layer. [Au atom] = 1.5×10^{-3} mol dm^{-3} in methanol, at room temperature.

ticles. Therefore, we adopted 15 cycles of surface sol–gel cycles in this study. After the preparation of TiO_2 gel, the resonator was immersed into a dispersion of gold nanoparticles in methanol ([Au] = 1.5×10^{-3} mol dm^{-3}) for given periods of time. It was then washed in methanol for 1 min and subjected to ultrasonication (Branson 1210) for a few minutes. The color of the resonator changed to slightly red after its immersion into the colloidal dispersion of gold, and indicated effective adsorption of particles. Ultrasonication was indispensable to obtain reproducible frequency decreases that corresponded to monolayer adsorption. SEM observation showed multilayer adsorption of gold particles without ultrasonication.

Figure 2 shows the frequency decrease of TiO_2-gel-modified QCM resonator against time immersed in a dispersion of gold nanoparticles ([Au] = 1.5×10^{-3} mol dm^{-3}). The adsorption process was very slow and it saturated only after immersion for as long as 10 h. In contrast, complexation of hydroxy groups of poly(vinyl alcohol) or starch and TiO_2 gel was saturated in 10 min.[26] When anionic gold nanoparticles were adsorbed onto a substrate covered with a cationic amphiphile layer, a close-packed layer was formed only after the substrate was immersed in a dispersion of gold nanoparticles (diameter = 19 nm, [Au] = 1.2×10^{-3} mol dm^{-3}) for 1 h.[12] Adsorption of SiO_2 nanoparticles onto cationic polyelectrolytes or amphiphile layers was saturated very quickly, in a few seconds.[28]

The adsorption rate may be varied by the particle concentration, the particle weight, the nature of the substrate, and the solvent used. The concentration of gold nanoparticles could not be made higher in our case, because coagulation of particles tended to occur in the dispersion. The dispersibility of gold nanoparticles was not as high in other solvents as in methanol or ethanol. The slow adsorption behavior of gold nanoparticles may be attributed at least partially to its low concentration.

The total frequency decrease due to the adsorption is ca. 1 100 Hz, as shown in Figure 2. If the ideal hexagonal packing is attained for a monolayer of gold nanoparticles with a diameter of 7.3 nm (including the stabilizer), a flat QCM resonator will give a frequency decrease (ΔF) of 950 Hz.[29] The excessive adsorption observed may be attributed to the surface roughness of the TiO_2 layer (ca. 10%),[25] to interpenetration of the stabilizer layer, and/or to three-dimensional aggregation of gold nanoparticles. The frequency decrease (ΔF) due to adsorption of the TiO_2 layer (15 cycles) and gold nanoparticles are comparable, and the overall film contains 50 wt % of gold. Thinner TiO_2 films can be prepared by decreasing the number of TiO_2 adsorption cycles to produce higher gold loading.

Figure 3 shows scanning electron micrographs (SEM) of the TiO_2-modified QCM resonator, before (Figure 3a) and after (Figure 3b) the adsorption of gold. The small dots observed in Figure 3a are attributed to the 2-nm platinum coating used for SEM observation, as evidenced by the accompanying size distribution. The surface of TiO_2 is relatively flat. After the adsorption, the surface became fully covered with densely packed spherical particles with a diameter of ca. 5–8 nm (white dots in Figure 3b). The particle size agrees with that of the gold nanoparticles employed.

Self-assembled monolayers (SAM) of thiol compounds onto flat gold substrates have been used for organization of gold particles. Despite the coordinative groups that are aligned on SAM surface, gold nanoparticles are adsorbed with scattered structures because of charge repulsion.[9,30,31] In our system, the particles are fully covered by neutral ligands and are devoid of charge repulsion. Thus, the particles can form a close and densely packed monoparticulate layer. However, a

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(29) The relationship between adsorbed mass (M, in grams) and frequency decrease (ΔF, in hertz) in this system is $\Delta F = 1.83 \times 10^8 \times M/A$, where A is the apparent area of the QCM. By using the coefficient of two-dimensional close packing: 0.9069, and the densities of gold (ρ_g) and stabilizer (ρ_s) (19.3 and 1.0 g/cm^3, respectively), the number of particles adsorbed on both sides of the resonator is $N_a = (0.9069 \times 2A)/\pi r_t^2$, where r_t is the average radius of the gold particles including the stabilizer (7.29 nm; estimated value). The adsorbed mass is $M = [\rho_g \times {}^4/_3(\pi r_g^3) + \rho_s \times {}^4/_3\{\pi(r_t^3 - r_g^3)\}] \times N_a$, where r_g is the average radius of the gold core (4.7 nm; from TEM observation).

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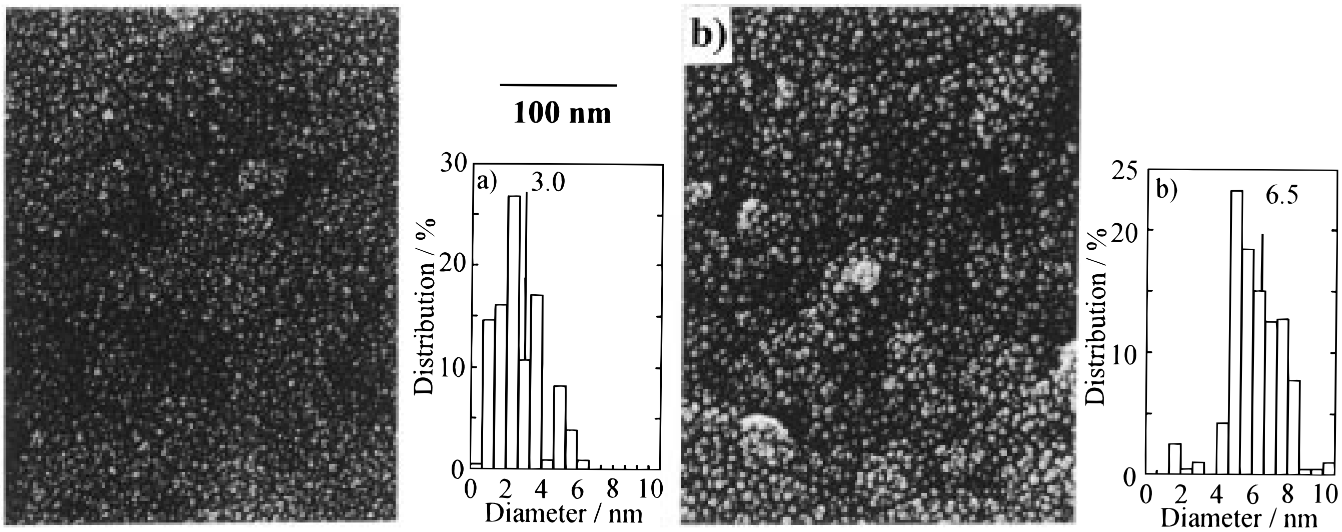

Figure 3. SEM photographs and the size distribution of white dots: (a) TiO_2 layer prepared by surface sol−gel technique and (b) gold nanoparticles adsorbed on TiO_2. SEM photographs were taken with a Hitachi S-900 at an acceleration voltage of 25 kV. A Pt film of ca. 2 nm thickness was deposited on the samples. White dots in a and b can be attributed to platinum particles generated by and gold nanoparticles adsorbed on TiO_2 by alternate assembly, respectively.

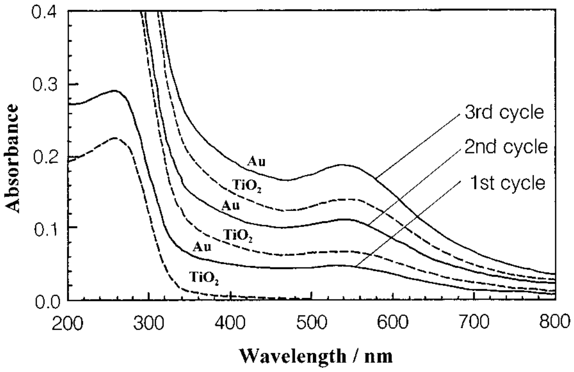

Figure 4. UV−vis spectra of the layer-by-layer assembly of gold nanoparticles and TiO_2 layer on a quartz substrate. Broken line: after the formation of TiO_2 gel layer. One cycle of TiO_2 contains 15 cycles of the surface sol−gel process. Solid line: after immersion of the substrate into the methanol dispersion of gold nanoparticles. [Au atom] = 1.5×10^{-3} mol dm^{-3}, at room temperature.

hexagonally packed layer could not be obtained, probably due to the lack of uniformity of the particle size.

UV−vis spectra of the nanocomposite films are shown in Figure 4. The adsorption was conducted on a quartz substrate that had been treated with concentrated aqueous NaOH. The strong absorption at 200−340 nm is characteristic of the TiO_2 layer, and the gold nanoparticle shows a strong adsorption peak at 500−600 nm due to the plasmon resonance. The absorption peak of gold nanoparticles was intensified in proportion to the cycle of adsorption. This is a strong indication of constant adsorption of gold nanoparticles on each TiO_2 overlayer. The physical nature of the surface plasmon resonance that gives colloidal gold its characteristically intensive ruby color is well-documented, as is its dependence on particle size and shape. It is known that aggregated gold nanoparticles exhibit red-shifted peaks. In our case, however, no typical red shift of the absorption peak was found after adsorption. The gold nanoparticles obtained here are fully covered with a monolayer of the 11-hydroxyundecylsulfide unit [$S(CH_2)_{11}OH$]. The whole size of the modified gold particles is estimated as 7.9 nm, while the size of the gold core is 4.7 nm. Because of the relatively thick, stable organic shell, gold metal cores do not directly contact with each other.

In conclusion, we demonstrated that nanocomposites of gold nanoparticles and TiO_2 ultrathin layers were successfully prepared by a combined use of layer-by-layer assembly and surface sol−gel process. Gold nanoparticles, being stabilized by a monolayer of the 11-hydroxyundecylsulfide unit, were effectively adsorbed on the surface of TiO_2 gel and close-packed monoparticulate layers were formed. Multilayer films of TiO_2/gold nanoparticles were also successfully prepared.

The extent of flexibility of the layer design that is possible in the present approach is a significant advantage in device preparation. In the current system, the number, order, and chemical species of the adsorption cycle can be varied flexibly. We believe that the present results expand the preparation of multicomponent nanodevices.

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