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Facile Fabrication of Gold Nanoparticle -Titanium Oxide Multilayer Assemblies by Surface Sol-Gel Processes

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1. Introduction

The surface sol-gel process is a well-known method for the facile fabrication of alternate films of organic-inorganic hybrids at ordinary temperatures and pressures, without using any sophisticated instruments.[1, 2)] Recently, we first reported the combined use of self-assembly and surface sol-gel methods in order to readily fabricate photoconductive films containing electron donor–acceptor photoredox pairs via titanium oxide (Ti(O)) layers.[3, 4)] However, the incorporation of organic layers has been suffered from keeping satisfactory conductivity in the film. Thus, a few other approaches to maintain the conductivity without loosing the photoredox activity should be taken into consideration in order to fully utilize the surface sol-gel method.

Meanwhile, the potential uses of metal nanoparticles have received considerable attention, such as its applications to catalysis [5, 6)] and optical devices [7, 8)]. In particular, gold nanoparticles (AuPs) with diameters of several to several tenths of nanometers can interact with visible light because they exhibit appreciable surface plasmon bands in the visible region. In addition, they are conductive and can function as photoredox nanomaterials.[9)] Thus, they are potentially useful as a component in photoconductive films.

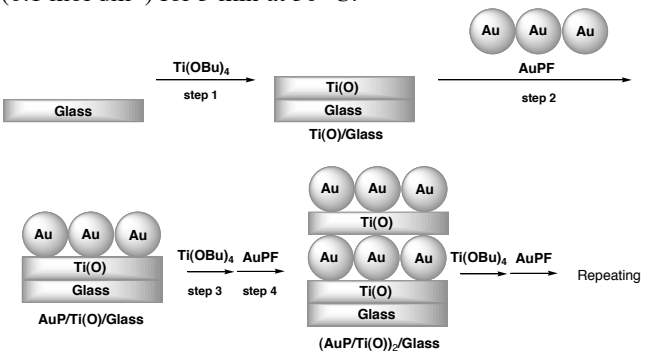
In the case of AuPs, they are capped with citrate ions when they are prepared by the chemical reduction of chloroauric acid with sodium citrate. Thus, they can possibly combine with titanium oxide by ester condensation during the surface sol-gel reactions by using titanium alcoxides. Recently, we reported the fabrication of AuP-titanium oxide alternate assemblies by the surface sol-gel process.[10)] However, the coverage of the alternate assemblies is below the level indicating the complete packing of the AuP-monoparticle layer.

In the present study, we fabricated multilayer assemblies of an ultrathin gold-nanoparticle film by using the surface sol-gel process.

2. Experimental

Chloroauric acid ($HAuCl_4$), titanium butoxide ($Ti(OBu)_4$), and other chemicals were used as received. An aqueous colloidal solution of AuPs was prepared by the reduction of $HAuCl_4$ with sodium citrate, as described in the literature,[11)]. The mean diameter of the resultant AuPs was ~15 nm.

Preparation procedures of multilayer assemblies of AuPs ultrathin film - titanium oxide $((AuPF/Ti(O))_n$ assemblies are shown in Scheme 1. First, a quartz glass plate was immersed into a toluene/ethanol (1/1) solution of $Ti(OBu)_4$ (0.1 mol dm^{-3}) for 3 min at 30 ºC.



Scheme 1. Preparation procedures of AuPF-Ti(O) multilayer assemblies

After withdrawal, the substrate is subsequently dipped into water and dried, yielding Ti(O)-modified quartz glass (Ti(O)/Glass) (step 1). The preparation of a gold nanoparticle film at the liquid/liquid interface has also been reported earlier.[12)] In particular, a liquid/liquid interface of an aqueous colloidal solution of AuPs (20 ml) and hexane (10 ml) was formed in a vial (ϕ = 30 mm), in which the Ti(O)/Glass was placed at its bottom. Then, methanol (10 ml) was immediately poured into the solution; this resulted in an instantaneous color change of the aqueous phase from wine-red to light pink, and at the same time, a liquid-like film of AuPs was formed at the liquid/liquid interface, as verified from the appearance of a gold color at the interface. Further, this liquid-like film was transferred onto the surface of the Ti(O)/Glass to yield an AuP ultrathin film (AuPF) modified substrate, AuPF/Ti(O)/Glass (step 2). Subsequently, Ti(O) was superimposed onto the surface of AuPF by the immersion of the AuPF/Ti(O)/Glass into a toluene/ethanol solution of $Ti(OBu)_4$ (step 3). Finally, the AuPF was modified on the surface of the outermost Ti(O) layer to yield $(AuPF/Ti(O))_2$/Glass (step 4). Further, multilayered assemblies were fabricated by repeating the above described surface sol-gel processes (step 3 and 4). In addition, multilayer assemblies of AuPF/Ti(O)-modified ITO transparent electrode were also fabricated by the same processes.

The structures of the assemblies were measured and evaluated by transmission absorption spectroscopy and scanning electron microscopy (SEM).

3. Results and Discussion

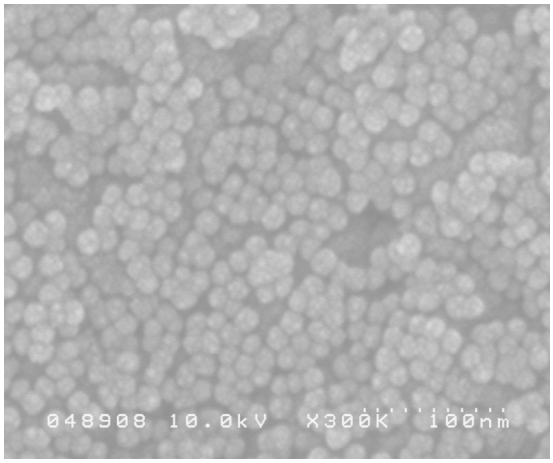


Figure 1. SEM image of the AuPF/Ti(O)/ITO

Figure 1 shows the SEM image of the AuPF/Ti(O)/ITO. As seen in the image, gold nanoparticles are deposited on the ITO electrode roughly at the level of the monoparticle layer. No appreciable fusion particles was observed. This result indicates that the Ti(O) layer plays an important role in immobilizing the AuPF on the surface of the substrate.

The transmission absorption spectra of AuPF/Ti(O)/Glass and Ti(O)/AuPF/Ti(O)/Glass are shown in Figure 2. A clear absorption peak (~700 nm) due to the AuPF is observed in the case of AuPF/Ti(O)/Glass. In the case of Ti(O)/AuPF/Ti(O)/Glass, the absorption peak is shifted to a longer wavelength and the absorption band is broadened. These results indicate that an aggregation of the AuPs occurs in the AuPF during the surface sol-gel process.

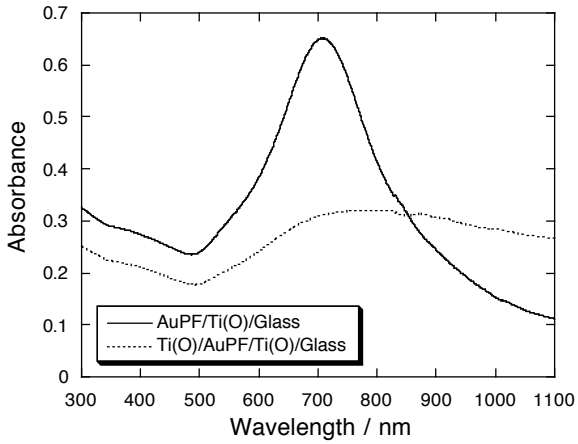


Figure 2. Transmission absorption spectra of AuPF/Ti(O)/Glass and Ti(O)/AuPF/Ti(O)/Glass

In addition, the multilayer assemblies $((AuPF/Ti(O))_n$/Glass were measured and evaluated. The absorption intensity of $((AuPF/Ti(O))_n$/Glass increased with the number of surface sol-gel process cycles. These results indicate that the multilayer assemblies of (AuPF/Ti(O)) were fabricated by the surface sol-gel process. Moreover, organic-dye (e.g., porphyrins) modified multilayer assemblies of AuPF were fabricated. We have conducted a preliminary investigation of the photochemical properties of the dye-modified AuPF assemblies. An appreciable enhancement of the fluorescence emission from the dye was observed, which may be due to plasmon excitation of the dye. The detailed preparation procedure and the results of the measurements will be discussed in the presentation.

Conclusion

We have performed a preliminary demonstration of a novel approach for the preparation of the multilayer assemblies of gold-nanoparticle ultrathin films. The structures of the assemblies were confirmed by absorption spectra and SEM. The enhancement of the photoexcitation of dyes on the surface of AuPF was also obtained.

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