Facile Fabrication of Gold Nanoparticle-Titanium Oxide Alternate Assemblies by Surface Sol-Gel Process and Their Photoresponsive Properties

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1. Introduction

Surface sol-gel process is a well-known method for facile fabrication of alternate films of organic-inorganic hybrids at ordinary temperature and pressure, without any sophisticated instruments.^{1, 2)} Recently, we have first reported the combined use of self-assembly and surface sol-gel methods in order to readily fabricate photoconductive films consisting of 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 Thus, some other approaches to keep the film. conductivity without loosing photoredox activity should be taken into consideration in order to make the most of the surface sol-gel method.

In the meantime, metal nanoparticles have received much attention as potentially useful nanomaterilas, such as applications to catalysis ^{5,6)}, optical devices ^{7,8)}, and so on. Especially, 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 have potential to utilize as a component of photoconductive films. However, the surface sol-gel method has not yet been applied to the fabrication of AuP films. As to AuPs, they are capped with citrate ions when they are prepared from the chemical reduction of chloroauric acid with sodium citrate. Thus, they possibility to combine with titanium oxide by ester-condensation reaction during the surface sol-gel reactions using titanium alkoxides .

In the present study, we have carried out the surface sol-gel method to fabricate AuP films, and have preliminarily investigated the photoelectrochemical activity of the films.

2. Experimental

Chloroauric acid (HAuCl₄), titanium butoxide (Ti(OBu)₄), and other chemicals were used as received. An aqueous colloidal solution of AuPs was prepared by the reduction of HAuCl₄ with sodium citrate, as described in the literature,¹⁰. The mean diameter of the resultant AuPs was 15 ± 2 nm. Preparation procedures of AuP-Ti(O) 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 °C. After withdrawal, the substrate was



subsequently dipped into water and dried, giving Ti(O)-modified quartz glass (Ti(O)/Glass) (step 1). Next, Ti(O)/Glass was soaked into the aqueous colloidal solution of AuPs for 60 min at at 30 °C, to give AuP-Ti(O)-modified glass plate (AuP/Ti(O)/Glass) (step 2). Then, Ti(O) was superimposed on the surface of AuPs by immersion of AuP/Ti(O)/Glass into a toluene/ethanol solution of Ti(OBu)₄ (step 3). Finally, AuPs were modified on the surface of outermost Ti(O) layer, to give (AuP/Ti(O))₂/Glass. Further multilayered assemblies were fabricated by repeating the above described surface sol-gel processes (step 3 and 4). As a control experiment, the quartz glass plate was immersed into the aqueous colloidal solution of AuPs, to give AuP/Glass.

The structures of assemblies were measured and evaluated by transmission absorption spectroscopy, quartz crystal microbalance (QCM) method, and X-ray photoelectron spectroscopy (XPS).

3. Results and Discussion

Transmission absorption spectra of AuP/Ti(O)/Glass and AuP/Glass are shown in Figure 1. A clear plasmon absorption band due to AuPs was observed in the case of AuP/Ti(O)/Glass, but no obvious peaks were observed in the case of AuP/Glass. The result indicates that the Ti(O) layer plays an important role for implanting AuP on the



Figure 1. Transmission absorption spectra of AuP/Ti(O)/Glass and AuP/Glass

surface of quartz glass plate. The peak profile of the plasmon band of AuP/Ti(O)/Glass is not changed even after 11 days in air or after treatment in an aqueous $NaClO_4$ solution (3 mol dm⁻³) for 24 hrs, indicating tight confinement on the Ti(O) layer without causing appreciable aggregation.



Figure 2. Transmission absorption spectra of alternate assemblies

Transmission absorption spectra of $(AuP/Ti(O))_n/Glass$ (n = 1 ~ 4), are shown in Figure 2. In each sample, the plasmon band of immobilized AuPs is clearly observed at around 520 nm. In addition, the absorption intensity increased with increasing the cycles of surface sol-gel processes. These results show that the citrate ions adsorbed on the surface of AuP are responsible to the surface sol-gel reaction with the Ti(O) layer.

The QCM measurements during the surface sol-gel procedures are shown in Figure 3. The frequency decrease (mass increase) by each surface sol-gel process clearly indicates the formation of alternate assemblies of AuPs and the Ti(O) layer.

We have preliminarily investigated the photoelectrochemical activities of the $(AuP/Ti(O))_n$ films by preparing them onto the surface of indium-thin oxide (ITO) substrate. Appreciable photocurrent responses were observed in the presence of AuPs in the films. Further studies are in progress.



Figure 3. Frequency change of the alternate assemblies by QCM

Conclusion

We have preliminarily demonstrated a novel approach for the preparation of alternate assemblies of gold nanoparticle-Ti(O) by the surface sol-gel process. The structures of assemblies were confirmed by absorption spectra, QCM, XPS, AFM measurements. Photoresponsive properties were also obtained from the films.

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