

금 나노입자 박막의 분광전기화학적 연구

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Spectroelectrochemical Study for Thin Film of Gold Nanoparticles

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요약. 아미노실리카이트로 안정화한 금 콜로이드 용액으로부터 산화인듐주석(ITO) 위에 전해석출법으로 금 나노입자의 박막을 만들고, 이 박막을 순환 전압전류법(CV), 주사전자현미경법(SEM), 자외선-가시선 및 에너지분산 X선 분광법(EDXS)으로 조사하였다. 박막 위 금 나노입자의 표면덮힘율은 1.2 나노몰/cm²였다. 금 박막을 0.10 M HClO₄ 용액에 든 0.1 mM anthraquinone-2,6-disulfonic acid, disodium 염(AQDS) 용액에 20시간 이상 담가서 AQDS의 자체 조립 단막층을 생성하였다. 그 결과 690 nm에서 다중층(AQDS/금박막/ITO)의 새로운 흡수 봉우리가 얻어졌다. 또한, +0.5V에서 -0.5V까지 전위를 변화시키는 시간전류법과 자외선-가시선 분광법으로 다중층의 표면 플라즈몬 흡수를 측정하였다. 음의 전위를 걸어주었을 때 550 nm에서 나타나는 최대 표면 플라즈몬 흡수띠가 감소하였다. 흡광도의 변화와 AQDS의 표면덮힘율과의 상관관계로부터 AQDS층의 유사용량 표면상태가 음전위를 걸어줄 때 플라즈몬 띠의 에너지준위와 연관되어 있음을 알았다.

주제어: 박막, 금 나노입자, 분광전기 화학적 연구, 표면 플라즈몬 흡수

ABSTRACT. Thin films of gold nanoparticles were formed on indium tin oxide (ITO) by an electrodeposition method from an aminosilicate stabilized gold colloid solution. The thin films were examined by cyclic voltammetry (CV), scanning electron microscopy (SEM), UV-visible, and energy dispersive X-ray spectroscopy (EDXS). The surface coverage of gold nanoparticles on the thin film was estimated to 1.2 nanomole/cm². An anthraquinone-2, 6-disulfonic acid, disodium salt (AQDS) self-assembled layer was generated by immersing gold thin film into 1 mM of AQDS in 0.1 M HClO₄ solution for over 20 hours. As a result, a new absorbance peak from the multi-layers (AQDS/thin film of gold /ITO) was obtained about at 690 nm. Also, the surface plasmon absorption of multi-layers was measured by UV-Visible spectrometer along with chronoamperometry by applying the various potentials from +0.5 V to -0.5 V. The maximum surface plasmon absorption band at 550 nm was decreased by applying negative potentials. The change of absorbance was correlated with the surface coverage of the AQDS indicating the pseudo-capacity surface state of the AQDS layer was coupled to the energy level of the plasmon band by applied negative potentials.

Keywords: Thin Film, Gold Nanoparticles, Spectroelectrochemical Study, Surface Plasmon Absorption

INTRODUCTION

Nanoparticulate materials can be applied in various areas such as solar energy conversion, chemical sensors, biological labeling, ultrafast data communication and optical data storage (1-3). In particular, thin films of gold nanoparticles have been applied to biomedical sensors (4). The organization of chemical assemblies of nanoscale dimensions has been extensively researched because of the potential impact on nanotechnology and miniaturized devices. These materials of nanoscale dimensions can give unique electronic, optical, and nonlinear properties (5). A particularly intriguing class of nanoparticles is noble metal nanoparticles such as gold and silver. Gold nanoparticles have been synthesized with various ligands. Gold thin films have been formed by an electrochemical deposition method from an aminosilicate-stabilized gold colloid solution. The electrochemical and optical properties of these thin films have been studied in detail (6-9). Gold nanoparticles have a characteristic surface plasmon absorption band that arises from the collective oscillation of conduction band electrons induced by interaction with an applied optical or electric field. The plasmon absorbance peak energies are a function of the dielectric constant of surrounding medium, embedding material or interparticle resonances. Finally, self assembled layers (SAM) of alkanethiols on gold nanoparticles have been studied extensively because of the possibilities of controlling the molecular architecture at the electrode-solution interface (10-15). The spectroelectrochemical characterizations of these thin films are highly important, as they are promising substrates for enzyme electrode and related biosensors. A novel the method for the detection of polynucleotides and oligonucleotides which utilizes the distance-dependent optical properties of aggregated gold functionalized nanoparticles with an agent has been reported. This method has the advantages of both rapid detection and good selectivity (16). The phenomenon of aggregation of the particles in a gold colloid solution upon the addition of a cross-linking agent is well documented (17-19). The posi-

tion and profile of the surface plasmon resonance peaks on silver nanoparticles in solution depends on the applied potentials (20). The optical properties of a colloidal gold solution were reported in response to potential modulation between 0.6 V and -1.0 V in the solution (21).

In this letter, gold thin films were formed on indium tin oxide (ITO) electrodes in gold colloid solution by electrochemical method and the surface was characterized by SEM and EDXS. The coverage of gold thin films on the ITO was evaluated by electrochemical measurement. The layer of AQDS on the gold thin film of ITO was formed by a self-assembly, and the coverage of AQDS calculated from electrochemical and spectroscopy measurements. The change of surface plasmon absorption of multilayers was measured with UV-Visible spectroscopy while varying applied potentials from +0.5 V to -0.5 V using chronoamperometry.

EXPERIMENTAL SECTION

Chemicals and instruments

Anthraquinone-2, 6-dissulfonic acid, disodium salt (AQDS), N-[3-(trimethoxysilyl) propylethylendiamine (EDAS), hydrogen tetrachloroaurate(III) trihydrate (HAuCl_4) and sodium borohydride were obtained from Aldrich Chemicals. All chemicals were of analytical grade. Distilled water was used throughout this study. AQDS was recrystallized using distilled water. Indium Tin Oxide (ITO) coated glass slides of 8-12 Ω resistance were obtained from Delta Technologies, Stillwater, MN. A CHI-650A potentiostat (CH Instruments, Inc., Austin, TX) was used in electrochemical measurements and in the electrochemical deposition of gold. ITO electrodes were cleaned with methanol and 0.1 M NaOH solution, then rinsed with water, dried with N_2 and stored under dry conditions. The electrochemical depositions of gold on ITO were performed in a gold colloid solution by cyclic voltammetry using an ITO working electrode, an Ag/AgCl reference electrode (saturated KCl solution) and a platinum wire counter electrode. After the electrochemical deposition, the gold electrodes were rinsed with water and dried

with a stream of N_2 . The absorption spectra of the gold electrodes were obtained using a computer controlled HP model 8425A diode array spectrophotometer (Hewlett-Packard Co., Palo Alto, CA). The surface of gold electrodes was examined by using Schottky Emission Scanning Electron Microscope (SEM) (S-4300 SE, Hitachi High - Technologies Corporation, Tokyo, Japan) which was integrated with Energy Dispersive X-ray Spectrometer (EDXS) (Gresham Sirius).

Preparation of gold colloid solutions (1-4) and self-assembled layers of AQDS

Gold solutions were prepared using previously reported procedures (4-7). Briefly, the EDAS was dissolved in 0.1 M KH_2PO_4 solution. Then 5 mL of 1.0 M EDAS in 0.1 M KH_2PO_4 , 35 mL of methanol, and 5 mL of 0.1 M solution of $HAuCl_4$ were placed in a clean 150 mL Erlenmeyer flask. A clear yellow solution resulted, which was sonicated for 10 minutes. After this procedure, 0.5 mL of 0.1 M HCl and 5 mL of distilled water was added to hydrolyze and condense of the solution. The solution was sonicated for another 10 minutes. 0.250 mL of 5% $NaBH_4$ was then added to reduce the solution, which was sonicated a further 10 minutes. The pH of solution was adjusted to 2.5 via dropwise addition of concentrated HCl. The self-assembled layers were formed by immersing the gold electrode into 1 mM of AQDS in 0.1 M $HClO_4$ solution for over 20 hours. The layer-covered gold electrode was rinsed with 0.1 M $HClO_4$ and water.

RESULTS AND DISCUSSION

A gold thin film on ITO was formed from gold colloidal solution after about 400 cycles of cyclic voltammetry between -0.4 V and 1.0 V with a scan rate of 100 mV/s. As the cyclic voltammograms are shown on Fig. 1, the gold thin film of nanoparticles grow in a cyclic-by-cyclic fashion. The electrochemical properties of the gold thin film on ITO electrode was obtained by CV in 0.1 M $HClO_4$ solution with a scan rate of 100 mV/s as shown on Fig. 2. The oxidation and reduction peaks of gold were obtained at

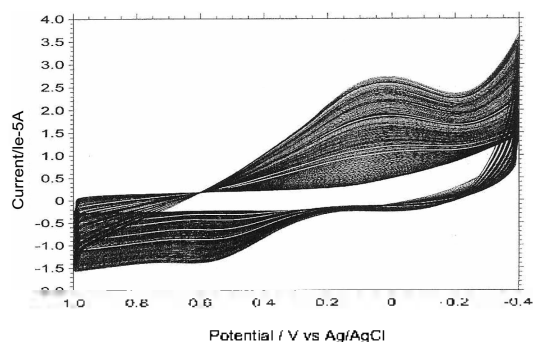


Fig. 1. Electrochemical deposition of gold nanoparticles on ITO.

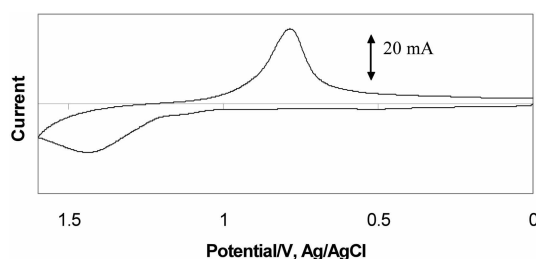


Fig. 2. The cyclic voltammogram of thin film of gold nanoparticles on ITO.

1.4 V and 0.7 V in 0.1 M $HClO_4$ solution, respectively. The surface coverage was calculated of 1.2 nanomole/cm² by measuring the area of the reduction peak of gold in 0.1 M $HClO_4$ solution. The UV-Visible spectrum of the gold film on the ITO was measured to indicate a characteristic maximum peak about 550 nm. The SEM image presented in Fig. 3 show a diameter of about 20 nm with isolated large clusters of gold particles. Thin film gold nanoparticles were confirmed by EDXS.

For comparison, the cyclic voltammograms of 10^{-5} M AQDS in 0.1 M $HClO_4$ with a glassy-carbon working electrode were obtained with a scan rate of 100 mV/s. The prominent peak at -0.12 V was due to the reduction of AQDS. The oxidation peak was shown at 0.03 V with a peak separation of 150 mV, the half peak widths of reduction and oxidation were 88 mV and 114 mV, respectively. The peak current and total charge of reduction was very close to that of oxidation. The CV of the self assembled AQDS layer on gold thin film was obtained in 0.1 M

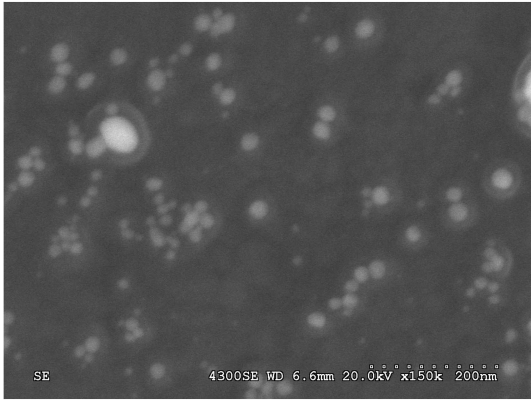


Fig. 3. SEM image of the gold nanoparticles on ITO.

HClO₄ with a scan rate of 200 mV/s. The CV exhibited a redox reaction of the self assembled layer AQDS at -0.006V for reduction and +0.080 V for oxidation. The peak-to-peak separation was 86 mV. The reduction and oxidation peak potentials of assembled AQDS layer on gold thin film were shifted to the positive potential direction compared with reduction and oxidation potentials of AQDS in 0.1 M HClO₄ solution by the glassy carbon electrode. Also, the UV-Visible maximum absorption peak of AQDS layer was obtained at 320 nm. The values of surface coverage for AQDS layer was obtained by CV (Γ_{CV}) and UV-Visible measurements (Γ_{UV}). They were calculated by the following equations: $\Gamma_{CV}=Q/2FS$, and $\Gamma_{UV}=A/1000\epsilon$, where S (cm²) is the area of electrode, Q (C) is the charge of the oxidation of AQDS, F (C/

mol) is the Faraday constant, A is the absorbance at 320 nm and ϵ is the molar extinction coefficient (2800 M⁻¹cm⁻¹) of AQDS in 0.1 M HClO₄. The Γ_{CV} and Γ_{UV} were calculated as 11.5 picomole/cm², and 17.8 picomole/cm², respectively. Various potentials were applied using chronoamperometry to study the effect of charge injection of AQDS self assembled layer on gold thin film. Gold thin film absorption band maxima were obtained at 540 nm, while the AQDS layer coupled the nanoparticles on the gold thin film and had absorption at 690 nm. The differences of surface plasmon absorption bands were obtained using UV-Visible spectrometer with various potential ranges from +0.5 V to -0.5 V of 300 seconds potential width. The potential dependent surface plasmon absorption spectra were shown on Fig. 4. The shapes of the plasmon absorption band of the self assembled layer AQDS on gold were changed to applied various potentials. By varying the potential, maximum surface plasmon band intensity was observed to decrease and broaden with increased applied negative potential. This is a result of thin film particle aggregation and the electron enrichment on the self assembled layer AQDS. The surface plasmon band of nanoparticle collide solution has been determined by the density of electrons, the effective electron mass, and the size and shape of the charge distribution. The peak positions are related directly to the relative electron concentration through $\lambda_r^2 = \lambda_i^2 N_f/N_i$ where N is the conduction electron concentration and i and f refer to initial and final

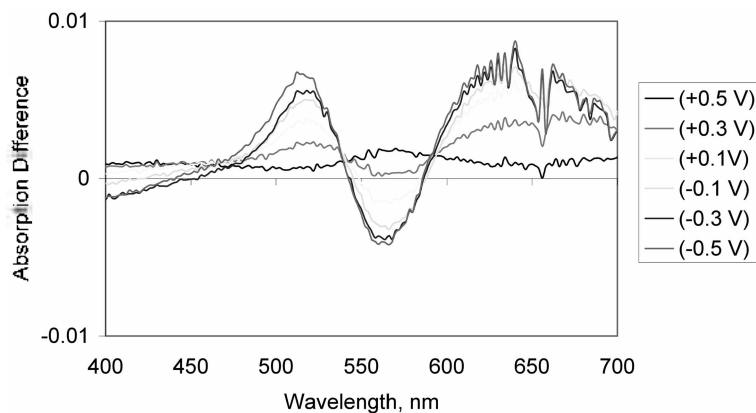


Fig. 4. The surface plasmon absorption differences of multi-layers with various applied potentials.

states, respectively (20). The self assembled AQDS layer on the gold thin film is able to accumulate charge which makes the blue shifts of plasmon peak a function of potential. This is in good agreement with previous observations (22). The change of optical properties of the multi-layers by changing their state of charge has been demonstrated. This system can be applied to measure the spectroelectrochemical responses as a sensor for a redox species on gold thin films in the future.

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