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Spectroelectrochemical phenomena on surface plasmon resonance of Au nanoparticles immobilized on transparent electrode

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Abstract

Different shapes (nanosphere or nanorod) of gold nanoparticles (Au-NPs) were synthesized with and without ultrasonic irradiation in the presence of citric acid. Spherical-shaped and rod-shaped Au-NPs showed different surface plasmon resonance (SPR) absorption bands. The Au-NPs with different shapes were immobilized on a monolayer of 3-aminopropyltriethoxysilane (APS) coated on an indium–tin oxide (ITO) electrode. The potential dependence of the SPR band of different shaped Au-NPs in an aqueous solution was explored. The SPR band and intensity changes of the Au-NPs were found to depend on the applied potential. The spherical-shaped and rod-shaped Au-NPs showed different SPR absorption behaviors when potential was applied. These behavior changes were interpreted as the result of the potential-induced changes of the local dielectric environment around the nanoparticles due to molecular absorption/desorption and the charging/discharging of the particles.

Keywords: Ultrasound; Gold nanoparticles; Surface plasmon resonance; ITO electrode; *In situ* UV–vis

1. Introduction

Metal nanoparticles (Me-NPs), which have a high specific surface area and a high surface-to-volume ratio, have been studied extensively because of their unique physicochemical characteristics [1]. Since the properties of Me-NPs can be adjusted by controlling their size, shape, composition, and crystallinity, there is a wide range of potential applications for Me-NPs in areas such as optics, electronics, catalysis, magnetic storage, biosensing, and biological labeling [2–4].

Covalently linked nanoparticles array using self-assembled monolayer is a general method to achieve effectively micron dimensions and to design nanoelectronic device, sensors. Thus, Colvin et al. have made use of a self-assembly of semiconductor nanocrystal to construct an optoelectronic device [5a]. Mallouk and coworkers have used a combination of layer-by-layer inorganic electrolyte and gold nanoparticles self-assembly methods to fabricate metal–insulator–nanocluster–insulator–bulk metal double tunnel junction (MINIM) devices [5b]. Dong and coworkers reported that Pt coated on Au nanoprticles monolayer electrodes show electrocatalytic activity in oxygen reduction [5c]. Osaka and coworkers reported that γ-Fe_2O_3 nanoparticles were modified with organosilane enhanced coercivity [5d]. Willner and coworkers reported that electrochemical sensors were built by the electrostatic cross-linking of gold nanoparticles with bipyridine complex [5e].

This is true especially of noble Me-NPs (e.g., Au, Ag), which have unique surface plasmon resonance (SPR) that originates from the collective oscillation of their conduction electrons in response to optical excitation [6]. The SPR is affected not only by the dielectric properties of the surrounding media but also by the size and the shape of the nanoparticles and the density of electrons [7]. Consequently, when the Me-NPs were fabricated, the shape and size were controlled, leading to different and highly sensitive SPR features [8,9].

Recently, special attention has been focused on the interaction between SPR and nanoparticles immobilized on a solid

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surface because of the importance of this interaction on practical problems relevant to micro-analytical sensor integration, microelectronics, photonics, and structural rational design of surface enhanced Raman scattering (SERS) substrates [10]. In addition, well-ordered, two and three-dimensional arrays of nanoparticles on conducting transparent surfaces permit the simultaneous study of optical and electrochemical measurements. Several reports have described the potential dependent shift and damping of the SPR band for Me-NPs immobilized on an electrode surface [11,12]. These studies demonstrated that the origin of the spectral change is due to the change of particle charge [13], the dielectric properties of the surrounding media [14], molecular absorption/desorption [15], and inter-particle interaction [16].

However, these studies dealt only with the transverse band of Me-NPs because of their spherical shape. The SPR change of longitudinal band reflecting the anisotropic nature of the rod and triangular types of gold nanoparticles (Au-NPs) and silver nanoparticles (Ag-NPs) was not reported. One of the most exciting properties of anisotropic Me-NPs (Au and Ag) is their polarization dependent response, either longitudinal SPR or transverse SPR, to incident light. For anisotropic nanoparticles (such as nanorods), two different resonance modes are possible: the resonance parallel to the long axis of the rods determines the longitudinal SPR band, or the resonance perpendicular to the long axis leads to a transverse SPR band [17]. The longitudinal SPR band is observed at lower energies (high wavelengths) and with a much higher absorption coefficient. When metal nanorods are dispersed in a solvent, the random orientation resulting from the continuous Brownian motion leads to a global absorption spectrum containing both bands.

Motivated by this previous work, we prepared different shapes (nanosphere or nanorod) of Au-NPs with and without ultrasonic irradiation in the presence of citric acid. Also, when potential was applied, we observed the SPR spectral change of different shapes of Au-NPs-immobilized ITO electrodes.

2. Experimental

2.1. Materials

Hydrogen tetrachloroaurate ($NaAuCl_4$) and citric acid were purchased from Aldrich and Wako, respectively. A 3-aminopropyltriethoxysilane (APS) and indium–tin oxide (ITO: surface resistance $10\,\Omega\,cm^{-2}$) electrode was purchased from Kanto. Water used throughout the experiments was purified by a Milli Q system (Millipore). All the chemicals were analytical grade and used without further purification.

2.2. Preparation of different shapes of Au-NPs

The citrate stabilized Au-NPs were prepared in the absence and presence of ultrasonic irradiation to control their shapes (nanosphere or nanorod). Nanorod-shape Au-NPs were prepared by reducing a 100 ml solution containing $NaAuCl_4$ (0.05 mmol dm^{-3}) with citric acid (10 mmol dm^{-3}) in the absences of ultrasonic irradiation. The citric acid works as both a capping agent and a reducing agent. On the other hand, nanosphere Au-NPs were prepared with ultrasonic irradiation using the above solution [18]. $NaAuCl_4$ (0.05 mmol dm^{-3}) was dissolved in distilled water containing citric acid (10 mmol dm^{-3}) placed in a water bath. Temperature of the solution was kept constant at 298 ± 0.5 K in a water bath. Ultrasonic irradiation was performed with a collimated 20 kHz beam emanating from a ceramic transducer with a titanium amplifying horn (13 mm Φ, Branson Sonifier 450D) directly immersed in the solution and operated with an input power of 41.6 W cm^{-2}, unless otherwise stated. The horn was vertically positioned 5.0 cm above the cell bottom. The power of ultrasound was determined by adiabatic measurement of the temperature rise of sonicated water.

2.3. Preparation of Au-NPs-immobilized electrodes

The Au-NPs-immobilized electrode was prepared using self-assembly onto an indium-doped tin oxide (ITO) electrode containing the 3-aminopropyl-siloxane (APS) primer monolayer [19]. Au-NPs immobilized ITO electrodes were prepared as shown in Fig. 1. The ITO electrodes were washed with ethanol and distilled water for 30 min with an ultrasonic bath and then transferred to a 1 M KOH solution for 30 min, to clean the surface and make it OH terminated. Next, the electrodes were rinsed with distilled water and dried. After rinsing, a self-assembled-monolayer (SAM) of organosilane (APS) was formed on the ITO by immersion in a dehydrated toluene solvent containing 1 wt% of APS liquid at 60 °C for 10 min, since the monolayer was formed easily in the liquid, rather than the gas phase. Subsequently, the ITO was cleaned again in a methanol solution and then dried at 100 °C for 10 min. Finally, the ITO electrode was APS-modified by immersion in 30 ml of citrate stabilized Au-NPs (nanosphere or nanorod) solution for 24 h.

2.4. Measurements

The colloidal suspensions of the Au-NPs (nanosphere or nanorod) were analyzed using a Shimadzu 1600 UV–vis

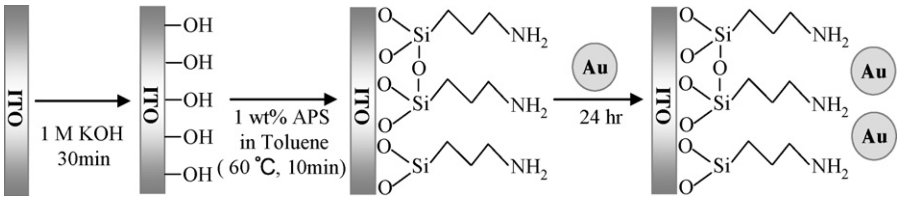

Fig. 1. Schematic illustration of process for formation of Au-NPs-immobilized-APS-modified ITO electrodes.