Bull. Soc. Photogr. Imag. Japan. (2018) Vol. 28 No. 1: 1–3

Letter

Preparation of ITO Electrode Modified with Au Nano-island by Pulse Electro-deposition

Katsumi Yamada, Fukuro Koshiji, Takayuki Uchida

Abstract: Au nanoparticles were immobilized on the ITO electrodes by electro-deposition with a pulse voltage, the optical properties of the resulting electrode were studied. It was found that the transmittance of the resulting electrode containing the plasmon scattering could be controlled without the change in the wavelength of the absorption maximum.

Key words: Au nano-island, Pulse electro-deposition, Plasmon scattering

Nanoparticles (diameter: 50 -100 nm) of noble metals, such as Au and Ag, show different colorations, such as red, violet and green, from their color in the bulk states. These colors are due to plasmon scattering of the nano-particle, and were dependent on the metal element, the diameter, the shape and the dielectric constant of the surrounding medium. These nanoparticles are utilized in stained glass as a pigment with a strong durability for long time. In recent years, these nanoparticles were integrated to improve the power generation efficiency of organic solar cells. [1)2)3)] A strong electric field (plasmon polariton) exists on the surface of the nanoparticles. When materials having an absorption band in the visible range, such as organic molecules and semiconductors, were incorporated into the electric field, the enhancement phenomenon of the coloration (absorption) would often be observed from the materials.

To utilize the enhancement phenomenon, it is required to arrange these particles on the electrode or into the layer. When thin layers (less than 100 nm) of Au or Ag were immobilized on a glass substrate by DC sputtering or evaporation technique, the resulting metal layer often showed an imperfect solid layer structure with space between the neighboring particles. A red or violet coloration was found from the thin layer, because of the plasmon scattering from the metal island-structures on a nano scale. Since no electric conductivity occurred from the thin layer, these nanoparticles were electrically in an isolated state. After immobilization of the nanoparticles onto the ITO glass, the conductivity and the transmittance of the electrode could be improved for an unmodified ITO glass. This is probably due to the presence of dielectric-metal-dielectric (DMD) or multi-layered structures on a nano scale.

In recent years, the comparison of the EC characteristics of the poly(3,4-ethylenedioxythiophene) [PEDOT] was carried out using the ITO electrode with Au nano-particle (Au-ITO) and an unmodified ITO as a control electrode. As a result, both the contrast between the colored state and the bleached state, and the switching speed of the color change were improved by using the Au-ITO. [4)] This is expected from the plasmon absorption enhancement and the DMD structures of the Au-ITO. [5)6)]

In this study, the preparations of the Au-ITO electrodes were carried out by a pulse electro-deposition in order to realize the effective plasmon enhancement of the various EC materials.

To optimize the reproducibility of the electro-deposition, a device for the metal Au formation was fabricated by interposing the electrolyte solution between two ITO electrodes through a silicon o-ring. The aqueous electrolyte solution (pH 10) was consisted of gold (I) trisodium disulfite (10 mM) and potassium sulfite (0.1 M). The Au layer were immobilized on the ITO surface by pulse voltage applications with a higher voltage for a short time and a constant lower voltage for a long time. In the ITO device, one side is the working electrode for depositing the Au layer, and the other side is the counter electrode. The voltage applied to the working electrode is defined as the potential difference to the counter electrode.

The transmittance spectrum in the visible band was obtained with a CCD spectrophotometer connected to fiber optics and a halogen light source. The surface observations of the resulting electrode were carried out using a field emission scanning electron microscope (FE-SEM).

Among the preparation methods of the Au nanoparticles, electrochemical deposition has many advantages, such as the direct immobilization of the particles onto the electrode surface, and no removal of protective surfactants, but has a disadvantage of a wide distribution of the resulting particle size. [7)8)] We choose a two-electrode electro-deposition system with the constant voltage mode for its simplicity.

As a result of our preliminary experiment, it was found that the Au deposit was not formed on the ITO electrode by an elec-

Received 4th August, 2018; Accepted 22nd August, 2018

Tokyo Polytechnic University,
E-mail: kyamada@chem.t-kougei.ac.jp

tro-deposition for a long time at the applied voltage of -1.2 V. On the other hand, the Au deposit was formed for a short time at a voltage over -2 V. During the general electro-deposition process of the metal, the adsorption of the Au metal on the surface of the electrode was caused by the electrochemical reduction of the metal ions during the initial step. The growth of the metal nucleus was then achieved by the electro-reduction of the metal ions on the surface of formed nuxleus in the following step. Because the activation energy for the nucleation is greater than that for the nuclear growth, both processes can be independently controlled. Namely, the electro-deposition at the higher negative voltages allows the both the nucleation process and the growth process, while at the lower voltages only the growth process occurs.

As an example of the electro-deposition, the time course of the applied voltage is shown in Figure 1. Since the degradation of the ITO was induced by application at the higher negative voltages, the higher voltage (V_P: from -7 V to -10 V) application would be momentarily performed for 2 ms as the nucleation process. The lower voltage (V_L: -1.2 V) application was then performed for 60 s as the nuclear growth process. As a result of this electro-deposition, the transmittance spectra of the ITO electrodes are shown in Figure 2. Their color was a pale violet; the absorption maximum was found at the wavelength of 580 nm. This wavelength was identified as the plasmon absorption of the Au nanoparticles having the diameter of around 100 nm. [9] In our results, only a decrease in the transmittance without the red shifting of the absorption maximum was observed by a change in the V_P. The control of the coloration for the plasmon scattering on the ITO electrode with immobilized Au nanoparticles was achieved without any color change by our pulse electro-deposition. In general, the red shifting of the plasmon absorption maximum is observed with an increase in the diameter of the Au nanoparticles. Furthermore, the decrease in the transmittance of the ITO electrode was induced with an increase in the number of Au nanoparticles due to the reduction of the effective open area for light transmission. Therefore, when both processes of the nucleation and the nuclear growth occur at the same time, the decrease in transmittance for the plasmon absorption was induced along with the red shifting of the absorption maximum. On the contrary, the shifting of the wavelength was not observed in our system. Since the voltage application in the nuclear growth process was performed at the same time, the particles formed might reach the same size. It is suggested from our results and this speculation that the number of Au nuclei on the electrode surface can be controlled by the V_P for this electro-deposition.

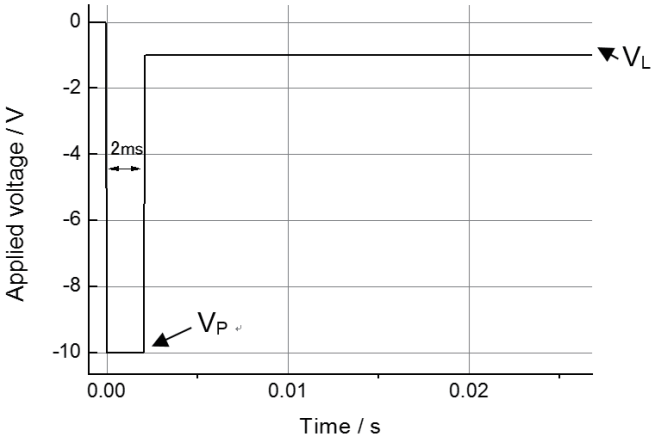

Figure 1 Change in applied voltage during Au electrodeposition.

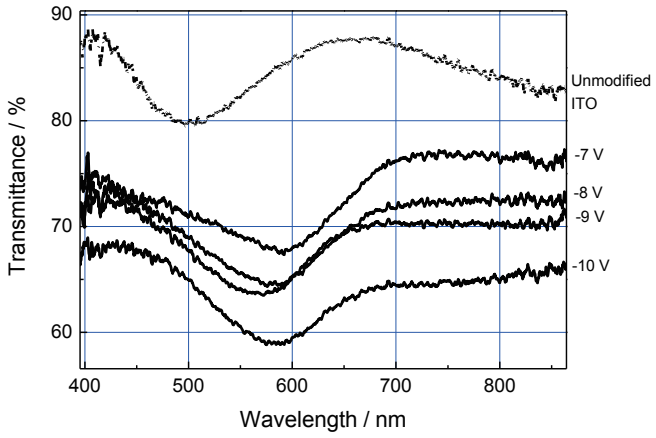

Figure 3 Transmittance spectra of ITO electrode with Au nanoparticles obtained by electro-deposition at various applied voltages.

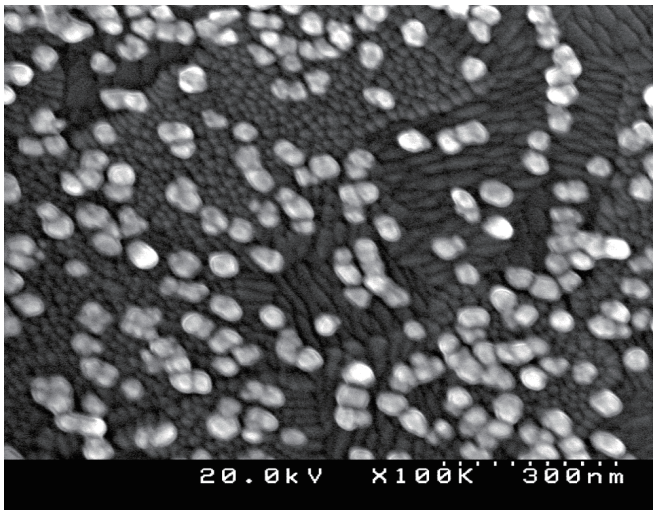

Figure 3 FE-SEM image of the ITO electrode after electrodeposition of Au with pulse voltage application of -8 V.

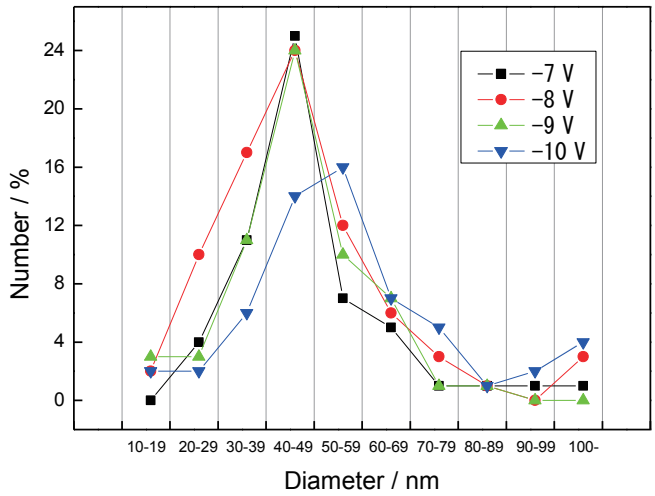

Figure 4 Size distributions of the Au nanoparticles obtained on the ITO electrode by electro-deposition at various applied voltages.

The FE-SEM image of the ITO electrode obtained by the electro-deposition with the V_P of -8 V is shown in Figure 3 in order to confirm the surface condition. The particle size distributions calculated from the image analysis of the FE-SEM images is shown in Figure 4. It was confirmed from Figure 3 that the Au depositions were particulate and immobilized on the ITO surface. We called this surface condition a "Au nano-island". From Figure 4, most of the diameters are around 50 nm for all the pulse voltages. This result indicates that the wavelength of the maximum absorption at 580 nm is attributed to the plasmon scattering of the nanoparticles having the diameter of 50 nm. However, this relationship between the particles size and the wavelength was a little different from that of the Au spherical nanoparticles. (diameter:100 nm and wavelength: 580 nm) Therefore, it is required to evaluate in detail the shape of the nanoparticle obtained from our system. From the observation of the FE-SEM images, it was confirmed that the number of the particles obtained in the same area by the electro-deposition with pulse voltages (V_P) of -7 V, -8 V, -9 V and -10 V were 601, 626, 660 and 696, respectively. Because of a progressive increment in the particle, the transmittance of the electrode will be smaller by enhancement of the light shielding. The discussion about the relationship between the V_P and the number of the Au nucleus in figure 2 is supported from these results. Namely, the V_P affected definitely the number of the Au nucleus, and did not affect the final size of the particles. As shown in figure 4, because of the same application time for electro-deposition with the V_L (nuclear growth process), the final size of the particle was also close to all sample. Other electro-depositions were carried out with the same V_P and the same application time of the V_P in order to evaluate the influence of the V_L application time on the final size of the particle. Increment of the particle size, and the red shift of the plasmon absorption maximum (accompanying the enhancement of the absorption) were induced by the elongation of the application time of the V_L.

About the relationship between the Au nucleation and the pulse voltage (V_P), and the shape of the resulting particles will be studied in detail in the near future. We believe that our studies of the plasmon scattering characteristics of Au nanoparticles immobilized on the ITO electrode can contribute to improvement of novel opto-electronic devices.

References

1) H.A.Atwater, A.Polman, Nat.Mater., **9**, 205 (2010).
2) S.Pillai, K.R.Catchple, T.Trupke, M.A.Green, J.Appl.Phys., **101**, 093105 (2007).
3) M.Ihara, M.Kanno, S.Inoue, Physica E, **42**, 2867 (2010).
4) Y.Tanaka, K.Yamada, J. Soc. Photogr. Sci. Technol. Jpn., **80**, 60 (2017).
5) Y.-C. Nah, J.Nanosci.Nanotech., **13**, 3470 (2013).
6) T.Xu, E.C.Walter, A.Agrawal, C.Bohn, J.Velmurugan, W.Zhu, H.J.Lezec, A.A.Talin, Nat. Commun., **7**, 10479 (2016).
7) N.Sasai, Y. Fujiwara, M.Arai, K.Yu, T.Tatsuma, J. Electroanal. Chem., **628**, 7 (2009).
8) Y.-C. Nah, S.-S. Kim, J.-H. Park, D.-Y. Kim, Electrochem. Solid-State Lett., **10**, J12 (2007).
9) P.K.Jain, K.S.Lee, I.H.El-Sayed, M.A.El-Sayred, J.Phys.Chem. B, **110**, 7238 (2006).