

Structural Control of Metal Nano-dot via Photo-induced Highly Localized Reduction of Metal Ions on Surface

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Metal nanoparticles possessing well-controlled structures have been widely employed for the preparation of various functionalized materials, such as catalysts, molecular sensors and optical devices. Precise control of metal nanoparticle structure in the nanometer region should be achieved in order to develop these functionalities. Precise control of metal nanoparticle structure in the nanometer region should be achieved in order to develop these functionalities. Although chemical synthetic techniques have been widely used for the preparation of metal nanoparticles with well-controlled size, further fine-tuning of the structure in the nanometer range following preparation can be quite difficult. Thus, novel approaches to control the structure of metal nanoparticles in this size region should be developed.

Recently, we proposed that selective excitation of a specific surface plasmon mode of metal nanostructures can be employed as a perturbation for effective structural control. Useful effects on particle-interaction and highly localized electrochemical reaction were observed in several nanostructured metal systems. Plasmon absorption is known to cause a highly localized electric field at the interface between the metal surface and surrounding medium. Thus, in instances where a localized field could be utilized to induce electrochemical reactions, the effect can be applied to alter and/or control the metal nanostructure. In this paper, the effect of photo-irradiation on metal deposition process was investigated.

Figure 1 shows photoelectrochemical responses Au polycrystalline electrode in electrolyte solution containing 0.1 M CuSO₄. Illumination of 830-nm laser light accelerated Cu deposition on to Au surface. Cathodic photocurrent was very sensitive to the potential of the electrode. As the electrode potential became negative, the photo-induced reduction current increased. Onset potential of the photocurrent was slightly negative for approximately 200 mV than that of bulk deposition. The result suggests that the photo-illumination accelerate the reduction of metal ions in solution. Apparent photocurrent efficiency depended on illuminated light intensity and optical properties of the electrode. Introduction of surface roughness to the Au electrode improved the efficiency significantly. These characteristics of the photocurrent in the present system imply that resonance excitation of the electrons via photo-absorption of Au electrode contributes the acceleration of metal deposition process.

The effect of photo-illumination at nano-gaps (tunneling junctions) between atomically flat Au (111) surface and the probe tips of a scanning tunneling microscope (STM) was also investigated under the comparable electrochemical condition in the same electrolyte solution. Illumination to the vicinity of the gap accelerated Cu deposition on to Au surface. In this case, illuminated light intensity was reduced to minimize the

effect of the heat caused by the photo-absorption by the tip. Total illuminated energy was adjusted to be in the order of < 1 mJ/cm². Photo-illumination at the gap in 0.1 M CuSO₄ resulted in the formation of a single Cu nano-dot formed just below the tip (Figure 2). During the experiment, the tip potential was kept at 0.7 V to avoid the effect of the deposition of Cu metal. Deposited dot on the electrode surface was dissolved when the electrode potential polarized to positive, indicating that the dot is Cu metal. The result proved that photo-induced metal deposition can be applied to construct small dot structure with the size range less than tens nm. Mechanism of the metal deposition under the photo-irradiation will be discussed in details.

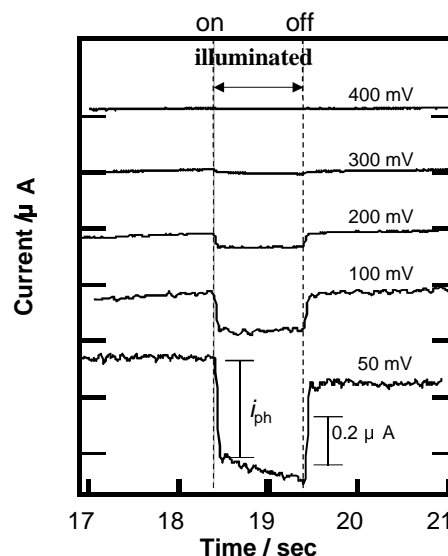


Figure 1. Photoelectrochemical response of Au polycrystalline electrode in 0.1 M CuSO₄ aqueous solution; Potentials was referred to the Ag/AgCl reference electrode.

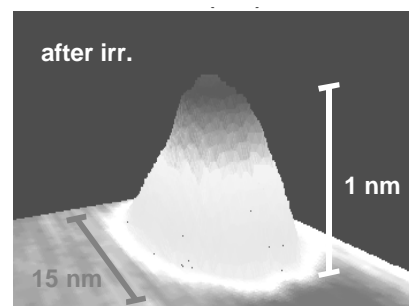


Figure 2. Cu nano-dot deposited on Au (111) surface by photo-irradiation in electrolyte solution.

References

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