$\label{eq:Electrochemical deposition of gold nanoparticles on rough TiO_2 surfaces$

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Metal nanoparticles have a lot of useful functions such as catalyst and plasmon resonance. The thermal decomposition method and dry processes such as the vacuum evaporation method are often used when metal nanoparticles are deposited on a substrate. However, these methods do not have the positional selectivity. The positional selectivity is important for integration of devices such as a sensor with various characteristics. On the other hand, the electrochemical method can deposit metal on the only region to which a current is applied, that is, it has the positional selectivity. However, it is difficult to homogeneously deposit metal nanoparticles on rough surfaces although it was reported that gold (Au) nanoparticles were homogeneously deposited on a flat surface such as HOPG or glassy carbon by the double pulse method [1-3]. In the case of the double pulse method, a higher pulse is applied to form nuclei of metal and the following lower pulse grows the nuclei in order to control nucleation and growth of nuclei.

In this study, we developed the electrochemical deposition method to homogeneously deposit Au nanoparticles on rough titanium oxide (TiO_2) surfaces. TiO_2 is one of metal oxide semiconductors. It has attracted great interest because of its superior properties such as high photocatalytic activity and high biological affinity and its application to solar cells or gas sensors has been investigated. We deposited a TiO_2 film on ITO layer. We employed pulse-train potential as an anodic potential to homogeneously deposit Au nanoparticles and the deposition process of Au nanoparticles was controlled by the waveform of which parameters are a pulse height, a pulse width and a rest time as shown in Fig. 1.

Figure 2 shows a SEM image of Au nanoparticles deposited on rough TiO₂ surfaces by the double pulse method. The first pulse of -1.5 V were applied for 100 ms and the second pulse of +1.0 V were applied for 300 s. An electrolyte was 1.2 M chloroauric acid (HAuCl₄) solution. A standard mercury/mercurous sulfate electrode was used as a reference electrode and a platinum (Pt) sheet was used as a counter electrode. From Fig. 2, we can see that Au nanoparticles were formed on lines and could not be deposited on rough TiO₂ surfaces. Figure 3 shows SEM images of Au nanoparticles deposited on rough TiO₂ surfaces by applying a potential of -1.5 V for (a) 5 s and (b) 12.5 s, respectively. From Fig.



Fig. 1: Parameters of a pulse train.



Fig. 2: A SEM image of Au nanoparticles on rough TiO_2 surfaces which were deposited by the double pulse method.



Fig. 3: SEM images of Au nanoparticles deposited on rough TiO_2 surfaces by applying a pulse of -1.5 V for (a) 5 s and (b) 12.5 s, respectively.



Fig. 4: A SEM image of Au nanoparticles deposited on rough TiO_2 surfaces by applying a pulse train.

3, we can see that larger particles preferentially grew and that the density did not change, that is, growth of small particles and formation of new nuclei were suppressed. Figure 4 shows a SEM image of Au nanoparticles deposited on rough TiO₂ surfaces by applying a pulse train. A pulse height and a pulse width and a rest time were -3 V, 250 ms, and 2 s, respectively. From Fig. 4, we can see that homogeneous Au nanoparticles were deposited on rough TiO₂ surfaces. This is because a rest time and a high potential prevented suppressing growth of small particles and formation of new nuclei.

Our results indicate that the pulse train method can control the electrochemical deposition process and is a powerful method to deposited homogeneous metal nanoparticles.

References

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