Oxygen reduction at Metal Monolayer Islands Deposited on Au Substrate

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It has been found in our previous studies that underpotential deposition (UPD) of several kinds metals on a gold electrode can be made even if the electrode was coated with a self-assembled monolayer (SAM) of alkanethiol. The metal monolayer is deposited between the SAM and the Au substrate, as schematically shown in Fig. 1. In the initial stage, numerous islands of metal atomic monolayers are generated and they grow gradually with polarization time. By using this way, we can prepare monolayer islands having a desired size.[1,2] After preparation of the metal islands, the SAM of alkanethiol can be removed by electrochemical reduction of alkanethiol molecules. This implies that we have got the technique allowing preparation of naked two-dimension metal islands having different sizes. As an example, an STM image obtained for Ag islands having the average diameter of 15 nm is shown in Fig. 2. Then, we initiated investigation for clarifying relationship between metal size and electrocatalytic activities.

As well known, Ag can do O_2 reduction with the 4-electron reaction in alkaline solution, whereas Au does with the 2-electron reaction. This fact was confirmed by the linear sweep voltammetry using Ag island-deposited Au electrodes, as shown in Fig. 3. The naked Au electrode shows a current peak at -0.4 V due to reduction of O_2 to HO_2^- and this species is further reduced to OH^- at -1.1 V. When Ag islands were deposited and their size increased, the former and the latter peaks increased and decreased, respectively, indicating that reduction of O_2 to OH^- with the 4-electron reaction was enhanced. However, close analysis of the electrocatalytic activities of the electrode has revealed that it is required for the Ag monolayer islands to contain number of Ag atoms larger than 750 to exhibit catalytic activities of 4-electron reaction.[3] Furthermore, it was found that Ag atoms over than 4000 was necessary to show the original activities for 4-electron reaction. Those results suggest strongly that band structure of metal is related to electrocatalytic activities of the metal.

Later we have developed several methods allowing preparation of monolayer islands of other metals including Pt and Pd on the Au substrate. Now electrocatalytic reactions such as O_2 reduction and H_2 oxidation are investigated by using those new electrodes.

Acknowledgement

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References

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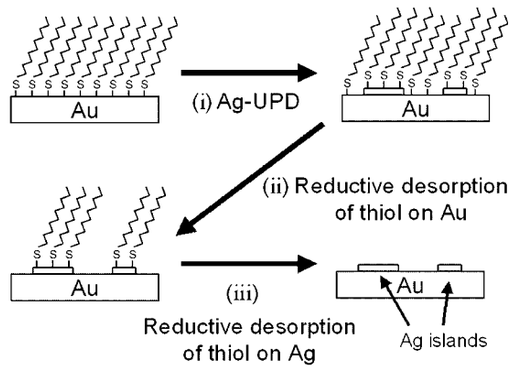

Fig. 1. Schematic illustration of procedures for preparation of Ag monolayer islands with use of underpotential deposition of Ag onto SAM|Au electrode.

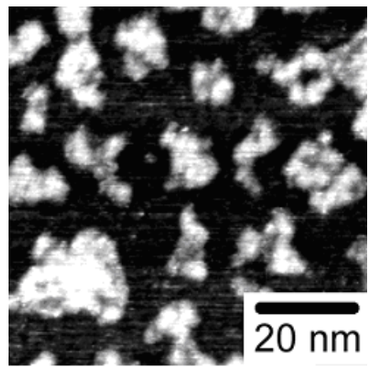

Fig. 2. STM images of Ag monolayer islands after reductive desorption of decanethiol. The polarization times for Ag deposition was 20 min.

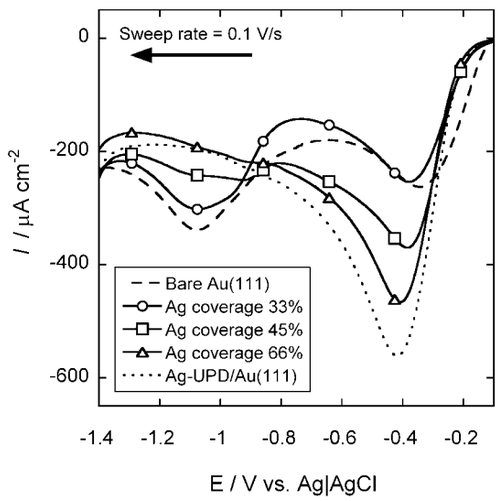

Fig. 3. Linear sweep voltammograms of oxygen reduction in O_2-saturated 0.5 mol dm^{-3} KOH solution at a sweep rate of 0.02 mV s^{-1}.