



Short communication

Size dependent lattice constant change of thiol self-assembled monolayer modified Au nanoclusters studied by grazing incidence x-ray diffraction

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ABSTRACT

Size and lattice constant of thiol self-assembled monolayer (SAM)-modified gold nanoclusters (GNCs) assembled on Au(111) surfaces after each electrochemical treatment were investigated using grazing incidence x-ray diffraction (GIXRD). When the potential was swept between 0 and 1.3 V (vs. Ag/AgCl), the size and lattice constant of GNCs slightly decreased due to the oxidative desorption of the SAMs. As the number of potential cycles increased, the size of GNCs started to increase due to the aggregation, while the lattice constant continued to decrease due to further desorption of the SAMs from the GNCs. After most of the SAMs were removed from the GNCs, the size and lattice constant monotonically increased with the number of potential cycles. The size dependent lattice constant change was observed when GNCs were smaller than ~35 Å.

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1. Introduction

It is very important to clarify the relationship between the size and interatomic layer distance, i.e., lattice constant, of nanoclusters, since these structural parameters are critical factors in determining the physical and chemical properties of nanoclusters, such as catalytic activity. Both theoretical predictions [1–6] and experimental results [6–15] have indicated that lattice constant of small metallic nanoclusters is smaller than that of the corresponding bulk crystals. However, the systematic study on the size dependent lattice constant change of metal nanoclusters has yet to be carried out because of the difficulty in precise control of the cluster size.

Previously, we succeeded [16–24] to synthesize gold nanoclusters (GNCs), of which surface was covered with the mixed self-assembled monolayers (SAMs) of mercaptoundecanoic acid (MUA), hexanethiol (C₆SH), and ferrocenylhexanethiol (FcC₆SH), using the methods by Brust et al. [25] and Hostetler et al. [26] and to construct the multilayers of GNCs on the solid surface, using the cation/anion electrostatic interaction [27–31]. When the potential was made more positive than that for the oxidative decomposition of the thiol SAM on gold [32–35], the

SAM was gradually removed from the GNCs and GNCs started to aggregate [22,23].

In this study, the size and lattice constant of GNCs were monitored using grazing incidence x-ray diffraction (GIXRD) after each electrochemical treatment, i.e., potential cycles between 0 and 1.30 V (vs. Ag/AgCl), where the thiol SAM is oxidatively decomposed. In the initial stage, the size and lattice constant of GNCs decreased from ca. 16 Å to ca. 12 Å and from ca. 4.19 Å to ca. 4.01 Å, respectively, due to the oxidative decomposition of the SAMs. Then, the size of GNCs increased to ca. 17 Å with the number of cycles due to the aggregation, while the lattice constant continued to decrease to ca. 3.93 Å due to further desorption of the SAMs. After most of the SAMs were removed from the GNCs, the size and lattice constant monotonically increased to ca. 40 Å and ca. 4.08 Å, respectively, proving the size dependent lattice constant change of GNCs during the aggregation. When the size of GNCs was larger than ~35 Å, the lattice constant became almost constant at around 4.08 Å which is identical to that of bulk gold.

2. Experimental

GNCs modified with the mixed SAMs of MUA, C₆SH, and FcC₆SH were prepared by the methods previously reported [16–19,21]. Multilayers of GNCs were prepared on a commercially available Au(111) substrate, which was annealed and quenched prior to use, by repeating the two-step dip and rinse cycles for 10 times

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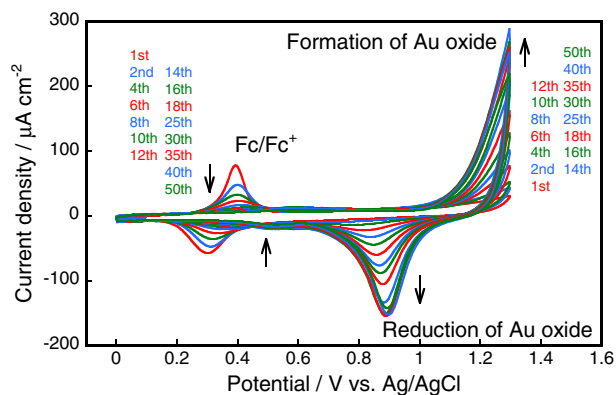


Fig. 1. CVs of the Au(111) electrode modified with the GNC/PAH layers, measured in a deaerated 0.1 M HClO₄ solution with a scan rate of 50 mV s⁻¹. Number of cycles is shown in the figure.

based on the carboxylate/poly(allylamine hydrochloride) (PAH)/carboxylate electrostatic interaction [16–19,21–23]. Cyclic voltammograms (CVs) of the Au(111) electrode modified with these mixed SAM modified GNC multilayers were measured in a deaerated 0.1 M HClO₄ solution at a scan rate of 50 mV s⁻¹ in the potential range between 0 and 1.30 V with respect to the Ag/AgCl electrode. The samples before and after a certain number of potential cycles were set on a six-circle diffractometer installed in an undulator-magnet beamline BL15XU at SPring-8 and GIXRD measurements were carried out in air with an x-ray energy of 11.5 keV and an incident angle of 0.2°. It was confirmed that x-ray irradiation during the GIXRD measurement did not cause any damage to the

sample, from the fact that no significant change was observed in the CVs after the GIXRD measurements. GIXRD profiles were fitted by summation of two Lorentzian functions to obtain the peak positions and fwhm (full width of half maximum).

3. Results and discussion

Fig. 1 shows CVs of the Au(111) electrode modified with GNC/PAH layers, measured in the 0.1 M HClO₄ solution. The CVs are almost the same as our previous reports [22,23]. Redox waves due to the redox of the ferrocene/ferrocenium couple (Fc/Fc⁺) observed at around 0.35 V gradually decreased by repeating the potential cycles between 0 and 1.30 V, confirming the oxidative decomposition of the thiol SAMs. Simultaneously, oxidation and reduction current due to the formation and reduction of Au oxide at around 1.2 V and 0.9 V, respectively, increased with the number of potential cycles.

Fig. 2 shows typical GIXRD profiles of the samples before and after several potential cycles. Before the potential cycles, a broad peak composed of two components due to the Bragg reflections of Au(111) and Au(200) around 2θ of 26.5° and 30.6° [36–40], respectively, was observed. It should be noted that the (111) reflection peaks were not from the Au(111) substrate but from GNCs because the measurements were carried out in an in-plane configuration. Azimuthal angle was fixed to avoid surface x-ray diffraction from the Au(111) substrate, such as <110> and <112>. As clearly seen in the profiles, these peaks became sharper as increase in the number of the potential cycles.

The size and interatomic layer distance of GNCs can be obtained by Scherrer's and Bragg's equations, respectively, as follows [41–46]:

$$D = (K \times \lambda) / (\beta \times \cos\theta) \quad (1)$$

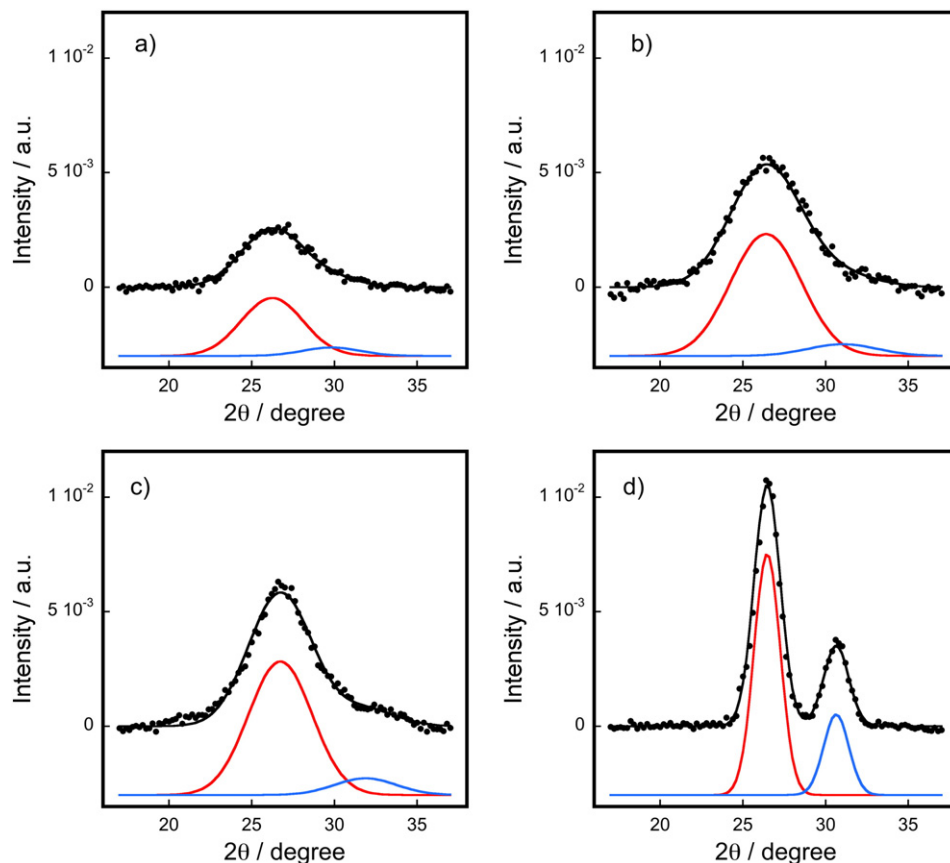


Fig. 2. Typical GIXRD profiles of the Au(111) electrode modified with the GNC/PAH layers (a) before and after the potential cycles (b) 1, (c) 8, and (d) 30 times. Black dots: experimental data. Red, blue, and black lines: fitting curves of the (111) reflection, the (200) reflection, and their summation, respectively.

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