Potential-Driven Dynamic Behavior of Surface Modified Gold Nanoparticles at a Au(111) Electrode Surface∗

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Potential-driven movements of a surface-modified Au nanoparticle at a Au(111) electrode/aqueous solution interface were examined. An interfacial capacity peak due to the reorientation of terminal 4-pyridyl groups of the surface modifier layer was observed when the Au(111) electrode was touched to the spread film of the particles on the surface of an aqueous solution at lower surface pressures than equilibrium spreading pressure. When the spread amount was increased, appearance of a capacity response presumably due to partial adsorption-desorption of the particles was observed. Implications of the results of electrochemical and electroreflectance measurements were discussed in regards to the reversible movement of the particles. [DOI: 10.1380/ejssnt.2005.141]

Keywords: Nano-Particle; Solid-Liquid Interface; Electrochemical Method; Dynamics at Electrified Interface; Adsorption-Desorption

I. INTRODUCTION

Much has recently become well clarified how water insoluble surfactants exhibit dynamic changes of their molecular assembling structures on well-defined electrode surfaces [1]. Achievement of reversible and drastic movements of entities greater in size driven by the change of electrode potential is an intriguing target. Such a movement may display to us the role played by the interplay of interactions in the surface dynamism and find applications to novel functional electrodes. The question we are addressing is how we can give potential-driven movements for bigger nano-entities at electrified interfaces. We previously reported the results of our preliminary study of the potential dependent behavior of a Au nanoparticle, the surface of which is modified with an organic monolayer possessing a terminal adsorption-active group [2]. When using a 6 nm Au nanoparticle co-modified with dodecanethiol (C12-SH) and isonicotinic acid 11-mercaptoundecyl ester (Py-(C=O)-O-C11-SH), we observed orientation change of the terminal 4-pyridyl groups at a Au(111) electrode surface, while adsorption-desorption of the particle itself did not take place. With an aim at realizing a sharp and multi-modal movement of a metal nanoparticle in mind, we prepare in this work a smaller core Au nanoparticle with shorter chain modifiers with an increased content of the terminal 4-pyridyl group.

It has been known that pyridine exhibits potential dependent adsorption-desorption and adsorption orientation change as a function of electrode potential [3]. We expect, therefore, that potential dependent interaction of 4-pyridyl groups with a Au(111) surface can induce the movement of Au nanoparticles.

We describe herein the potential-driven behavior of newly prepared surface-modified Au nanoparticle (Py-C4-MPC; see Fig. 1) at a Au(111) electrode in contact with an aqueous electrolyte solution using the results of voltammetric and electroreflectance measurements.

II. EXPERIMENTAL

n-Butanethiol-modified Au nanoparticles synthesized by the Brust reaction [4] were added in chloroform solution of n-butanol and 4-pyridine ethanethiol (mol/mol = 1:1), and the solution was stirred for 72 h at room temperature. Resulting particles were purified by precipitation-centrifugation-decantation-resolution cycles. Obtained Py-C4-MPC was characterized by TEM, XRD, TG, XPS, DLS, and IR and UV-vis spectroscopies. Chloroform solution of Py-C4-MPC was spread on a Ar gas/electrolyte solution (G/S) interface. After chloroform was allowed to evaporate, an anneal-cooled single crystal Au(111) electrode (surface area: 0.283 cm²) was horizontally touched to the spread film of Py-PMC at the G/S interface. At a hanging meniscus configuration of the Au(111) electrode, electrochemical and spectroelectrochemical measurements were conducted as described before [2].

III. RESULTS AND DISCUSSION

The particle size (diameter) of Py-C4-MPC as determined by TEM was 2.45±0.92 nm, in accordance with the results of DLS measurements. The XRD primary crystalline size based on the Debye-Scherrer equation was 1.26 nm at (111) diffraction. Addition of I₂ in the chloroform solution of Py-C4-MPC made the Au particles completely precipitate in a period of 1 h, because surface modifier thiols were decomposed to disulfides and displaced from the particle surface into the solution phase. The supernatant after solvent evaporation was subjected to ¹H NMR measurement in d₆-DMSO. The NMR peak areas of pyridyl

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FIG. 1: Schematic depiction of Py-C4-MPC.

FIG. 2: Cyclic voltammograms (CVs: upper) and $C - E$ curves (lower) for a Au(111) electrode horizontally touched to the spread film of Py-C4-MPC at Ar gas/0.05 M KClO$_4$ aqueous solution interface at four different spread amounts of the particles. Potential sweep rate for CVs was 20 mV s$^{-1}$. Interfacial differential capacity was obtained by AC measurements at 14 Hz and 5 mV$_{rms}$-ac amplitude. Spread amounts were (a) 0.96 µg cm$^{-2}$, (b) 1.96 µg cm$^{-2}$, (c) 2.94 µg cm$^{-2}$(= ESP), and (d) 3.92 µg cm$^{-2}$. Green line $C - E$ curves were obtained in the absence of Au nanoparticles.

and methyl protons allowed us to determine the molar ratio of butanethiol and 4-pyridine ethanthiol on the particle surface as being 52:48 (mol/mol). Full coverage of the particle with the modifiers was supported experimentally by TG thermogram. The absence of free thiol in the spread solution was confirmed by chemical analysis using 5,5'-dithiobis(2-nitrobenzoic acid). The Py-C4-MPC sample was stable under refrigerator storing in the dark in approximately 18 months.

When water-insoluble Py-C4-MPC was spread on the surface of 0.05 M KClO$_4$ aqueous solution, the film pressure ($\pi$) was saturated at 12.3 mN/m. The $\pi - A$ curve ($A$ is the area of the G/S interface per particle) at the 0.05 M KClO$_4$ sub-phase supported the formation of a Langmuir film of Py-C4-PMC and showed a sudden steep rise of $\pi$ at 6.6 nm$^2$/particle, in accordance with the estimation of the modified particle size including the modifier layer thickness using the TEM and DLS diameters. Therefore, we determined the equilibrium spreading pressure (ESP) as being 12.3 mN/m, to attain which a minimum spreading amount of 2.94 mg of Py-C4-PMC per 1 cm$^2$ sub-phase surface is required.

Figure 2 shows typical cyclic voltammograms (CVs) and interfacial differential capacity ($C$)-potential ($E$) curves for a Au(111) electrode at various spread amounts of Py-C4-PMC. The value of $C$ was obtained from AC voltammetry measurement. At all spread amounts shown here, the capacity level was lowered compared to a bare Au(111) electrode surface, indicating that the particles are adsorbed on the electrode surface by contacting the surface organic layer to the electrode surface. At a spread amount much lower than ESP (Fig. 2(a)), a capacity peak was observed around 0.05 V. At the same potential, CV peaks were clearly observed. This capacity peak is due to
the potential dependent reversible orientation change of 4-pyridyl groups that are in contact with Au(111) substrate surface, as reported previously [2]. On the other hand, the $C - E$ curve around $-0.7$ V, the potential region where pyridine desorption can take place, was almost flat. That is, desorption of the particles did not take place.

With the increase of the spread amount, the capacity peak of orientation change disappeared (Fig. 2(b)), while a rise of capacity at the potential region more negative than $-0.5$ V commenced (Fig. 2(b)) and was progressively enhanced (Figs. 2(c) and (d)). In line with this observation, CV peaks around $0.05$ V disappeared, while cathodic current rise at more negative potentials than $-0.6$ V and anodic bump at $-0.7$ V appeared in CVs. The rise of capacity is ascribable either to the increase of the area of Au(111) surface directly exposed to the electrolyte solution by the partial displacement of Py-C4-MPC or to the increase of the amplitude of charging-discharging of Py-C4-MPC. It has been known that the latter process exhibits characteristic electroreflectance (ER) signal at the plasmon light absorption wavelength of the Au particle core [5, 6]. Although a slight increase of the ER signal was observed at negative potentials relative to that at $0.0$ V, blue shift of the ER plasmon peak indicative of the enhancement of charging-discharging process [5, 6] was not observed [7]. Therefore, the capacity rise is most likely due to the partial adsorption-desorption of Py-C4-MPC depending on the electrode potential. The permeation of electrolyte solution in between the electrode surface and organic layer covering the particle was allowed, giving rise to the increase of capacity and voltammetric current. The potential region exhibiting the capacity rise actually well corresponds to the potential at which adsorption-desorption of pyridine [3] and a periphery-modified PA-MAM dendrimer with 4-pyridyl groups [8] take place. Since the rise did not reach the capacity value of a bare Au(111) surface, the desorption is 'partial' at these conditions. On a speculative basis, the potential driven changes of the state of the Py-C4-MPC film were pictured in Fig. 3.

Note that one may suspect the stability of modifiers under negative potential scan whether the thiols were partly desorbed into solution, transferred to Au(111) surface from the particle surface or not. Usually, reductive desorption of a thiol adsorption layer takes place in strong alkaline aqueous solution at more negative potentials, and the desorption brings about irreversible change of CV curve [9]. In the present experiments, no change of CV curve upon multiple potential scans to $-0.8$ V was observed, indicating that the reductive desorption did not take place. Experiments are currently underway in our laboratory to confirm the absence of the flip-flop inversion of some thiol molecules in the gap between Au particle and Au(111) surface.

When the spread film of Py-C4-MPC at the G/S interface takes the ESP, the area occupied by one particle is approximately $12.5$ nm$^2$/particle, nearly twice of the area for a 2D close packing. Unless the 2D density changes largely upon touching, the relative amounts of the particles on the Au(111) electrode are approximately 17%, 33%, and 50% of the 2D close packing, respectively, for Figs. 2(a), (b), and (c). In the case of Fig. 2(d), such estimation is not applicable, since the spread amount exceeded that necessary to establish the ESP. The spread amount dependence may point to the importance of inter-particle interaction. When the relative amount is over ca. 30%, adsorption orientation of 4-pyridyl group on the Au(111) surface is insensitive to the potential, on one hand. This may connote the absence of isolated particles free from interparticule interaction. On the other hand, enhanced adsorption-desorption at increasing spread amounts points to the emergence of cooperativity in the movement to displace the particles from the electrode surface.

It may be worth noting that, during the movements of the particles, aggregation of the particles did not take place, since otherwise the ER spectrum should have shown a drastic plasmon peak wavelength shift as well as spectral curve change at longer wavelengths. Such an ER spectral change was in fact not observed.

In comparison to our previous work [2], at least one of the three factors, namely smaller core, shorter chain lengths of modifier molecules, and greater fractional content of the adsorption active groups, effects the achievement of partial desorption of the particles. Interestingly, the modified particle used in our previous work [2] still ex-
hibits reorientation response of the 4-pyridyl group even when the spread amount is greater than that necessary to establish ESP, in contrast to the results of the present work. Evaluation of the extent of the contribution of these three factors to the dynamics remains as the future work.

IV. CONCLUSIONS

In conclusion, we observed in this preliminary investigation that both surface group orientation change and partial adsorption-desorption are achieved. These processes were found to be chemically reversible. The behavior of the particles were stable and long-lived. Taken the results of our previous study [2] together, we can point out the availability to control the movements through the design of the surface-modified metal nanoparticle. However, the direct observation of the movements of the particles by the use of nano-level techniques and clarification of the driving force and mechanism remain to be fully investigated. Design of surface-modified Au nanoparticles exhibiting sharper and greater amplitude movement as well as spectroelectrochemical studies are currently underway in our laboratory.

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[1] D. Bizzotto, V. Zamlynny, I. Burgess, C.A. Jeffrey, H.-Q. Li, J. Rubinstein, R.A. Merril, J. Lipkowski, Z. Galus, A. Nelson, B. Pettinger, in: A. Wieckowski (Ed.), Interfacial Electrochemistry: Theory, Experiment, and Applications, (Marcel Dekker, New York, 1999), p. 405.
[2] T. Sagara, F. Kai, N. Kato, Electrochem. Comm. 5, 853 (2003).
[3] T. Sagara, K. Uematsu, K. Nagata, J. Electroanal. Chem. 550-551, 219 (2003), and references therein.
[4] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, J. Chem. Soc., Chem. Comm. 1994, 801 (1994).
[5] T. Sagara, N. Kato, N. Nakashima, J. Phys. Chem. B 106, 1205 (2002).
[6] A. Toyota, N. Nakashima, T. Sagara, J. Electroanal. Chem. 565, 335 (2004).
[7] For optics for ER measurements and ER spectra, see supporting information. Electroreflectance measurements were conducted at normal incidence of the monochromatic light to the Au(111) electrode surface using ac potential modulation of 14 Hz and 5 mV_{rms}-ac amplitude at the same conditions as Fig. 2(d).
[8] T. Sagara, K. Nagata, H. Tsuruta, N. Nakashima, Chem. Comm. 2002, 2116 (2002).
[9] C. A. Widrig, C. Chung, M. D. Porter, J. Electroanal. Chem. 310, 335 (1991).