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Electrocatalytic activity of three-dimensional monolayer of 3-mercaptopropionic acid assembled on gold nanoparticle arrays

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Abstract

3-Mercaptopropionic acid (MPA) was assembled on gold nanoparticle arrays to form three-dimensional monolayer. The electrochemical behavior of small biomolecules such as NADH, ascorbic acid (AA), uric acid (UA) and dopamine (DA) on the as-prepared three-dimensional monolayer was studied. The cyclic voltammetric results indicated that three-dimensional MPA monolayer promoted the electron transfer between NADH and electrode, which was similar to two-dimensional MPA monolayer assembled on planar gold electrode. However, to the electrooxidation of AA, although two-dimensional MPA monolayer exhibited a blocking effect, three-dimensional MPA monolayer showed an obvious promotion. The catalytic activity of three-dimensional MPA monolayer towards UA and DA was also observed, which was attributed to its three-dimensional structure that might effectively prevent the poison of the electrode surface by the oxidation products.

Keywords: 3-Mercaptopropionic acid; Three-dimensional monolayer; Gold nanoparticle arrays; Electrocatalytic activity; Biomolecules

1. Introduction

Self-assembled monolayers (SAMs) based on the strong chemisorption between organic molecules and substrates have been extensively studied because they offer an effective and flexible approach controlling the properties of interfaces [1]. The simple route of SAMs to functionalize electrode surfaces makes the technique of SAMs particularly useful in developing chemically modified electrodes and electrochemical biosensors. By employing the well-defined structures of SAMs as well as their functional terminal groups, the feature of SAMs as a tunable platform for biosensor applications [2] and the advantages of SAMs for enzyme immobilization [3] have been demonstrated. The SAMs-modified planar gold electrodes showing high selectivity and sensitivity, fast response or anti-fouling properties for voltammetric determination of small biomolecules such as NADH, ascorbic acid (AA), dopamine (DA) and other neurotransmitters have been described [4–7].

With the development of nanotechnology, SAMs have been utilized in nanomaterial-modified electrode, which extends the characteristics of monolayer from two-dimensional planar to three-dimensional cluster surfaces. The most important application of SAMs in this field is to synthesize metal nanoparticles, in which SAMs are utilized as stabilizer for nanoparticles, namely monolayer protected clusters (MPCs) [8]. Another application of SAMs is to connect nanoparticles with substrates, in which SAMs act as molecular linkers between electrode substrates and metal nanoparticles [9]. Compared with SAMs on planar metal surfaces, monolayers assembled on nanoclusters have different characteristics although there are significant similarities between two-dimensional and three-dimensional monolayer systems [10]. The unique feature of three-dimensional monolayers offers promising applications in nanomaterial-based electrochemistry. When

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three-dimensional monolayers are functionalized with electroactive molecules such as anthraquinone [11] and polyanthraquinone [12], monolayer protected gold clusters have been shown as useful electrochemical catalysts. On electrode surfaces, electroactive three-dimensional monolayer transferred from 4-hydroxythiophenol (4-HTP) immobilized on gold nanoclusters exhibits excellent catalytic properties towards the electrooxidation of 3,4-dihydroxyphenylalanine (DOPA) and AA, which is more efficient than when the same two-dimensional monolayer is assembled on the planar gold substrate [13,14].

On the other hand, many monolayers are electrochemically inactive. Thus, studying the three-dimensional monolayers assembled on nanoparticles without electroactive groups is more practical in developing nanoparticle-based electrochemical catalysts and biosensors. It has been demonstrated that alkanedithiolate-capped gold nanoparticles have shown electrocatalytic activity towards the oxidation of CO [15]. In the present work, we prepared three-dimensional MPA monolayer assembled on gold nanoparticle arrays for investigating the electrochemical behavior of small biomolecules such as NADH, AA, uric acid (UA) and DA. The results indicated that, although MPA was electroinactive, the three-dimensional MPA monolayer always showed obvious electrocatalytic activity to promote the electron transfer between these biomolecules and electrode, which was different from the two-dimensional MPA monolayer assembled on planar gold electrode.

2. Experimental

2.1. Reagents

Cetyltrimethylammonium bromide (CTAB), 3-mercaptopropionic acid (MPA) and $HAuCl_4 \cdot 3H_2O$ were purchased from Aldrich. Dopamine (DA) and NADH were obtained from Sigma. Trisodium citrate, ascorbic acid (AA), uric acid (UA), $NaBH_4$, KCl and 0.1 M NaOH solution were obtained from Wako Pure Chemicals Ltd. Ultrapure fresh water obtained from a water purification system (Millipore WR600A, Yamato Co., Japan) to a specific resistivity >18 MΩ cm was used in all runs.

2.2. Construction of gold nanoparticle arrays

The gold nanoparticle arrays were fabricated upon ITO substrates, based on a modified seed mediated growth approach [16]. Prior to construction, ITO substrates (CBC Ings Optics Ltd.) were ultrasonically cleaned with acetone, ethanol and distilled water for 15 min followed by drying with a stream of high purity nitrogen. Then, the ITO substrates were soaked in an Au precursor complex solution composed of 0.5 ml of 0.01 M $HAuCl_4$, 0.5 ml of 0.01 M trisodium citrate and 18 ml H_2O. After stabilizing for 15 min, 0.5 ml of fresh ice-cold 0.1 M $NaBH_4$ aqueous solution was added into the Au precursor complex solution. The substrates were taken out of the Au precursor complex solution and thoroughly rinsed with distilled water and dried with nitrogen and then immersed in a glass tube containing a gold growth solution. The growth solution was prepared by mixing 90 ml of 0.1 M CTAB, 2.5 ml of 0.01 M $HAuCl_4$, 0.5 ml of 0.1 M AA and 0.5 ml of 0.1 M NaOH solutions. After 24-h immersion in the growth solution, the substrates were removed from the tube and flushed several times with distilled water and dried with nitrogen.

2.3. Self-assembly of MPA on electrode surfaces

A polycrystalline gold electrode (BAS Inc.) surface was polished with 2000 mesh and 3000 mesh emery papers and 0.05 μm alumina slurry. The polished electrode was then electrochemically cleaned by cycling the electrode potential between 0 and 1.5 V in 0.5 M H_2SO_4 until a stable voltammogram was obtained. After thoroughly rinsed several times with distilled water and ethanol and dried with nitrogen, the electrode was immersed in an ethanol of 1% (V/V) MPA solution for 2 h. Thus, a gold electrode modified with two-dimensional MPA monolayer was prepared. A three-dimensional MPA monolayer was prepared by soaking gold nanoparticle arrays in the MPA ethanol solution instead of the polycrystalline gold electrode.

2.4. Apparatus and procedures

A field emission scanning electron microscopy (FE-SEM) instrument (JSM-7400F, JEOL, Japan) was employed to observe SEM images. Electrochemical experiments were carried out on an EG&G M263A potentiostat/galvanostat (Princeton Applied Research, USA) with a three-electrode cell. A platinum wire was employed as the counter electrode. All potentials were referred to an Ag|AgCl (saturated KCl) electrode. Gold nanoparticle arrays constructed on an ITO electrode surface (exposed geometry area of ca. 0.0314 cm^2) and a polycrystalline gold electrode (1.6-mm diameter) were used as the working electrodes. All measurements were performed in 0.1 M KCl at room temperature.

3. Results and discussion

Fig. 1 shows the morphology of gold nanoparticle arrays fabricated on ITO substrate through the modified seed mediated growth approach. It is clearly seen that many gold nanoparticles in the diameter of ca. 22 nm are deposited on the ITO surface with this two-step wet-chemical method.

To characterize the electrochemical features of the as-prepared gold nanoparticle arrays, the electrooxidation behavior of some biomolecules on the bare ITO and gold nanoparticle-modified ITO electrodes was studied. Fig. 2A compares the CVs of NADH recorded on an ITO electrode with or without the deposition of gold nanoparticles. The oxidation peak potential (E_{pa}) for NADH