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In situ detection and removal of metal ion by porous gold electrode

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ABSTRACT

A sensing electrode for the detection of heavy metal ions in aqueous solution selectively measured the concentrations of target materials on its functionalized surface, which has affinity to target metal ions. Target ions were adsorbed simultaneously on the functionalized electrode during the sensing process. Therefore, to understand this, experiments on the amperometric response and isotherms with an initial concentration of Hg^{2+} were tested. Detection current was dependent on the concentration of Hg^{2+}, and the equilibrium concentration of Hg^{2+} adsorbed to the electrode showed a Langmuirian shape. Correlation between the detection current and removal capacity for Hg^{2+} revealed that it is possible to estimate the adsorbed concentration on the electrode during the sensing step. Although the macroporous gold electrode prepared herein showed relatively low adsorption performance compared to conventional adsorbents, when we prepare nanoporous gold electrodes with a uniform nanopore structure and large surface area, in situ detection and simultaneously removal of metal ions by nanoporous gold electrode will be possible.

1. Introduction

Commonly used adsorbents for detection of heavy metal ions in aqueous solutions have micro- to macro-porous structures with larger surface areas, but conventional adsorbents such as charcoal and clay show inherent disadvantages; irregular pore structure, low selectivity, and low uptake capacity for metal ions [1]. Therefore, some promising ceramics with nanoporous structures (mesoporous silica and alumina) were developed via templating method [2,3], and their uptake capacities for heavy metal ions were found to be several times larger than those of conventional adsorbents.

The uptake capacity of these adsorbents is calculated based on the difference between the initial and final concentration of target ions, which is measured by ICP spectroscopy (post-analysis) or sensing electrode (in situ analysis). Colorimetric sensor (e.g. pregnancy tester) or electrode-system (e.g. pAg meter) has been suggested for real-time and in situ analysis of target materials. However, a colorimetric sensor can be used only once for qualitative (i.e. presence of target ions and range of concentration) not quantitative investigation [4,5]. Therefore, an electrochemical electrode system is generally used in field applications.

The adsorption procedure is generally separated from the sensing procedure. To detect and simultaneously remove target materials in liquid phase, it is helpful that the detecting electrodes have porous structure (large surface area), functional groups (selective detection), and electrical conductivity (electrochemical detection). Therefore, herein, we proposed an in situ detective and adsorptive electrode composed of porous gold (PAu) based on previous reports [6,7]. Porous metal is generally fabricated by selective dealloying or templating method. In the dealloying method, white-gold (Au–Ag) alloy is employed, and Ag elements are selectively removed by chemical etching [8,9]. In the templating method, multi-processing steps are involved. The metal is deposited into the artificial templates with different sizes, followed by removal of the templates to form the porous structure with an adjustable pore size [10]. In our previous report, porous gold electrode was shown to be very effective and promising for the development of high performance electrochemical and biological sensors. PAu/ITO electrode functionalized with thiol groups (HDT, 1,6-hexanedithiol) have been successfully applied to the detection of mercury ion at very low concentration and display high linearity from 7 to 150 ppb [6]. In addition, Pt nanoparticle-deposited PAu-pellet electrode also exhibits an extremely low working potential, a detection limit of 50 μM of H_2O_2, and a fast response time within 10–20 s [11].

As a proof-of-concept test, the submicron-sized porous gold electrode prepared by the templating method was used to detect and simultaneously remove mercury ion from aqueous solutions. For electrochemical sensing, PAu/ITO substrate was modified with functional groups and then evaluated by measuring the current according to concentration of mercury ion. When we used the correlation curve for uptake capacity (mg/g) by HDT/PAu/ITO electrode with detection current, equilibrium uptake capacity was estimated. The results of these experiments will be helpful to

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understanding how much of the target ion was adsorbed simultaneously on the electrode during the sensing process. Therefore, these experiments for detecting the removal capacities and amperometric responses were carried out at several different concentrations of mercury ion.

2. Experimental

2.1. Fabrication of HDT/PAu/ITO electrode

Preparation of free-standing porous gold was carried out by following the templating method using aluminum alkoxide, which acts as both a pore generator and reinforcement agent for the reverse network of porous gold [6]. Scheme 1 shows a simplified version of the preparation procedure for HDT/PAu/ITO electrode. Dried powder before calcinations was prepared by following a previously reported method. After calcinations, calcined PAu powder including alumina was obtained. ITO glass was immersed in the bottom of a beaker containing the calcined materials during the etching process, which was carried out to remove the alumina network. A mixture of 11.8 M H_3PO_4 and 0.6 M HNO_3 was used as an etchant for alumina. After etching, thin film of porous gold was deposited on the ITO glass, and then additional heating was conducted at 150 °C for 20 min to remove defects in the PAu thin film. PAu/ITO electrode was dipped into 1 mM HDT for 24 h, followed by washing with ethanol and DI water. Surface morphology of PAu was analyzed by scanning electron microscopy (SNE-3000M, SEC).

2.2. Measurement of amperometric response

Amperometric (current–time) response was recorded with a potentiostat (WEIS-500, WonA Tech) at −50 mV after successive additions of 5 μM Hg^{2+} solution with continuous stirring in 0.5 M H_2SO_4 solution. Pt substrate and Ag/AgCl were used as counter and reference electrodes, respectively. Then, the current response according to concentration of Hg^{2+} was measured corresponding to collapsed time. The used electrode was dipped into 1 M NaOH solution to remove the attached mercury ions on the substrate.

2.3. Adsorption test

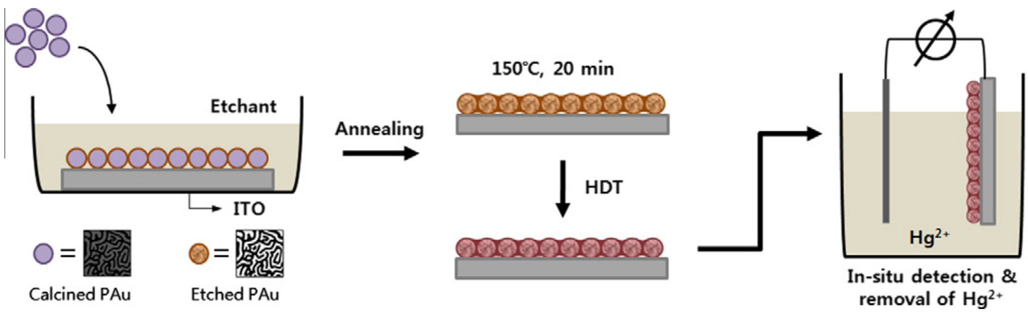
The equilibrium concentrations for Hg^{2+} by the HDT/PAu/ITO substrate were controlled at 1–100 mg/L. Approximately 0.03 ± 0.005 g of PAu loaded on ITO was added to 20 mL of a solution prepared with a predetermined ion concentration using deionized water, followed by shaking at room temperature for 1 h. The adsorption capacities were calculated based on the difference between the initial and the final concentrations. The mercury concentration was analyzed with inductively coupled plasma mass spectrometer (ICP-820 MS, Varian). Two isotherms, i.e. Freundlich and Langmuir, were examined to establish the most appropriate correlation for the equilibrium curves. The maximum uptake capacity was calculated by the Langmuir equation.

3. Results and discussion

As shown in the SEM image in Fig. 1, porous gold (Fig. 1a) showed a coral-like structure, which is helpful to transport target materials into the inner space. On the other hand, electrolytic-deposited gold (EAu) on ITO glass (Fig. 1b) showed rough surface morphology with no pore structure. PAu showed a window pore size of 200–400 nm and a framework thickness of 100–300 nm. PAu has many window pores formed due to the overlapping of the branched gold networks, which is the foundation of the interconnected pore system. Formation of submicron-sized window pores was induced by the removal of the alumina framework during the etching step. In XRD analysis, etched PAu showed the same characteristics peaks at (1 1 1), (2 0 0), and (2 2 0) as compared to bulk gold. XRD pattern of etched PAu was consistent with previously reported data [6]. Primary particle size of etched PAu was easily calculated to be ca. 40 nm by the Scherrer equation. Therefore, the framework of PAu was prepared by aggregation of primary gold particles during successive calcination, etching, and sintering processes.

As-made PAu/ITO substrate was modified with thiol groups to increase affinity for mercury ion. In our previous test, HDD/PAu/ITO was used at low concentration (ppb level) [6]. Herein, to determine the maximum current per unit area, excess concentration of mercury ion was successively added in the form of 5 μM Hg^{2+} solution to the working vessel. As shown in the inset of Fig. 2, amperometric responses of the as-made electrode showed a typical stair-form of current change. As comparison with HDT/PAu/ITO, electrolytic-deposited gold electrode (HDT/EAu/ITO) showed very unstable amperometric responses (not shown here). The current response was linearly dependant on the mercury concentration in the range from 0 to 30 μM, but it approached maximum current density (80 μA per 2 cm^2 of electrode). Namely, for the full concentration range of mercury ion, the curve of the amperometric response was similar to that of Langmuir adsorption, which was due to adsorption of mercury ion on the thiol groups with oxo-bridge bonding (S–Hg–O–Hg–S) [2,12]. Since ionic conductivity correlated with $C^{1/2}$ by the Kohlrausch equation and current density was linearly dependent on ionic conductivity [13], the Langmuirian current response was obtained in the full range of concentrations.

Since the current response according to concentration originated from adsorption of Hg^{2+} on the HDT/PAu/ITO substrate, the maximum uptake capacity of the substrate should be analyzed by the adsorption isotherm test. To optimize the design of the adsorption system for the removal of mercury ion, it is important to establish appropriate correlation between the equilibrium



Scheme 1. Schematic diagram of the preparation of porous gold electrode functionalized with thiol groups for in-detection and removal of mercury ion from aqueous solution.