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A strategy for fabricating nanoporous gold films through chemical dealloying of electrochemically deposited Au-Sn alloys

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Abstract
We report a novel strategy for the fabrication of nanoporous gold (NPG) films. The fabrication process involves the electrodeposition of a gold–tin alloy, followed by subsequent chemical dealloying of tin. Scanning electron microscopy (SEM) images show a bicontinuous nanoporous structure formed on the substrates after chemical dealloying. Energy dispersive x-ray (EDX) analysis indicates that there are no impurities in the Au–Sn alloy film with an average composition of 58 at. % Au and 42 at. % Sn. After dealloying, only gold remains in the NPG film indicating the effectiveness of this technique. X-ray diffraction (XRD) results reveal that the as-prepared Au–Sn alloy film is composed of two phases (Au₅Sn and AuSn), while the NPG film is composed of a single phase (Au). We demonstrate that this approach enables the fabrication of NPG films, either freestanding or supported on various conductive substrates such as copper foil, stainless steel sheet and nickel foam. The resulting NPG electrode exhibits enhanced electrocatalytic activity toward both H₂O₂ reduction and methanol oxidation compared to the polished Au disc electrode. Our strategy provides a general method to fabricate high quality NPG films on conductive substrates, which will broaden the application potential of NPG or NPG-based materials in various fields such as catalysis, optics and sensor technology.

Keywords: nanoporous gold, electrodeposition, chemical dealloying

(Some figures may appear in colour only in the online journal)

1. Introduction

In the past few decades, considerable attention has been devoted to the production of various gold nanostructures owing to their unique physicochemical properties, such as nanoparticles [1], nanoshells [2], nanowires [3], nanorods [4] and nanocages [5]. Realizing their potential versatility for real-world applications requires the assembly of nanoscopic elements into 3D macroscopic structures. There has however been limited success in obtaining macroscopic arrays of gold nanostructures [6–9]. Recently, nanoporous gold (NPG) has attracted increasing interest because it can exhibit exemplary catalytic and optical properties resulting from its monolithic bicontinuous porous structure [10, 11]. NPG is an attractive...
candidate as a next generation material for a wide range of applications such as heterogeneous catalysis [12, 13] electrochemical biosensing [14, 15] optical sensing, [16, 17] energy storage [18, 19] and drug delivery [20]. An effective method for fabricating NPG is by dealloying, in which nanoporosity is formed through the chemical or electrochemical dissolution of less noble metals present in gold alloys [21]. Typically, NPG films are fabricated by chemically dealloying commercially available Au–Ag alloy leaves [10, 14, 16–19, 22], leaving behind a freestanding NPG film. However, these ultra-thin films are difficult to handle, are readily available in only standard compositions (for example, 9 carat: 25 at. % Au, or 12 carat: 35 at. % Au), and require extremely careful transfer methods to be transferred onto various substrates for practical applications. All of these factors culminate in substantial material integration challenges to be realized for a wide array of potential applications, and alternative synthesis methods for NPG films are highly desirable for overcoming these issues. There have been some studies that report the synthesis of NPG by alternative fabrication routes such as sputtering [23], electron beam evaporation [24] and electrodeposition [25]. While methods such as sputtering and electron beam evaporation require complex and costly high vacuum apparatuses, electrodeposition represents the most attractive technique for depositing metal alloy films owing to the low temperature and ambient operation, low equipment costs and easy scalability. Synthesis methods based on electrodeposition are expected to hold promise in extending the application potential of NPG in various fields.

In this paper, we report a unique approach to fabricate NPG films. The process allows for the preparation of NPG films that are either: (i) free-standing, (ii) supported on various conductive substrates, or (iii) patterned on flat substrates. This simple but highly effective technique involves electrochemical co-deposition of Au and Sn to form Au–Sn alloy films which are then subjected to chemical dealloying. Au–Sn alloy is one of the most promising lead-free solders [26]. The Au–Sn solder possesses excellent mechanical and thermal properties making it well suited to optoelectronic packaging [27]. To date, there are few reports on the synthesis of NPG based on Au–Sn alloy [28]. To the best of our knowledge, this is the first report on the formation of NPG films from electrodeposited Au–Sn alloy films. Our strategy provides a general, simplistic and cost-effective method to fabricate high quality NPG films on conductive substrates, which will broaden the potential applications of NPG or NPG-based materials in various fields.

2. Experimental section

2.1. Materials and substrate preparation

Au–Sn alloy plating solution was obtained from Huizhou Leadao Electronic Material Co., Ltd (Huizhou, China, website: www.leadao.cn). HCl (36%), H2O2 (30%), NaOH, NaCl, Na2HPO4·12H2O, NaH2PO4·2H2O, CH3OH, KOH and HNO3 (70%) were purchased from Xilong Chemical Co., Ltd (Guangzhou, China). All the reagents are of analytical grade and used as received without further purification. Ultrapure water with a resistance of 18.2 MΩ·cm from a Millipore Milli-Q purification system was used throughout this work. Copper foil and stainless steel sheets were cleaned ultrasonically successively in acetone, ethanol and distilled water for 15 min each before use. Nickel foam was carefully cleaned with a 5 M hydrochloric acid solution in an ultrasonic bath for 30 min in order to remove the nickel oxide layer potentially existing on the surface, and then thoroughly rinsed with distilled water. The pre-patterned stainless steel substrate was prepared by a standard photolithography technique. In brief, photoresist (Microposit S-1818, Shipley, Marlborough, MA) was spin-cast at 4000 rpm for 50 s onto the stainless steel sheet surface and then baked for 1 min at 95 °C. Utilizing a contact mask aligner (Q2000, Quintel Corp. San Jose, CA), the photoresist was exposed to UV (345 nm) light for 6 s and was subsequently developed for 40 s (MF-CD-26, Shipley, MA).

2.2. Electrodeposition of Au–Sn alloy films

The electrodeposition was performed in a two-electrode electrochemical cell using the freshly pretreated substrates as the working electrodes and a platinum sheet as the counter electrode. A KR-3001 30 V/1 A programmable DC source-meter (Kingrav Electronic Technology Co., Ltd, Shenzhen, China) was used as a power supply. The deposition was performed at a cathodic current density of 5 mA cm−2 for 5 min in an aqueous electrolyte containing 500 mL L−1 Au–Sn alloy plating solution. After deposition, the substrates were thoroughly rinsed with distilled water, and then dried in air.

2.3. Fabrication of NPG films

For Au-Sn alloy films deposited on stainless steel sheets, the substrates were immersed into 35 wt.% HNO3 at room temperature for 3 days. For Au-Sn alloy films deposited on nickel foam, the substrates were immersed in 5 M NaOH + 1 M H2O2 solution at room temperature for 3 days. For Au-Sn alloy films deposited on copper foil, the samples were treated using the above-described two procedures, respectively. After free corrosion, the substrates were thoroughly rinsed with distilled water and dried in air. In the case of the copper substrate dealloyed in HNO3 solution, the substrate was dissolved in the solution, leading to the formation of a freestanding NPG film floating on the solution surface, which was carefully picked up by a glass slide.

2.4. Characterization

The microstructure and chemical composition of the Au–Sn alloy films and NPG films were investigated using a field-emission scanning electron microscope (SEM, JEOL, JSM-6700F, 15 keV) equipped with an energy-dispersive x-ray spectrometer (EDX). X-ray diffraction (XRD) measurements were carried out on a Rigaku D/max-2200/PC diffractometer using Cu Kα radiation. All electrochemical characterizations
were carried out using a Gamry REF 600 potentiostat and a conventional three-electrode electrochemical cell, with Pt plate as the auxiliary electrode, Ag/AgCl electrode or saturated calomel electrode (SCE) as the reference electrodes, NPG or Au disc electrodes as the working electrodes, respectively. The electrocatalytic activity of NPG electrodes toward H₂O₂ reduction was evaluated in 0.1 M phosphate buffer (pH 7.2) and methanol oxidation in 0.1 M KOH solution.

3. Results and discussion

The fabrication procedure of NPG films through electrodeposition and chemical dealloying is schematically illustrated in figure 1. First, Au–Sn alloy films were electrodeposited onto conductive substrates (e.g. copper foil, stainless steel sheet, Ni foam, etc). Second, the as-deposited Au–Sn alloy thin films were subjected to a chemically dealloying process to selectively remove the Sn component, which then resulted in formation of supported NPG film under the condition that the substrate can survive after the dealloying process, or freestanding NPG film in the case when the substrate cannot withstand the etching. Such an electrodeposition–dealloying procedure for fabricating NPG film is simple to conduct, and can be used to obtain freestanding NPG films as well as NPG films supported on a wide variety of conductive substrates.

Figure 2(a) shows a representative optical image of the Au–Sn alloy film galvanostatically deposited on a copper foil substrate. It is clearly shown that the deposited area uniformly turned to a silvery white color after alloy deposition. The as-prepared samples were then dealloyed in two different solutions. In the first case, a square of side length 1.5 cm was cut from the deposited area and immersed into a 35 wt. % nitric acid bath. After a long enough time period (e.g. 3 days) of free corrosion, both the tin component and the copper foil substrate were etched away, thereby leaving a freestanding film floating on the water surface (figure 2(b)). In comparison to the Au–Sn alloy film, the freestanding thin film is gold colored, highlighting the fact that the non-noble elements have been leached out. This thin film is furthermore mechanically robust enough to be picked up by various substrates such as silicon and glass. In the second case, the Au–Sn alloy-deposited copper foil was immersed into 5 M NaOH + 1 M H₂O₂ solution. After dealloying for 3 days, the color of the deposited film changed from silver white to gold yellow (figure 2(c)), suggesting the formation of gold-based materials.

Further characterization of the films was conducted using scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) spectroscopy. Figure 3(a) shows SEM images of the Au–Sn alloy film deposited on a copper foil substrate. It is revealed that the alloy film consists of numerous diamond-like grains with an average size of ca. 300 nm densely packed on the substrate surface. Figure 3(b) presents a typical EDX spectrum of the Au–Sn alloy film with the determined composition shown in the inset. It clearly shows that the as-deposited film contains only Au and Sn (the Cu signal comes from the copper foil substrate). The atom ratio of Sn to Au in the film is 42:58, as derived from the EDX analysis. These results verify that gold and tin were successfully co-deposited on the copper substrate, with gold present in a higher atomic concentration in the alloy film. Figures 4(a) and (b) show low- and high-magnification SEM images of the Au–Sn alloy films after chemical dealloying in 35 wt. % nitric acid solution. It is shown that a very uniform porous structure, with an average ligament diameter of about 150 nm was formed as a result of the dealloying process. The cross-sectional SEM image (figure 4(c)) reveals that the continuous porous network was formed across the entire thickness of the film. Representative EDX spectroscopy (figure 4(d)) of the NPG film reveals that the porous structure consists of almost pure gold and the tin content is below the EDX detection limit (~0.5 wt. %). This reveals that tin can be nearly completely etched away from the Au–Sn alloy in nitric acid, leading to the formation of an open bicontinuous nanoporous structure comprised entirely of gold. It is worth mentioning that, in the majority of previous studies [16, 29–31], there are always some residual less-noble metal component (e.g. Ag) trapped in the NPG films after the dealloying process. The possible reason for this discrepancy in results is that the difference of the standard electrode potentials between Au and Sn (1.83 V) is much greater than that between Au and Ag (0.9 V).

X-ray diffraction (XRD) measurements were conducted to further examine the crystal phase of the Au–Sn alloy films before and after chemical dealloying. Samples prepared with longer electrodeposition time (30 min) were employed in order to overcome the issue of weak diffusive patterns obtained when using an electrodeposition time of only 5 min.
Figure 2. Representative optical images of the Au–Sn alloy film deposited on a copper foil substrate (a) before and (b), (c) after chemical dealloying in (b) 35 wt. % HNO₃ solution for 3 days or in (c) 5 M NaOH + 1 M H₂O₂ solution for 3 days.

Figure 3. (a) SEM image of Au–Sn alloy film deposited on copper foil substrate before chemical dealloying and (inset) high-magnification image with a scale bar of 300 nm. (b) EDX spectrum of the Au–Sn alloy film.

Figure 4. (a) Low-magnification SEM, (b) high-magnification SEM and (c) cross-sectional SEM images of NPG film after chemical dealloying. (d) EDX spectrum of the NPG film.
Figure 5 shows XRD patterns of the Au–Sn alloy film (black) before and after chemical dealloying. The XRD results reveal that the as-prepared Au–Sn alloy film is composed of two phases: Au5Sn (PDF No. 31-0568) and AuSn (PDF no. 08-0463). The peaks located at 2θ values of 35.2°, 37.8°, 39.9°, 52.4°, 62.9°, 69.7°, 74.1° and 77.2° can be indexed to the diffractions from (110), (006), (113), (116), (300), (119), (220) and (223) crystal planes of Rhombohedral Au5Sn, while the peaks located at 2θ values of 41.7°, 48.7°, 51.5°, 59.5° and 75.5° can be indexed to the diffractions from (110), (200), (201), (202), and (223) crystal planes of hexagonal AuSn. The diffraction pattern of the NPG film matches well with that of Au (PDF no. 04-0784). Such NPG films are expected to have a large electrocatalytic activity owing to the presence of highly porous and rough nanostructures. We take NPG films supported on stainless steel substrate as an example with which to evaluate the electrochemical properties of the NPG electrode. The ECSA of NPG electrode was determined in comparison with Au disc electrode. The cyclic voltammogram (CV) curves of these electrodes were recorded in N2-saturated 0.5 M H2SO4 and are presented in figure 7. These voltammograms display the current peaks associated with the formation of surface gold oxide during the anodic scan and the subsequent gold oxide reduction during the cathodic scan. The ECSA of these electrodes was calculated by the charge integration of the gold oxide reduction peak by assuming a value of 390 μC cm−2 as the conversion factor [32]. The ECSA of the NPG electrode was 35.8 cm2 in comparison to 6.7 cm2 of the Au disc electrode. The increased ECSA value of NPG electrode can be attributed to its special porous structure with more active sites exposed to the solution. The electrocatalytic performance of the NPG electrode was investigated through the electrochemical reduction of H2O2 and oxidation of methanol. Figure 8(a) displays CV curves of the H2O2 reduction activities of the NPG and Au disc electrodes in a 0.1 M phosphate buffer (pH 7.2) with 5 mM H2O2 solution. The onset potential of H2O2 reduction appears at 0 V at the NPG electrode while an onset potential of ~0.1 V is obtained at the Au disc electrode. The lower onset potential at the NPG electrode reveals its higher electrocatalytic activity, which is consistent with a previous report [33]. Figure 8(b) shows the CV curves of the methanol oxidation activities of the NPG and Au disc electrodes in a 0.1 M KOH with 1.5 M methanol solution. The catalytic activity of the NPG electrode is superior to that of the Au disc electrode, which agrees well with a previous study [34]. The peak current density of methanol oxidation on the NPG electrode is 1.81 mA cm−2, which is about 3 times higher than that on the Au disc electrode (0.65 mA cm−2). Obviously, the increase in peak current density of methanol oxidation at the NPG electrode was not as much as that in ECSA. Similar results were obtained in previous studies [34–36]. This phenomenon may be attributed to the fast kinetics of the reaction species which fully reacts at the outer porous layer before these species can diffuse into the inner porous surface. The above results confirm that the NPG nanostructure exhibits a higher catalytic activity which may
be attributed to the presence of more active sites associated with its bicontinuous porous structure.

4. Conclusions

In conclusion, we have reported the fabrication of high purity NPG structures by chemical dealloying of electrochemically deposited Au–Sn alloy films. This novel synthetic strategy is new, simplistic, rapid and readily reproducible. Moreover, this technique is efficient for the preparation of not only freestanding NPG films, but also NPG structures supported on various conductive substrates such as non-patterned or pre-patterned stainless steel sheet, copper foil and nickel foam. The resulting NPG electrodes displayed enhanced electrocatalytic activity toward the H2O2 reduction and methanol oxidation than the Au disc electrode. Further investigation may pave the way to wider applications of these NPG nanostructures in biosensing, surface-enhanced Raman scattering (SERS) and energy storage.
Figure 8. The electrocatalytic activity of the NPG electrode (red) and Au disc electrode (black): (a) H$_2$O$_2$ reduction in 0.1 M phosphate buffer (pH 7.2) and (b) methanol oxidation in 0.1 M KOH solution at a scan rate of 50 mV s$^{-1}$. Current densities are normalized to the geometric electrode area.

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