Gold leaf: From gilding to the fabrication of disposable, wearable and low-cost electrodes

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ABSTRACT

Gold is among the most used materials in electrocatalysis. Despite this, this noble metal is still too expensive to be used in the fabrication of low cost and disposable devices. In the present work, gold-leaf sheets, usually employed in decorative crafts and wedding candies, is introduced as an inexpensive source of gold. Planar-disc and nanoband gold electrodes were simply and easily manufactured by combining gold leaf and polyimide tape. The planar disc electrode exhibited electrochemical behavior similar to that of a commercial gold electrode in $0.2 \, mol \, L^{-1} \, H_2SO_4$; cyclic voltammetry of a $1 \, mmol \, L^{-1}$ solution of potassium ferricyanide ($K_3[Fe(CN)_6]$) in $0.2 \, mol \, L^{-1} \, KNO_3$, using this novel electrode, displayed an 80 mV difference between the oxidation and reduction peak potentials. The electrode also delivers promising prospects for the development of wearable devices. When submitted to severe mechanical deformation, this electrode exhibited neither loss of electrical contact nor significant variation in electrode response, even after fifteen bending and/or folding cycles. The thickness of the gold-leaf sheet facilitates the production of nanoband electrodes with behavior similar to that of ultramicroelectrodes. The electrode surface is easily renewed by cutting a thin slice off its end with a razor blade; this process led to limiting currents that were reproducible, presenting a relative standard deviation (RSD) of 3.8% (n = 5).

1. Introduction

Although many electrocatalysts have been developed, mainly over the past few decades, including those composed of nanoparticles [1,2], metallic films and metal alloys [3], and non-noble metals [4,5], among others [6,7], polycrystalline (and/or single crystal) platinum and gold electrodes are still widely used in electrochemical and electrocatalytic applications [8–11]. These noble metals are inert to many classes of chemical compound, are easy to machine, and can be obtained in high purity.

In addition to its applications in the determination of inorganic ions by stripping analysis [12,13] and the electrooxidation of small organic molecules [8,14,15], gold electrodes are particularly attractive due to their interactions with thiols that provide interesting ways of modifying the electrode surface through self assembly. These modified surfaces can be used to either improve selectivity and sensitivity [16,17], or to serve as substrates for the immobilization of biochemical species, such as enzymes [18,19], antibodies [19,20], proteins [21,22], and DNA [19,23], during biochemical/bioelectrochemical studies [18,19,22,24].

Due to strong interactions, thiols are not easily removed from gold surfaces; their removal may require time-consuming cleaning steps that include polishing with an abrasive slurry (e.g., alumina). In addition, the high cost of gold electrodes has fostered the search for alternative strategies and/or less expensive sources of this metal [25,26], driven by the development of disposable and low-cost devices. With this in mind, Angnes and coworkers [26] reported a simple method for the fabrication of gold electrodes (CDtrodes) using recordable CDs as the source of gold. Apart from planar gold electrodes, the exposed thin gold film that covers a recordable CD (~50–100 nm thick) can be used to fabricate nanoband electrodes [26]. Angnes' group also demonstrated that gold microelectrodes (or arrays of microelectrodes) can be obtained from integrated-circuit chips by simply splitting and sanding the surfaces of the chips with sandpaper to expose the circuit contacts [25].

In this context, gold-leaf sheets, already used for gilding by the Egyptians in the pyramids and now predominantly used in decorative crafts and wedding candies, is an interesting commercially available material and can be procured with the desired purity [27,28]. Interestingly, 12 kt white-gold leaf (1:1 w/w Au:Ag ratio) has been dealloyed to produce nanoporous gold leaf (NPGL) with a high surface area and well-defined structure [27]. However, concentrated acid is required

during the dealloying process [27]. The NPGL has been applied as a substrate for molecularly imprinted polymers [29], has been surface-covered by platinum nanoparticles to improve sensitivity [30,31], has been used in electroanalysis [32,33] and during the fabrication of organic solar cells [34]. On the other hand, to date 23 kt gold leaf has been used only to prepare electrodes for electrophoretic separation in microdevices [28]. Despite the advantages of gold leaf, the handling of 0.1 µm sheets is not trivial, which has probably contributed to its lack of use for analytical purposes.

The present work describes an easy and simple method for the fabrication of gold electrodes from gold leaf and single or double-sided polyimide tape. The electrochemical performance of planar disc and nanoband gold electrodes are presented and compared with that of gold CDtrodes and commercially available gold electrodes. The flexibility and mechanical resistance of the fabricated electrodes, which allow bending and twisting without loss of electrochemical response, provide promising prospects for the development of wearable devices.

2. Experimental section

2.1. Chemicals and solutions

All solutions were prepared using analytical-grade reagents and water with a resistivity > 18.1 MΩ cm (NANOpure Diamond, Barnstead, Dubuque, IA, USA). Potassium ferricyanide ($K_3[Fe(CN)_6]$) and potassium nitrate were purchased from Sigma-Aldrich (Saint Louis, MO, USA). Sulfuric acid was purchased from J. T. Baker (Phillipsburg, NJ, USA). The supporting $0.2\ mol\ L^{-1}\ H_2SO_4$ or $0.2\ mol\ L^{-1}\ KNO_3$ electrolyte solutions used in the cyclic voltammetry (CV) experiments were prepared from analytical grade reagents without further purification.

2.2. Apparatus

The 23 kt gold leaf (79 × 79 mm) was purchased from Nazionale Battitura Metalli s.r.l. (Milan, Italy). The single and double-sided polyimide (Kapton™) tape was purchased from Polyimide Tape Online (Frisco, TX, USA). To define the dimensions of the disc electrodes, a paper punch (ProPunch™) from Paper Pro Inc. (West Columbia, SC, USA) was used, however cork borers can also be used. A new double-edge razor blade (Wilkinson Sword, Shoreham-by-Sea, West Sussex, UK) was used to cut the nanoband electrodes after first being degreased with acetone. Cyclic voltammetry (CV) experiments were performed using a µAUTOLABIII/FRA2 low-cost impedance analyzer from Metrohm-Autolab (Utrecht, The Netherlands). Platinum wire (1 mm diameter) and a miniaturized $Ag/AgCl_{(KCl\ 3M)}$ [35] electrode were used as auxiliary and reference electrodes, respectively, in all CV experiments. A Metrohm-Autolab polycrystalline gold-disc electrode (2 mm diameter) and a gold CDtrode [26], prepared from gold-recordable 650 MB CD-Rs, (Mitsui, Chiyoda-ku, Tokyo, Japan) were used for comparison purposes.

2.3. Electrode design and fabrication

A schematic diagram depicting the fabrication of the planar-disc gold-leaf electrode and the nanoband gold-leaf electrode is shown in Fig. 1A. To fabricate the planar-disc electrode, gold leaf was placed onto non-stick paper on a flat surface, after which it was transferred to a strip of polyimide tape (10 × 25 mm) through contact of the gold leaf with the tape, followed by light pressing (steps **i** to **iii** in Fig. 1A). Subsequently, another piece of polyimide tape (10 × 20 mm) was punched with the paper punch and placed over the gold film to define

the electrode surface area (3 mm diameter), as detailed in steps **iv** and **v** on the right side of Fig. 1A. Silver ink was used to reinforce the gold film for the purpose of creating a terminal for the electrical contact. The exposed area of the disc electrode, defined by the hole punched in the polyimide tape, can be varied by choosing paper hole punchers (or cork borers) of different diameters. Images of the front view of the gold-leaf disc electrode and its side view during bending are shown in Fig. 1B and C, respectively.

The nanoband electrodes were fabricated following the same initial steps used in the fabrication of the planar electrode, by pressing the polyimide strip lightly against the gold leaf, as depicted in steps **i** to **iii** in Fig. 1A. Subsequently, the gold film was covered with another piece of polyimide tape (not punched), with a strip at one end left uncovered as a terminal, which was then reinforced with silver ink. Finally, a section of the gold film was exposed by cutting the edge of the sandwiched gold leaf with a razor blade, as depicted in steps **iv** to **vi** in the left side of Fig. 1A. This procedure can be repeated many times to renew the exposed gold nanoband in case the electrode becomes blocked, for example, due to strong adsorption, electropolymerization, deposition of species on the surface, or electrode corrosion. Taking into account the electrochemical area of the electrode and by weighing a gold leaf sheet, nanoband electrodes of approximately 230 nm thick are expected. The Kapton polyimide film has high chemical resistance, excellent dielectric properties and is thermally stable [36].

3. Results and discussion

In order to compare the electrochemical behavior of the gold-leaf disc electrode with other polycrystalline gold electrodes, cyclic voltammetry experiments were performed in $0.2\ mol\ L^{-1}\ H_2SO_4$. Similar behavior was observed for the commercial disc electrode, the CDtrode, and the gold-leaf disc electrode, corresponding to the well known characteristic CV profiles found in the literature (data not shown). The anodic peak that appears during scanning to more positive potentials, at approximately 1.35 V, is attributed to oxide formation, and the cathodic peak, observed during the reverse scan, at approximately 0.90 V, is attributed to the reduction of the formed oxide [37].

Cyclic voltammograms (triplicates) of $1\ mmol\ L^{-1}\ K_3[Fe(CN)_6]$ in $0.2\ mol\ L^{-1}\ KNO_3$, obtained using the gold-leaf disc electrode at different scan rates, are shown in Fig. 2A. The plot of peak current as a function of the square root of the scan rate is linear (insert, Fig. 2A), as expected for a diffusion-controlled electrochemical process. In addition, under the given experimental conditions, the difference between the two peak potentials was observed to be about 80 mV (at room temperature, 25 °C), irrespective of scan rate, which is a good experimental value, although 59 mV is expected at 25 °C for a reversible one-electron process [37,38].

To demonstrate the potential of the gold-leaf electrode fabricated on polyimide tape for the development of wearable devices [39,40], a 6-mm-diameter planar disc electrode was submitted to severe mechanical deformation. After each mechanical deformation (i.e., bending and/or folding of the electrode), a cyclic voltammogram of $1\ mmol\ L^{-1}\ K_3[Fe(CN)_6]$ in $0.2\ mol\ L^{-1}\ KNO_3$ was recorded using the electrode. The 15 overlaid cyclic voltammograms shown in Fig. 2B exhibit neither loss of electrical contact nor significant variation in electrode response, even after repeated folding/unfolding, although wrinkles caused by the mechanical stress are clearly apparent in the images of the gold-leaf electrode (Fig. 2C).

To evaluate the performance of the nanoband electrode, cyclic voltammograms were recorded with increasing concentration of potassium ferricyanide in $0.2\ mol\ L^{-1}\ KNO_3$, as shown in Fig. 2D. As presented in the insert of Fig. 2D, the limiting current increases linearly