Published in final edited form as:

Anal Chim Acta. 2015 January 1; 853: 207–213. doi:10.1016/j.aca.2014.09.030.

Selective detection and recovery of gold at tannin-immobilized non-conducting electrode

Khaleda Banu^{a,b,*}, Takayoshi Shimura^{b,c}, and Saman Sadeghi^{a,}**

^aDepartment of Molecular & Medical Pharmacology, University of California, Los Angeles, CA 90095, United States

^bVenture Business Laboratory, Center for Advanced Science and Innovation, Osaka University, Suita, Osaka 565-0871, Japan

^cDepartment of Material & Life Science, Division of Advanced Science and Biotechnology, Graduate School of Engineering, Osaka University, Japan

Abstract

A tannin-immobilized glassy carbon electrode (TIGC) was prepared via electrochemical oxidation of the naturally occurring polyphenolic mimosa tannin, which generated a non-conducting polymeric film (NCPF) on the electrode surface. The fouling of the electrode surface by the electropolymerized film was evaluated by monitoring the electrode response of ferricyanide ions as a redox marker. The NCPF was permselective to HAuCl_4 , and the electrochemical reduction of HAuCl_4 to metallic gold at the TIGC electrode was evaluated by recording the reduction current during cyclic voltammetry measurement. In the mixed electrolyte containing HAuCl_4 along with FeCl_3 and/or CuCl_2 , the NCPF remained selective toward the electrochemical reduction of HAuCl_4 into the metallic state. The chemical reduction of HAuCl_4 into metallic gold was also observed when the NCPF was inserted into an acidic gold solution overnight. The adsorption capacity of Au(III) on tannin-immobilized carbon fiber was $29 \pm 1.45 \text{ mg g}^{-1}$ at 60°C . In the presence of excess Cu(II) and Fe(III), tannin-immobilized NCPF proved to be an excellent candidate for the selective detection and recovery of gold through both electrochemical and chemical processes.

Graphical abstract

*Corresponding author at: Department of Molecular & Medical Pharmacology, University of California, Los Angeles, CA 90095, United States. Tel.: +1 310 825 8113. kbanu@ucla.edu, kbanu05@yahoo.com (K. Banu). **Corresponding author. Tel.: +1 310 825 3170. samsadeghi@mednet.ucla.edu (S. Sadeghi).

Keywords

Non-conducting electrode; Selective detection; Selective recovery; Permselective diffusion; Gold; Tannin

1. Introduction

Precious metals such as gold have extensive applications in many areas, such as catalysis, electrical and electronics industries, medicine and in jewelry. Given the limited primary resources and rapidly increasing prices, it is important to investigate the selective detection and recovery of gold from secondary sources, such as electronic waste, in the presence of excess interfering metallic species, such as copper(II) and iron(III) [1–4].

Various conventional methods have been employed for the recovery of precious metals, including chemical precipitation, membrane filtration, ion exchange, carbon adsorption, and co-precipitation [1–4]. However, these methods are not efficacious, economical (high price, high reagent and/or energy requirements) or environmentally friendly. Consequently, more cost-efficient and environmentally friendly alternative technologies for the detection and recovery of precious metals are required.

Tannins are natural polyphenolic antioxidants with molecular weights between 500 and 3000 Da (see Fig. S1) [5,6]. Tannins contain multiple adjacent hydroxyl groups and exhibit specific affinities for many metal ions [5–9]. Thus, tannins hold promise as good biomass materials for effective and efficient adsorption of metal ions. However, tannins are water-soluble compounds and must be chemically modified or immobilized in water-insoluble matrices [5–11]. The immobilization of tannic acid and other tannins has been described, and the synthesis and characterization of water-insoluble tannin resins have also been reported [5–11]. For example, tannin adsorbed on collagen fiber, cross-linked in the form of a gel or adsorbed on silica powder or activated carbon has been applied for the recovery of different metal species. Nevertheless, these methods are time consuming and require 2 days to several weeks to prepare the substrate. Another two major drawbacks of the existing methods are the considerable leakage of tannin due to its poor physical or chemical adsorption on the solid surface and the application of toxic glutaraldehyde as the cross-linking agent [1–11].

Similar to other polyphenolic compounds, tannins are irreversibly oxidized on electrode surfaces to form a compact, non-conducting, insoluble polymeric film (NCPF) (10–100 nm)

[12,13]. The NCPFs of various polymers containing different functional groups exhibit permselectivity, which is useful in preventing interfering species from approaching or contaminating the electrode surface. This property has enabled the use of non-conducting electrodes as sensors for the selective detection of approximately 60 metal ions, including several transition metal ions [14]. However, the electrochemical detection of gold using NCPF has not been described [14].

In this study, we immobilized tannin on a glassy carbon (GC) electrode or a carbon fiber (CF) electrode within 15 min through electrochemical oxidation. The as-prepared solid polymeric coating had superior mechanical strength due to its chemical adsorption onto the electrode surface. The tannin-immobilized NCPF prepared using this method was found to be an excellent candidate for the selective detection and recovery of HAuCl_4 in the presence of excess Cu(II) and/or Fe(III) by both electrochemical and chemical methods.

2. Experimental

2.1. Materials

All compounds were used as received. Hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), iron(III) chloride trihydrate ($\text{FeCl}_3 \cdot 3\text{H}_2\text{O}$), potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$), potassium ferrocyanide ($\text{K}_4[\text{Fe}(\text{CN})_6]$) and HClO_4 were purchased from Sigma–Aldrich (USA). Mimosa tannin (trade name Fintan OP) was obtained as a gift from Silvateam (CA, USA).

2.2. Electrochemical measurements

All of the electrochemical measurements were performed in an undivided or divided cell with a three-electrode system using an Autolab PGSTAT101 electrochemical analyzer (Methrom Autolab B.V., The Netherlands) connected to a personal computer and controlled by NOVA software version 1.8 (Methrom Autolab B.V., The Netherlands). A GC electrode (model no. MF-2012, 3.0 mm diameter, BASi) or a CF electrode was used as the working electrode. Prior to experiments, the GC electrode was polished with 0.3 and 0.05 mm alumina and then ultrasonically cleaned for 5 min in water and acetone. The GC electrode was then electrochemically treated by scanning the potential between -0.7 V and 1.75 V (vs. SSE) for 5 repeated cycles in aqueous solution (pH 1). After the treatment, the GC surface became hydrophilic in nature due to the increase of oxygen to carbon ratio on the surface [15,16]. During a typical CV measurement, the reduction peak potential for the reduction of HAuCl_4 shifted to a more positive potential when recorded at the electrochemically treated electrode than at the untreated electrode (see Fig. S2). The CF electrode was electrochemically treated in a 0.5 M H_2SO_4 solution by scanning the potential between -0.7 V and 1.75 V for 10 cycles. The CF with a thickness of 0.19 mm was obtained as a gift from TORAY, Japan. The mass density of the carbon fiber cloth was 0.44 g cm^{-3} . The average diameter of each carbon fiber was 10 μm . A platinum wire was used as a counter electrode, and all potentials were recorded against a Ag/AgCl (SSE) electrode (model no. 11-2020, BASi). The electrical connection of CF was made by Pt wire (0.3 mm diameter). An undivided cell with a three-electrode system was used for all of the cyclic voltammetry (CV) measurements. Tannin-immobilized carbon fiber (TICF) was prepared in a divided cell

consisting of two glass compartments separated by a Nafion[®] membrane. The CF electrode and the RE were placed in the WE compartment, and the CE was placed in the CE compartment. Unless otherwise specified, all of the electrochemical experiments were conducted using a scan speed of 20 mV s⁻¹. All of the CV experiments were performed at room temperature (25 °C) in an aqueous solution at pH 1. The chemical adsorption of gold on TICF was conducted in 20 mL of a solution with pH 1 at 60 °C. Potential was scanned to the negative direction for a typical CV measurement when an electroactive species was reduced at the electrode surface. Potential was scanned to the positive direction for a typical CV measurement when electroactive species was oxidized at the electrode surface. For all background current measurements, potential was scanned to the positive direction.

2.3. Preparation of the tannin-immobilized electrode

Aqueous solutions containing 10% tannin were prepared. The prepared solution was slightly turbid in nature. After filtration or centrifugation (10 min, 6000 rpm), the solution remained turbid and did not precipitate any solid residues. The initial pH values of the solutions were adjusted to 1 by adding concentrated HClO₄ and were measured using an Orion EA940 pH meter. The tannin-immobilized GC electrode (TIGC) was prepared via the electrochemical oxidation of tannin by scanning the potential between 0.2 V and 1.1 V for 10 repeated cycles, which generated a non-conducting polymeric film (NCPF) on the electrode surface [17]. The tannin-immobilized carbon fiber (TICF) was prepared in the same manner, in which electropolymerization occurred on the GC electrode. In another procedure, TIGC was prepared by applying a constant potential at 0.8 V for 10 min, and the initial current (20 μA) decreased to 500 nA. The TIGC prepared using the electrolysis method did not possess sufficient mechanical strength and gradually showed a redox response to the redox marker after 10 cycles. The polymeric film prepared through 10 repetitions of CV was mechanically stable and did not exhibit a redox response after 10 or more cycles with the redox marker. The as-prepared TIGC electrode was dipped in distilled water prior to electrochemical measurements.

2.4. Selective electrochemical reduction of HAuCl₄ at TIGC

In a typical procedure, the CV of a 1 mM (10 mL, pH 1) HAuCl₄ solution was recorded at the TIGC electrode by scanning the potential from 1.1 to 0.0 V. To investigate the selective electrochemical reduction in the presence of Fe(III) species, the CV of a mixture containing 1 mM HAuCl₄ and 3 mM FeCl₃ was recorded at the TIGC electrode. Similarly, the CV of a mixture containing 1 mM HAuCl₄ and 5 mM CuCl₂ recorded at the TIGC electrode was used to investigate selective electrochemical reduction in the presence of Cu(II) species.

2.5. Selective chemical reduction of HAuCl₄ at TICF

In a typical procedure, TICF (0.134 g) was dipped into a 1 mM (20 mL) HAuCl₄ solution (pH 1) at 60 °C for 80 h. One hundred microliters of the solution was collected at different time intervals (2 h, 5 h, 10 h, 20 h, 40 h, and 80 h) for elemental analyses. After adsorption, the TICF was washed thoroughly with water and dried at 60 °C for 1 h. The color of the TICF became blackish-yellow when dipped in the HAuCl₄ solution. In another procedure, to determine the effect of the co-existence of Cu(II) and Fe(III), 0.134 g TICF was dipped into a 1 mM HAuCl₄ solution containing 5 mM CuCl₂ and 3 mM FeCl₃.

2.6. Characterization of gold metal

SEM measurements were performed on a Hitachi S-3000N scanning electron microscope with an accelerating voltage of 15 kV. Optical microscopy measurements were performed on an Olympus model IX70 optical microscope. The oxidation state of the metal species was characterized using an XPS spectrometer (Quantum-2000, ULVAC-PHI Inc., Japan) with a monochromatic Al source. All binding energies were referenced to the C1s hydrocarbon peak at 284.6 eV. The SEM, optical microscopy, and XPS measurements were performed directly on the metal species deposited on the TICF or on a tannin-immobilized carbon plate (TICP). The contents of Au(III), Cu(II) and Fe(III) in the solutions were determined by an Agilent 7500c quadrupole inductively coupled plasma-mass spectrometry (ICP-MS) equipped with an H₂/He octapole reaction/collision cell. The % relative standard deviations for all the data were at or below our lower quantifiable limits for each element at less than or equal to 10%.

3. Results and discussion

3.1. Modification of the GC electrode-TIGC

Fig. 1(a) shows the cyclic voltammogram of 10% mimosa tannin at pH 1 recorded at the GC electrode for 3 repeated cycles. An irreversible oxidation peak for the first scan was observed at 0.80 V. This peak current (24 μ A) was markedly decreased in the repeated cycle and completely disappeared after 10 cycles due to the passivation of the electrode surface with an electropolymerized non-conduction coating (TIGC), thereby inhibiting the further oxidation of tannin. The oxidation of tannin at pH 7 (Fig. 1(b)) shows a similar irreversible oxidation, with the peak potential shifted by approximately 400 mV in the negative direction. This result indicates that the oxidation of tannin, similar to a typical phenol, is associated with the release of protons and is energetically favorable at high pH [20]. The non-conducting nature of the prepared electrode was further characterized by monitoring the redox response of a 1 mM K₃[Fe(CN)₆] solution at the TIGC electrode. Fig. 2 shows the voltammogram of 1 mM K₃[Fe(CN)₆] at the bare GC (a) and the TIGC electrodes (b). The reduction current of the ferricyanide was absent in the CV recorded at the TIGC electrode (b). Similarly, no oxidation current was observed when the CV of 1 mM K₄Fe(CN)₆ was recorded at the TIGC electrode. This result illustrates the non-conducting nature of the immobilized tannin polymer on the electrode surface. Other electroactive species, such as Fe(III) and Cu(II), showed similar results and did not generate a reduction current at the TIGC electrode during the CV measurements.

The electrochemical oxidation of a typical polyphenol at pH 1 is a 2 electron process that produces the corresponding quinone as the oxidation product (see Fig. S1) [16–18]. However, oxidation at pH 7 follows a 1 electron oxidation process and mainly generates a polymer through free radical polymerization. Mimosa tannin primarily has the pyrogallol group in the B ring of the repeating monomer unit (see Fig. S1). Therefore, the oxidation of mimosa at pH 1 will form a more compact quinone-rich coating on the electrode surface [16–18].

3.2. Diffusion of ionic and molecular species in the non-conducting polymer matrix

Fig. 2(c) shows the background current of the cyclic voltammogram measured at pH 1 at the TIGC electrode for 2 repeated cycles. The background current was similar to the background current at the bare GC electrode (Fig. 2(b)). A similar result was observed for different values of the solution pH (1–7), and the potential window did not change after modification of the electrode. The polymerization of a typical polyphenol coats the electrode surface with an approximately 38 nm non-conducting coating [12,13]. Therefore, direct electron transfer at the NCPF/solution or GCE/solution interface should not be possible. The observed final increase and final decrease in Fig. 2(c) is due to the redox process at the electrode/membrane interface, indicating that the coated polymer is permeable to the corresponding redox species [21,22]. Here, the final increase (–1.3 V) recorded at the TIGC is due to the oxidation of water, and the final decrease (~ -0.6 V) is due to the evolution of hydrogen because of the proton reduction. A reduction pre-peak associated with molecular oxygen reduction always appeared (-0.45 V) before the final decrease [23]. This peak disappeared when the CV was recorded under deaerated conditions.

This result indicates that the NCPF is permeable to small molecules or ions such as water, molecular oxygen, H_2O_2 , protons and hydroxyl ions. However, the polymer membrane was not permeable to relatively larger molecules, such as $\text{K}_3[\text{Fe}(\text{CN})_6]$, $\text{K}_4[\text{Fe}(\text{CN})_6]$, $\text{Cu}(\text{II})$ and $\text{Fe}(\text{III})$, but rather served as an insulator to these species [20,22].

3.3. Selective electrochemical reduction of HAuCl_4 at TIGC electrode

Fig. 3(a) shows the cyclic voltammogram of 1 mM HAuCl_4 recorded at the bare GC electrode for 2 repeated cycles. The first reduction peak appeared at 0.68 V and shifted to a more positive potential (0.76 V) for the repeated cycle. During the repeated cycles, HAuCl_4 deposited on the gold surface that was generated on the surface of the GC electrode during the previous scan. The peak potential gradually shifted to a more positive potential and did not change further after 8 repeated cycles. This peak potential was identical to the reduction peak observed at the bare gold electrode (see Fig. S2(c)). This result indicates that the reduction of HAuCl_4 at a metallic gold electrode is an energetically favorable process compared to the reduction at the GC electrode. Fig. 3(b) shows the cyclic voltammogram of 1 mM HAuCl_4 recorded at the TIGC electrode for 2 repeated cycles. The irreversible reduction peak current for the first scan was observed at 0.27 V and is due to the reduction of HAuCl_4 to metallic gold. This peak is 410 mV more negative than the peak at the GC electrode (Fig. 3(a)). Here, the oxidation state of the deposited gold species was confirmed to be metallic gold by XPS measurement. Fig. S3 shows the Au 4f region that corresponds to the binding energy of metallic gold. The Au 4f_{7/2} peaks were at 84.0 eV and 84.12 eV before and after the Ar^+ sputter etching process, respectively. These values are consistent with metallic gold in the Au^0 state [24,25]. For the XPS measurement, gold was electrochemically deposited at the TIGC. In the second cycle, a 20% decrease in the peak current was observed, and the peak potential remained unchanged. For the subsequent 8 cycles, no noticeable changes in the peak potential or peak current were observed. The TIGC after the deposition of gold for 10 repeated cycles was thoroughly washed with water, and the response of this (Au-TIGC) electrode to a redox marker was investigated. Fig. 3(c) shows the voltammogram of 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ at Au-TIGC for 2 repeated cycles. No

reduction current was recorded, and a similar result was observed for 10 repeated cycles. Similarly, no reduction current was observed when the CV of a solution containing 3 mM FeCl_3 was recorded at the Au-TIGC electrode for 10 repeated cycles.

3.4. Selective electrochemical reduction of HAuCl_4 in the presence of Fe (III) and Cu(II)

The results in Section 3.3 illustrate that although HAuCl_4 electrochemically reduces at the TIGC electrode, FeCl_3 is not electroactive and does not show any reduction current for the formation of Fe(II). Fig. 4(a) depicts the CV of 1 mM HAuCl_4 and 3 mM FeCl_3 measured at bare GC electrode. During the first scan, the reduction current of HAuCl_4 overlaps with the reduction current of FeCl_3 , preventing the selective and accurate detection of Au(III) in the presence of Fe(III) ions. The total reduction current measured at the bare GC electrode was the sum of the reduction currents from HAuCl_4 and FeCl_3 with a single peak at 0.42 V. Starting with the second scan, 2 reduction peaks associated with Au(III) (peak potential 0.76 V) and Fe(III) (peak potential 0.5 V) appeared during the CV measurement (see Fig. S4). In the presence of Fe(III), the reduction of HAuCl_4 at the carbon electrode is an overpotential process and overlaps the reduction current of Fe(III) [26]. Beginning with the second scan, Au(III) and Fe(III) reduced on the gold surface generated during the first scan and exhibited two reduction peaks during the CV measurement. Fig. 4(b) shows the cyclic voltammogram of 1 mM HAuCl_4 and 3 mM FeCl_3 recorded at the TIGC electrode. The irreversible single reduction peak for the first scan was observed at 0.27 V, and the observed CV was similar in nature to the CV shown in Fig. 3(b). This peak was associated with the reduction of Au(III) to metallic gold and was confirmed by XPS measurement. The presence of Fe(II) or Fe(III) was not confirmed by XPS measurement. The reduction peak did not increase, and no noticeable changes in the peak potential or peak current were observed with repeated cycles at the TIGC electrode. In the mixed system containing both HAuCl_4 and FeCl_3 , the presence of a single peak matching the reduction potential and current of HAuCl_4 alone at the TIGC, as well as the XPS results showing the absence of signals from Fe species, strongly support the selective reduction of HAuCl_4 at the TIGC electrode.

Similarly, the selective reduction of HAuCl_4 in the presence of CuCl_2 was also observed at the TIGC electrode.

3.5. Selective diffusion and reduction process of HAuCl_4 at TIGC

The reduction of HAuCl_4 at the TIGC electrode supports the permselective nature of the NCPF toward acidic gold species. Figs. 3(b) and 4(b) show the CVs for the reduction of HAuCl_4 at the NCPF. The peak potential remained constant throughout repeated cycles. Because the reduction of HAuCl_4 at the gold surface is energetically favorable compared to deposition at the GC electrode surface, i.e., it occurs at a more positive potential, the constant peak potential indicates that further reduction of HAuCl_4 did not occur on the deposited gold surface (see Fig. S2). Moreover, the formation of gold oxide was not observed at approximately 1.0 V when reduced at the TIGC electrode, which also indicates that gold was not directly deposited on the GC electrode surface.

The quinone derivative generated on the GC electrode surface by the electrochemical oxidation of tannin can form complexes with precious metal species [27–29]. The

electrochemical reduction of quinone-metal ion (QM^+) species to the corresponding hydroquinone in the acidic medium will be facilitated in the presence of an electron-deficient metal ion. The generated hydroquinone (phenol) can chemically reduce metal ions to their metallic state and can regenerate the quinone, which becomes available to form a complex with another metal ion species. We hypothesize that the observed reduction current in Fig. 3(b) is due to the mediated reduction of Au(III) to metallic gold via a quinone–hydroquinone (Q–HQ) redox couple (see Scheme 1). According to this hypothesis, the observed reduction current in Figs. 3(b) and 4(b) is due to the reduction of a QM^+ species, while the subsequent deposition of gold is enabled by chemical reduction with the electrochemically generated hydroquinone species. To maintain electrical neutrality, the electrochemical reduction of QM^+ at the GCE/NCPF interface will be coupled with proton (H^+) transfer from the solution to NCPF or with anion transfer (Cl^-) from NCPF to the solution. Thus, gold does not directly deposit on the GC electrode surface but remains in the polymer matrix.

3.6. Selective chemical reduction of $HAuCl_4$ in the presence of Fe(III) and Cu(II): adsorption capacity of tannin-immobilized carbon cloth

The electrochemical reduction of $HAuCl_4$ is possible due to the mediated electron transfer through a Q–HQ redox couple in which HQ was the responsible species for the chemical reduction of the metal ions. Mimosa tannin is a polyphenolic compound rich in pyrogallol rings (see Fig. S1) with three adjacent phenolic groups attached to the benzene ring. The electrochemical polymerization employed in this study generates an approximately 38 nm thick film on the electrode surface [12,13]. The two electron oxidation peak current of a typical polyphenol for a 1 mM solution is in the range of 10–20 μA [18,19]. Fig. 1 shows the irreversible oxidation of 10% mimosa tannin at the GC electrode during a typical CV measurement in which the peak current was 24 μA . This result indicates that only a fraction of the pyrogallol ring of the mimosa tannin, which is a flavonoid polymer, was converted to the quinone derivative and was adsorbed on the GC electrode surface. Most of the pyrogallol ring in the polymer matrix did not convert to the quinone moiety upon the electrochemical oxidation and could remain free to participate in the chemical reduction of $HAuCl_4$ to metallic gold. It has been reported that tannin adsorbed on different solid matrices, such as collagen, can reduce metal ions to their metallic state, and it is reasonable to anticipate that the immobilized tannin film on the GC electrode would do the same [30,31].

To determine the reducing capacity of the NCPF, tannin was oxidized on the CF electrode rather than the GC electrode. CF was used as the electrode to increase the surface area of the polymeric film. TICF (0.134 g) was dipped in 20 mL of a $HAuCl_4$ solution for 24 h, and the presence of gold on the electrode surface was investigated by XPS measurement. The solution temperature was held constant at 60 °C throughout the procedure. The TICF was removed from the solution and dried after thorough washing. The presence of metallic gold on the TICF was confirmed by XPS measurement. Fig. 5(a) shows the Au 4f region that corresponds to the binding energy of metallic gold. The Au 4f_{7/2} peaks were observed at 84.0 eV and 84.15 eV before and after the Ar⁺ sputter etching process, respectively. These values are consistent with metallic gold with the Au⁰ state. $HAuCl_4$ was completely reduced to its metallic state, and the presence of ionic gold species was not identified by XPS

measurement. The presence of deposited particles was further characterized by SEM (see Fig. 5(b) and (c)) and optical microscopy measurements (see Fig. 5(d) and (e)). The presence of golden colored particles on the TICF supports the presence of metallic gold on the electrode surface.

The adsorption capacity of the tannin-immobilized solid matrix prepared using the reported methods for Au(III) has been reported and varies considerably depending on different adsorption parameters [1–7,28,29]. To investigate the adsorption capacity of the TICF, the adsorption of Au(III) was recorded as a function of the contact time. Fig. 6 shows that the adsorption of 1 mM HAuCl₄ increased with increasing contact time and reached equilibrium at approximately 20 h. An adsorbent with faster uptake is better for the recovery of gold. Fig. 6 reveals that over 93% of adsorption occurred within 20 h and that equilibrium was reached within 24 h. In another experiment, the adsorption of Au(III) was recorded as a function of the contact time when Cu(II) and Fe(III) were present in the solution. The adsorption of Cu(II) and Fe(III) was negligible compared to the adsorption of gold. The concentrations of Fe(III) and Cu(II) in the solution, measured by ICP-MS, did not change after treatment for 24 h or 80 h, indicating that Fe(III) and Cu(II) were not reduced or adsorbed on the TICF but remained entirely in the aqueous solution phase. The XPS data also supported the absence of copper and iron species on the TICF.

The complexation of tannin with different metal ions depends on the stability of the formed complex and on the solution pH. Different metals have different binding affinities for the flavonoid structure of tannin. For example, iron has the highest binding affinity for the 3-OH group of ring C and the 5-OH group of ring A, whereas copper ions bind to the first ring catechol group B (see Fig. S1) [32–36]. Both of these ions form stable complexes at a solution pH greater than 5. Mimosa tannin is a flavonoid polymer, in which the major components are the resorcinol A ring and the pyrogallol B ring. Therefore, iron cannot form stable complexes with mimosa tannin due to structural limitations. The pyrogallol B ring can form complexes with copper at higher pH. However, at pH 1, copper cannot form stable complexes, making chemical separation of gold possible in the presence of copper and iron species.

4. Conclusion

This paper describes a method for the selective detection and recovery of gold in the presence of excess Fe(III) and Cu(II) at a tannin-immobilized non-conducting electrode through both electrochemical and chemical methods. Naturally occurring mimosa tannin, a pyrogallol-rich polyphenolic compound, was immobilized through electropolymerization on the electrode surface for the preparation of TIGC or TICF. The electrochemical detection and deposition of gold at the non-conducting electrode was possible due to the permselective diffusion of HAuCl₄ in NCPF and the subsequent mediated electron transfer promoted by the Q/HQ redox couple. The chemical reduction of HAuCl₄ to metallic gold was due to the reducing ability of the pyrogallol-rich NCPF. The adsorption capacity of Au(III) on tannin-immobilized carbon fiber was $29 \pm 1.45 \text{ mg g}^{-1}$ at 60 °C.

The experimental findings described in this article demonstrate that the non-conducting film formed by natural biopolymer tannin adsorbed on an electrode surface is an excellent candidate for the selective detection and recovery of gold in the presence of excess Fe(III) and Cu(II) using either an electrochemical or chemical step. GC is promising for the detection of gold while CF has very large surface area, making it better applicable for the recovery of gold from industrial waste. The method presented here may also be applicable for the detection of other precious metals such as Pt and Pd. Tannin-based substrates prepared through the proposed electrochemical method do not require the application of toxic aldehydes as the cross-linking agents. This presents an attractive environmentally friendly alternative for preparation of tannin-based substrates. Moreover, the surface can be prepared within 15 min with superior mechanical stability. However, further studies on parameters such as effect of a wide range of concentration encountered in commercial scales, pH, presence of various anions and cations and scale up, are necessary prior to commercial application for the recovery of precious metals from industrial waste.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The authors thank Yasuo Kanematsu, Hiroshi Uyama, Susumu Kuwabata, and Samuele Giovando for their interest, suggestions and support for this research. The authors acknowledge the ICP Facility in the Department of Environmental Health Sciences, UCLA and Research Center for Ultra-Precision Science and Technology of Osaka University for the ICP-MS and XPS measurements, respectively. K. Banu acknowledges financial support from VBL, Osaka University.

References

1. Mack C, Wilhelmi B, Duncan JR, Burgess JE. *Biotechnol Adv.* 2007; 25:264–271. [PubMed: 17293076]
2. Cui J, Zhang L. *J Hazard Mater.* 2008; 158:228–256. [PubMed: 18359555]
3. Robinson BH. *Sci Total Environ.* 2009; 408:183–191. [PubMed: 19846207]
4. Paleologos EK, Giokas DL, Tzouwara-Karayanni SM, Karayannis MI. *Anal Chim Acta.* 2002; 458:241–248.
5. Amarowicz R. *Eur J Lipid Sci Technol.* 2007; 109:549–551.
6. Haslam E. *J Nat Prod.* 1996; 59:205–215. [PubMed: 8991956]
7. Wang R, Ru X, Liao B, Shi B. *Ind Eng Chem Res.* 2005; 44:4221–4226.
8. Banu K, Shimura T. *New J Chem.* 2011; 35:1031–1041.
9. Banu K, Shimura T. *New J Chem.* 2011; 35:1503–1514.
10. engil IA, Özacar M. *J Hazard Mater.* 2009; 166:1488–1494. [PubMed: 19188018]
11. Bailey SE, Olin TJ, Bricka RM, Adrian DD. *Water Res.* 1999; 11:2469–2479.
12. Yuqing M, Jianrong C, Xiaohua W. *Trends Biotechnol.* 2004; 22:227–231. [PubMed: 15109808]
13. Barlett PN, Cooper JM. *J Electroanal Chem.* 1993; 362:1–12.
14. Faridbod F, Norouzi P, Dinarvand R, Ganjali MR. *Sensors.* 2008; 4:2331–2412.
15. Pleskov VY. *Russ J Electrochem.* 2002; 38:1275–1291.
16. Fagan DT, Hu IF, Kuwana T. *Anal Chem.* 1985; 57:2759–2763.
17. Kuramitz H, Nakata Y, Kawasaki M, Tanaka S. *Chemosphere.* 2001; 1:37–43. [PubMed: 11572589]
18. Janeiro P, Brett AMO. *Anal Chim Acta.* 2004; 518:109–115.

19. Hotta H, Ueda M, Nagano S, Tsujino Y, Koyama J, Osakai T. *Anal Biochem.* 2002; 1:66–72. [PubMed: 11906152]
20. Firuzi O, Lacanna A, Petrucci R, Marrosu G, Saso L. *BBA-Gen Subjects.* 2005; 1721:174–184.
21. Kur un S, Ekinci BZ, Pa ahan A, Ekinci E. *J Appl Polym Sci.* 2011; 1:406–410.
22. Guerrieri R, Ciriello D. *Biosens Bioelectron.* 2009; 24:1550–1556. [PubMed: 19022646]
23. Panchompoo J, Aldous L, Kabeshov M, Pilgrim BS, Donohoe TJ, Compton RG. *New J Chem.* 2012; 5:1265–1272.
24. Sangeetha NS, Narayanan SS. *Anal Chim Acta.* 2014; 828:34–45. [PubMed: 24845813]
25. Banu K, Shimura T. *New J Chem.* 2012; 36:2112–2120.
26. Zhou DL, Wang RZ, Zhang M, Weng X, Chen JR, Wang AJ, Feng JJ. *Electrochim Acta.* 2013; 108:390–397.
27. Pierpont CG, Buchanan RM. *Coordin Chem Rev.* 1981; 38:45–87.
28. Chaudhuri P, Verani CN, Bill E, Bothe E, Weyhermüller T, Wiegardt K. *J Am Chem Soc.* 2001; 10:2213–2223. [PubMed: 11456867]
29. Ferraz PA, de Abreu FC, Pinto AV, Glezer V, Tonholo J, Goulart MO. *J Electroanal Chem.* 2001; 507:275–286.
30. Liao X, Zhang M, Shi B. *Ind Eng Chem Res.* 2004; 43:2222–2227.
31. Ma HW, Liao XP, Liu X, Shi B. *J Membrane Sci.* 2006; 278:373–380.
32. Rice-Evans CA, Miller NJ, Paganga G. *Free Radic Biol Med.* 1996; 20:933–956. [PubMed: 8743980]
33. Cotellet N. *Curr Top Med Chem.* 2001; 1:569–590. [PubMed: 11895132]
34. Kaurinovi , B.; Popovi , M. *Liposomes as a Tool to Study Lipid Peroxidation.* Catala, A., editor. InTech; Rijeka, Croatia: 2012. p. 155-180.
35. Kurek-Górecka A, Rzepecka-Stojko A, Górecki M, Stojko J, Sosada M, Swierczek-Zi ba G. *Molecules.* 2013; 19:78–101. [PubMed: 24362627]
36. Feng S, Tang A, Jiang J, Fan J. *Anal Chim Acta.* 2002; 455:187–191.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.aca.2014.09.030>.

HIGHLIGHTS

- Selective detection of gold at non-conducting (NC) polymer modified electrode.
- Mimosa tannin oxidized on glassy carbon electrode surface as NC polymeric film.
- Permselective diffusion and mediated electron transfer at NC electrode surface.
- Chemical recovery of gold is due to the reducing ability of the NC polymeric film.
- Adsorption capacity of Au(III) on carbon fiber was $29 \pm 1.45 \text{ mg g}^{-1}$ at 60°C .

Fig. 1.

Cyclic voltammograms of 10% mimosa tannin recorded at the GC electrode for solution pH 1 (a) and pH 7 (0.1 M phosphate buffer) (b). Background current measured at the GC electrode for solution pH 1 (c). The scan speed for all measurements was 20 mV s^{-1} .

Fig. 2. Cyclic voltammogram of 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ recorded at the GC electrode for solution pH 1 (a). Background current measured at the GC electrode for solution pH 1 (b). Background current recorded at the TIGC for solution pH 1 (c). Arrow sign indicates the direction of scan for a typical CV measurement.

Fig. 3.

Cyclic voltammograms of 1 mM HAuCl_4 recorded at the bare GC electrode ((a) gray line) and at the TIGC electrode ((b) black line) with a solution pH 1. (c) Cyclic voltammogram of 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ recorded at the Au-TIGC electrode.

Fig. 4.

Cyclic voltammograms recorded at the bare GC electrode ((a) gray line) and at the TIGC electrode ((b) black line) with a solution containing 1 mM HAuCl₄ + 3 mM FeCl₃ (pH 1). Cyclic voltammogram recorded at the TIGC electrode (c) in a solution containing 3 mM FeCl₃ (pH 1). The stoichiometries balance of the chemical equations presented in the graph was ignored for the sake of simplicity.

Fig. 5.
 (a) X-ray photoelectron spectra of the Au 4f region of the deposited gold particles on the TICF. Data obtained before (1) and after (2) the Ar^+ sputter etching process. ((b) and (c)) SEM images of the deposited gold particles on the TICF. ((c) and (d)) Optical microscopy images of the gold particles deposited on the TICF.

Fig. 6.

The effect of contact time on the adsorption of gold on NCPF when 0.134 g TICF was soaked in a 1 mM HAuCl_4 solution (pH 1) at 60 °C. Inset shows the ICP-MS data obtained for the quantity of gold remaining in solution during the adsorption process. The error bars present the relative standard deviation, which was at or below 10%, the lower quantifiable limit of our ICP-MS measurements.

Scheme 1.

Reduction of metal ion at a non-conducting polymer-modified electrode via mediated electron transfer coupled with a Q/HQ redox couple. The precious metal species, which is permselective to the polymer matrix, can form a complex with the quinone derivative. The electrochemical reduction of QM^+ will form hydroquinone, which can subsequently reduce the metal ion species via a chemical reaction. Proton/metal ion or chloride transfer at the NCPF/solution interface will be associated with electron transfer at the electrode/NCPF interface to maintain the overall electrical neutrality.