An Undergraduate-Level Electrochemical Investigation of Gold Nanoparticles-Modified Physically Small Carbon Electrodes
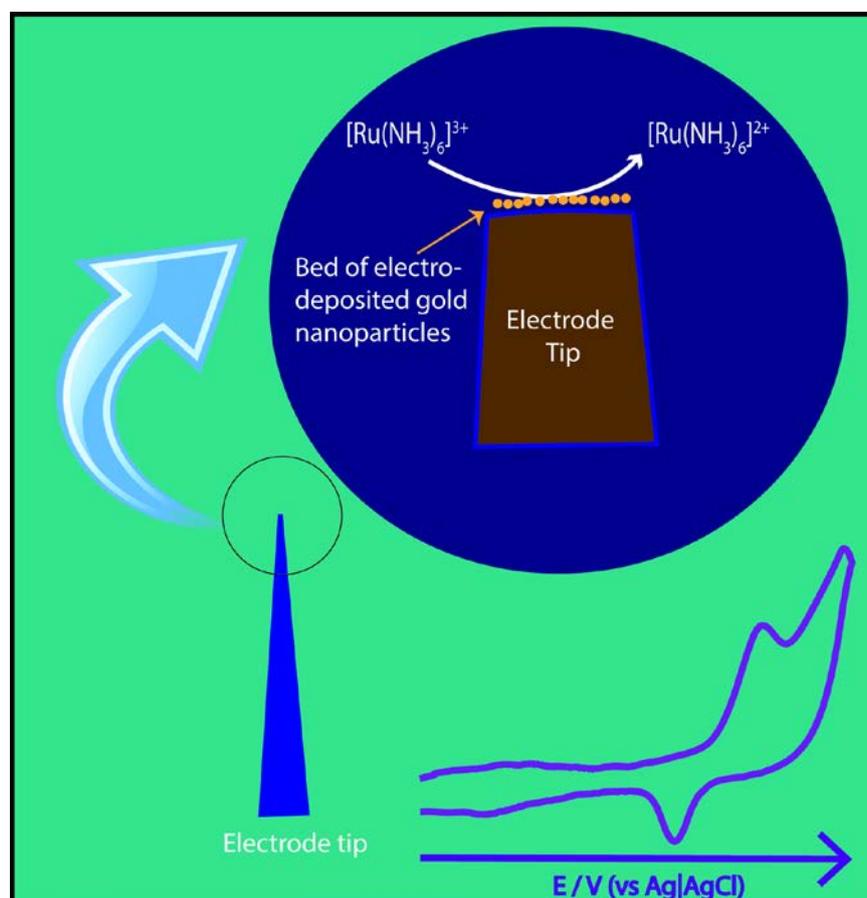
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Abstract This paper reports an undergraduate experiment based on analytical chemistry, electrochemistry and materials science of carbon microelectrodes. The modification of the electroactive surface of the carbon microelectrode was done using gold nanoparticles electrodeposited from gold solution. To determine the changes on the surface, the electrode was subjected to simple optical microscopy. Next, the electrode was characterized using fast-scan cyclic voltammetry of two known electrochemical redox markers: hexaamineruthenium(III) chloride and potassium hexacyanoferrate (III), i.e. potassium ferricyanide. The redox behavior of both markers demonstrated the change in electrode surface. After modification, the ferricyanide reduction peaks were observed to increase significantly, as a consequence of accelerated electron transfer. Furthermore, changes in wave slope and half-wave potentials ($E_{1/2}$) of the redox waves also confirmed an altered electrode surface that students can logically trace back to the modification. The electrode tip dimension was also determined using a modified form of the Cottrell equation, confirming the tip size to be 2.0 µm. The discussion of these results enables an understanding of electrochemistry, analytical chemistry and materials chemistry, and presents an excellent opportunity to apply these in an undergraduate setting.

1. Introduction

The development of modified electrodes has been a focal issue in the fields of electrochemical sensors [1]. Electrodes, particularly of the structurally small variety of different geometries and sizes have reportedly been constructed from various electrode materials such as tungsten, aluminum, various forms of carbon (doped diamond, pyrolyzed carbon, carbon fibers and gold nanoparticles deposited on glassy carbon) and gold nanoparticles (AuNPs) deposited on aluminium [2]. Some recent work based on electrochemical platform for instance include determination of the neurotransmitter dopamine [3], carbamate pesticides in food [4], determination of peroxide using nanoparticles-based sensors [5] and histamine quantification in fish sauce for example [6].

Electrochemical detection has numerous advantages such as detection of heavy metals present at trace levels with low cost, ease of use, high sensitivity and suitability for in-situ monitoring [7]. However one of the challenges is the need to improve selectivity and sensitivity of electrochemical sensors. This is because interfererents can decrease the response of electrodes with time and preclude the possible analysis of untreated samples. Therefore, the electrode surface needs protection against electroactive interfering species that may have irreversibly adsorbed on the electrode surface or similarly affect its functioning. In this manner, modifying the electrode surface can ensure the protection of the electrode from the interfering agents [8] and accordingly, achieve the otherwise difficult detection of low concentration of analytes such as As(III) in natural waters [9]. For instance, when determining trace elements, the presence of intensive matrix background or interfering peaks results in poorer detection limits and/or inaccurate quantitative results [10].

Electrode surface modification can allow for sensitive and selective detection of trace analytes such as neurotransmitters [11], pesticides[12] and even difficult species such as As(III) [13]. This is due to the increased sensitivity and repeatability which results in marked enhancement of peak current response of the target analyte. For instance, in the detection of As(III) in water, interference can be reduced at electrodes modified with gold. In this case, greater sensitivity is realized when detecting As(III) compared to that at normal (i.e. unmodified) electrodes, where the interfering Cu(II) on gold modified electrodes often affects the analysis, and led to higher limits of detection [9]. The use of physically small electrodes, such as microelectrodes allows for hemispherical pattern of mass transfer of analyte, thereby reducing diffusion time [14]. As a result excessive capacitive current is minimized [15]. Since diffusion time is reduced, it is suitable for the analysis of large quantities of samples at a faster rate. The slow response of many

sensing devices is one of the challenges of the electrochemical platform. To keep up with more rapid chemical reactions, sensors are required that could monitor reactions in smaller time scale [16]. Therefore, there has been high demand for miniaturized electrodes to measure the small currents generated [17].

The modification of carbon surfaces on electrodes has led to ease of analysis of challenging species such as As(III). Since electrochemistry is a fast growing tool of convenience for analysts, it is becoming increasingly useful to be able to study the mechanisms of electrode surface alteration to achieve sensitive and selective measurements at yet lower levels in undergraduate studies [18]. The widespread availability of modified sensors such as in glucometers is an ever-pressing reminder that scientific understanding of such vital surface modifications is becoming as important as the electroanalytical detection platform itself. Such advances raise the necessity to expose undergraduate students to such concepts enabling them to gain knowledge and skills in the use and applications of current advances in nanotechnology in electroanalytical chemistry. As has been alluded to previously, electrochemistry lab experiments are usually focused in the use of techniques, and utilizing such experiments can bridge the gap between theory and practice, improving the feeling of students on electrochemistry and highlight the importance of the theoretical lectures in experimental applications [19]. Indeed, using techniques such as cyclic voltammetry, information on electrode surfaces, reaction kinetics and even information on a redox couple [20] can be easily obtained. Furthermore, it utilizes simple instrumentation and equipment such as a potentiostat, inexpensive electrodes and mico-volumes of solutions, and is therefore simple to apply and cost-effective. The appeal of these favorable attributes towards teaching has been captured by other educators of electrochemistry recently as well [21].

In this work, therefore, we propose a simple electrode modification and characterization procedure that can be safely and easily applied at upper-division undergraduate levels. The experiment is one we created and implemented in our third-year chemistry course at the University of the South Pacific that covers nano-sized sensors and electrochemistry. The results from one group of students in 2014 form the basis of this shared experience. The practical focuses on both the technique as well as evaluation of the modification procedure electrochemically without resorting to the usual high-end spectroscopic and microscopic technologies usually associated with such surface science studies. We also present the results obtained in our characterization in this manner and offer guidance on their interpretation. This is a simple technique that can be achieved in a matter of three practical sessions. Its simplicity and applicability to recent and cutting-edge research work also lends the experience of new scientific work being included in

teaching curricular to reflect the dynamism of both electroanalytical chemistry as well as materials science.

2. Experimental Section

Fifty four students successfully completed this experiment in three weeks using all the experimental techniques described herein. The goals of this experiment were to reinforce the theory of electrochemistry, electrode surface modification and re-characterization to assess the changes onto the electrode surface. No data was externally sourced for the students and this ensured a real research experience was gained by each student. It was found that groups of 3-4 students work well in such investigations, and the final outputs included a report formatted to a specified journal format, the adherence to which formed part of the assessment criteria. Not only did the exercise impart a cutting edge aspect to their undergraduate learning, but the students also learnt the value of carefully handling fragile and sensitive electrochemical equipment including the electrodes. The auxiliary learning in the exercise was also teamwork, which is one of the graduate attributes of the University.

The experiment accompanies theory of electrochemical characterization of surfaces using known redox markers. Voltammetric behavior of the redox markers can provide useful information on analyte mass transport regime, extent of capacitance, the thermodynamics such as reversibility of the redox process. All these concepts were covered in the theory during lectures and tutorials before the students embarked on the practical exercise.

The laboratory session began with a 30-min prelab that outlined the objectives for the session as well as logistics and safety issues to consider. The sessions were for four hours, respectively.

Scientifically, in this experiment, there are several aspects of science encompassed that makes it suitable for students specializing in various disciplines (such as applied chemistry, analytical chemistry, physical chemistry and materials chemistry). Through the electrochemical experiments involving $[Ru(NH_3)_6]^{3+}$, students will be able to observe and learn how to assess the functioning of a microelectrode. The electrodeposition section teaches students at an early level the use of a powerful, robust method of attaching AuNPs to a carbon surface, thereby introducing a new surface altogether. This is one of the multidisciplinary aspects of the exercise, drawing on electrochemistry and materials chemistry. The subsequent electrochemical and microscopic characterization of the surface to determine the changes therein presents an exciting, approach of examining the changes to the electrode surface and correlating observations to scientific theory. To correlate the waveforms obtained in each electrochemical step with the underlying theory of electron transfer across the electrode/solution interface draws on principles of chemical kinetics.

2.1. Electrochemical Characterization of Electrodes

Electrochemical measurements involved cyclic voltammetry and chronoamperometry and were undertaken using a potentiostat capable of measuring down to nanoampere-range currents, provided by eDAQ Pty Ltd, Sydney, Australia and controlled using an EChem version 2.1.15 software. A single compartment, three electrode glass cell containing the working electrode, a platinum counter electrode and an Ag|AgCl reference electrode (eDAQ Pty Limited, Sydney, Australia) was used. All measurements were carried out at controlled room temperature (25 °C). All electrochemical measurements and characterization were carried out in a grounded Faraday cage. For microelectrodes, any commercially-available electrode with a micrometer of smaller tip-dimension should suffice.

Ultrapure (Milli-Q) water (18.2 MΩ cm at 25^oC) was used to prepare all solutions. Analytical grade potassium chloride, potassium ferricyanide, gold(III) chloride trihydrate, sulfuric acid and hydrochloric acid were purchased from Sigma Aldrich. Hexamineruthenium(III) chloride, was obtained from Stremm Chemicals (Newport, USA). All chemicals and reagents were used without further purification. All redox solutions and supporting electrolytes were prepared daily and purged with nitrogen for 5 min preceding any analysis.

Week 1: Electrode modification and re-characterization

Electrodes were screened for electrochemical functioning to isolate non-working electrodes. Cyclic voltammetry of 1.0 mM $[Ru(NH_3)_6]Cl_3$ in 1.0 M KCl was performed at each electrode. Only those electrodes that yielded a sigmoidal-shaped cyclic voltammogram from the reduction and subsequent re-oxidation of the species were deemed to be suitably-working electrodes and kept aside for further electrochemical assessment. The redox system here serves as a useful marker for screening electrode functionality as it is relatively insensitive to the electrode surface [22].

Next, working electrodes were subjected to characterization using 1.0 mM potassium ferricyanide $K_3[Fe(CN)_6]$, in 1.0 M KCl. Voltammetric behavior of $K_3[Fe(CN)_6]$ at different electrode surfaces can be used to evaluate the extent of surface activationand also to probe the effects of surface oxides via changes to reaction kinetics [22].

Week 2: Electrode surface modification and re-characterization using cyclic voltammetry

AuNPs deposition was achieved by reduction of 1.0 mM $AuCl_4^-$ solution (prepared in 1.0 M HCl). The deposition parameters used a reducing pulse (height: 1000 mV, duration: 1 s) applied onto a resting potential of 0 mV (vs Ag|AgCl). The modified electrodes were then re-subjected to characterization by cyclic voltammetry of 1.0 mM $K_3[Fe(CN)_6]$ in 1.0 M KCl.

Week 3: Microscopy and data analysis

For visual examination of the electrode tips, a compound microscope was used at the magnification of 20× objective. The diameter of the electrode tip was also visually estimated using the microscope's in-built scale. For perspective, a human hair was also compared together with the electrode tip to allow for tip size comparisons.

Diffusion-limited currents from all sigmoidal waveforms were determined through subtraction of the residual current from the limiting current. All cyclic voltammograms were background subtracted to isolate non-Faradaic currents and noise contributions. Furthermore, waveslopes of all cyclic voltammograms were estimated

from a plot of potential versus $\log_{10}[(I_{lim}- I)/I]$ (where I denotes current at a specific potential and I_{lim} is the limiting current on the voltammogram), with the half-wave potential ($E_{½}$) being the intercept on the potential axis. The statistical significance of all correlation coefficients at the 95% confidence level was evaluated based on Student's t-test. Uncertainties associated with the slope and ordinate intercept of all linear plots were expressed as confidence intervals at the 95% level. Sigma Plot was used to perform statistical analysis.

2.2. Data Analysis

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3. Hazards

Chloroauric acid trihydrate is irritating to skin, and poses the risk of causing serious damage to eyes.

Hexamine ruthenium chloride can be irritating to eyes, respiratory system and skin. Potassium ferricyanide has limited information available on risks, but its product (as formed in this experiment) can be used as a guide. It may cause irritation to the respiratory tract. Skin contact may cause irritation with redness and pain, while eye contact may cause irritation, redness and pain. Potassium chloride is slightly hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion and inhalation. Sulfuric acid is very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive), of ingestion, of inhalation. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Hydrochloric acid is very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive), of ingestion. It is slightly hazardous in case of inhalation (lung sensitizer). Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath.

4. Results and Discussion

Completed electrode size determination

Figure 1 depicts a completed electrode. The impression of the impression of multi-geometric aspects of the electrode are also shown.
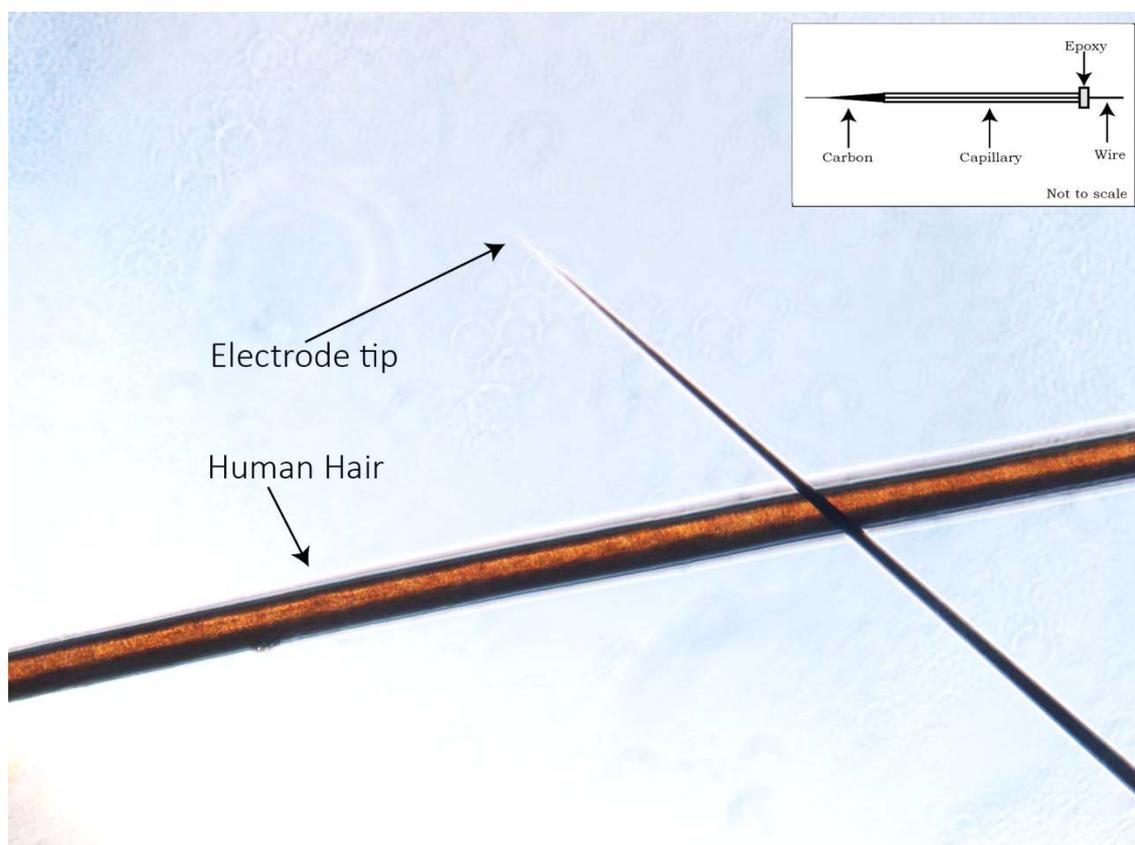
Figure 1. Comparison of the tip dimensions of the completed electrode against a human hair and schematic representation of a carbon electrode (inset)

The dimensions of the electrode tip, which is at the end of the conic section can be determined using guiding work done on such electrodes previously [23]. Based on our preparation and chronoamperometric experiments using 1.0 mM $[Ru(NH_3)_6]Cl_3$ in 1.0 M KCl, the average radius of these electrodes was estimated to be 6.9 µm with a standard deviation of 2.0 µm (N = 6).

As also shown in Figure 1, the tip of the electrode is much smaller in comparison to a human hair. This serves as a comparison for illustration purposes and provides a valuable perspective of how small these tips can be. The diameter of the human hair was 2.04 µm and while that of the electrode tip was too small to be accurately estimated from the compound microscope image, another valuable measurement – that of the diameter of the electrode along the shank was estimated to be approximately 0.1 cm.

Deposition of Au

Modification of the carbon electrodes was undertaken next, using a reducing potential as per published procedure. [24] Briefly, a reducing pulse of 1.0 V (vs Ag|AgCl) and of 15 ms duration was applied to a resting potential of 0 mV within 1 s of commencing the experiment.

The current generated in the reduction experiment can be measured as a function of time as shown in Figure 2. This shows a characteristic chronoamperometric response from the experiment where a sharp reduction current feature is observed corresponding to the reduction of gold from solution onto the carbon electrode surface which corresponds to the reaction of $Au^{3+} + 3e^- \rightarrow Au$.
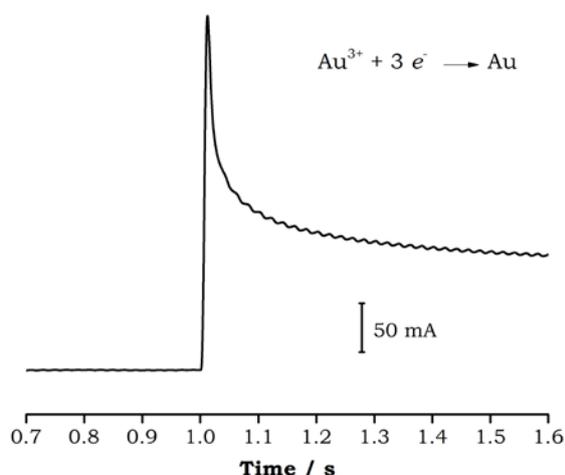

Figure 2. Transient current signal obtained from pulse application in 1.0 mM $AuCl_4^-$ solution prepared in 1.0 M HCl

The sudden rise of current between the 10.00 – 10.02 s region in Figure 2 corresponds to the deposition of a primary layer of gold particles on a bare surface. The large current spike is characteristic of the extensive electron transfer phenomenon associated with such deposition processes. Subsequent decay of the current is symbolic of blockage of active sites of the electrodes due to primary layer of deposition and impurities causing a gradual slowing of electron transfer kinetics [25,26].

To identify functioning electrodes, the hexaamineruthenium (III) chloride, $[Ru(NH_3)_6]Cl_3$ redox system has previously been employed by numerous researchers [27,28,29]. Reduction of the outer sphere, cationic complex is expected to be insensitive to the type of carbon surface,

thus eliminating surface-induced variations. Therefore, it serves as a basic, stable marker at the outset of the experiment prior to any surface modification of a functioning microelectrode, such as of the type employed in this study. Accordingly, we performed reduction of 1.0 mM $[Ru(NH_3)_6]Cl_3$ in 1.0 M KCl at the electrodes to identify working electrodes. Figure 3 shows a typical voltammogram indicative of the current-potential response during reduction of $[Ru(NH_3)_6]Cl_3$. A sigmoidal shape, characteristic of the hemispherical diffusion pattern of mass transport at the electrode surface (tip in this instance) confirmed the small nature of the electrochemical area [30].
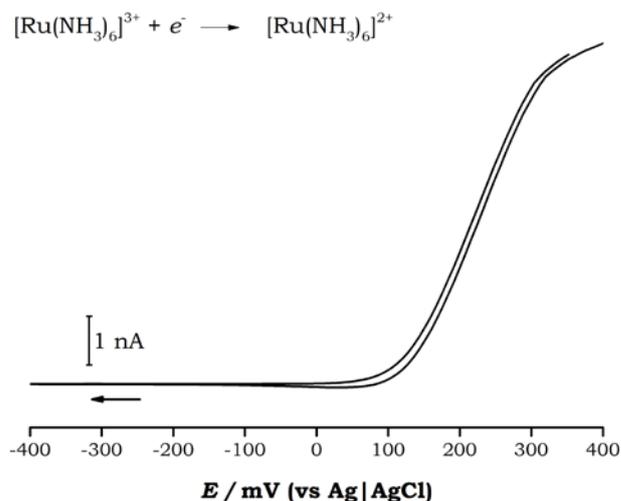
Figure 3. Current-potential plot of 1.0 mM $[Ru(NH_3)_6]Cl_3$ in 1.0 M KCl supporting electrolyte. Scan rate: 100 mV s^{-1}

Working electrodes screened through the ruthenium (Ru^{3+} to Ru^{2+}) reduction experiment were then subjected to further characterization in 0.5 M H_2SO_4 as per the work of Dai and co-workerswhere the presence of a peak at 1300 mV (vs Ag|AgCl) was used as a marker for deposited AuNPs on the electrode surface [24]. As shown in Figure 4, initially there was no current feature observed in the current-potential plot. However, following modification, re-characterization using identical parameters revealed the presence of sharp oxidation and reduction peaks at 1240 mV and 860 mV, respectively.
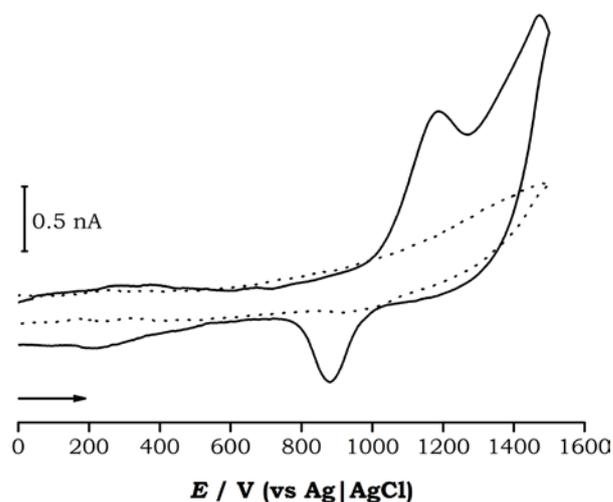
Figure 4. Current-potential plots of 0.5 M H_2SO_4 before (dashed line) and after (solid line) electrode modification. Scan rate: 100 mV s^{-1}

The reduction is that of the gold oxide on the surface, while the oxidation peak usually is manifested in electrodes demonstrating gold "macro" electrode behavior attributed to the presence of a gold film as has been described previously[9]. For this work, the oxidation peak is indicative of necessitating either a reduction in the $AuCl_4^-$ concentration or that of the deposition time in order to restrict the deposition environment. Failing these, instead of discrete gold nanoparticles, a film may result.

Electrode characterization using the $K_3[Fe(CN)_6]$ redox system yields a wealth of information about the altered electrode surface. Figure 5 depicts the results obtained, and an examination of the corresponding waveforms presents some interesting results that are summarized in Table 1.
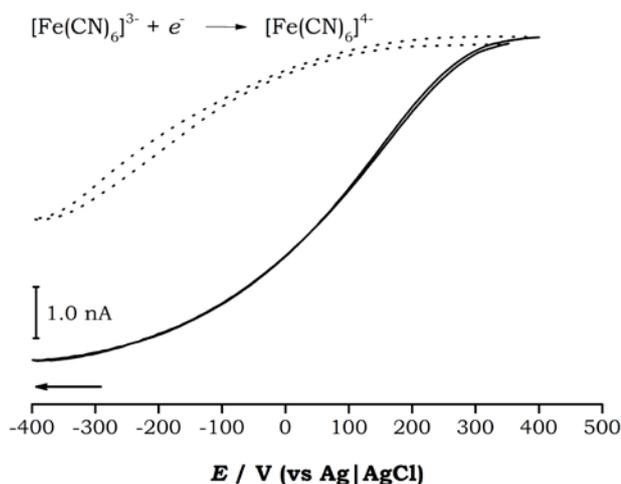
Figure 5. Current-potential plots of 1.0 mM $K_3[Fe(CN)_6]$ in 1.0 M KCl before (dashed line) and after (solid line) electrode modification. Scan rate: 100 mV s^{-1}

Table 1 presents the waveslope and $E_{1/2}$ of the system before and after electrode modification. Here, an increase of 80% in reduction current is observed following modification. This amplified current response is also accompanied by a 36% reduction in waveslope following the electrode surface modification from 198 ± 69 mV decade^{-1} to 125 ± 42 mV decade^{-1}.

Table 1. Waveslope and half-wave potential ($E_{1/2}$) determined from cyclic voltammetry of the $K_3[Fe(CN)_6]$ redox system prior to and following modification

Electrochemical parameters	$E_{1/2}$(mV)	Waveslope (mv decade^{-1})
Bare carbon electrodes	-149 ± 61	198 ± 69
AuNPs-modified carbon electrodes	76 ± 55	125 ± 42

All values denote the variability for five replicates.

A change in the waveslope is indicative of changing electrochemical reversibility of the redox process at the electrode surface [31]. Generally, an electrochemically-reversible redox reaction is denoted by a waveslope value corresponding to 59/n mV decade^{-1} where n equals the number of electrons associated with the redox process [32]. Therefore, the one-electron transfer process of the reduction of $K_3[Fe(CN)_6]$ would be expected to yield a waveslope close to 59 mV decade^{-1}, indicative of an electrochemically reversible reaction [33]. In this experiment, the remoteness of the waveslope values from 59 mV decade^{-1} confirms that there is little change

brought about by the electrode modification step using AuNPs. The electrochemical reversibility depends on the ratio of edge-base planes in the highly oriented graphitic surface of electrodes such as those in the study. An electrode with more basal planes tends to exhibit an irreversible reaction compared to an electrode with edge planes which exhibits a reversible reaction. Edge planes are defect sites on an otherwise smooth surface and thus present sites of expedited reaction kinetics [34]. While the incorporation of a gold film may impart little improvement towards the ratio of edge to base planes on a carbon surface, the introduction of high-surface-area, small particles of another excellent conductor such as gold would nonetheless reasonably be expected to expedite electron transfer and promote electrochemical reversibility. The waveslope shift to a value more aligned towards that of an electrochemically reversible surface reinforces this hypothesis.

Following modification, the $E_{1/2}$ of the waveform was observed to increase from -149 ± 61 mV initially to 76 ± 55 mV. This 151% increase symbolizes the altered kinetics of the electron transfer reaction associated with this reduction at the modified surface. It is quite likely to be a consequence of the increased surface area imparted by the deposited AuNPs. Such a profound change onto the electrode surface is expected to greatly expedite electron transfer, naturally resulting in increased currents at redox processes undertaken at the modified electrode surface. The accelerated electrode kinetics are also contributing to larger current responses in the redox processes as has been previously reported [35]. Overall, these AuNPs allow for far more rapid electron transfer across the modified electrode surface, thus resulting in greater Faradaic component currents.

All results presented in this work were generated by our students. Carbon microelectrodes were first subjected to cyclic voltammetry of 1.0 mM $[Ru(NH_3)_6]Cl_3$ in 1.0 M KCl to identify electrodes that were well functioning as proper microelectrodes. Such electrodes tend to characteristically display a sigmoidal-shaped cyclic voltammogram for $[Ru(NH_3)_6]Cl_3$ reduction with a small charging current between the forward and the backward scans [36].

The availability of a scanning electron microscope for undergraduate experiments would provide greater resolution, particularly in studying smaller aspects of the tip of the orifice. Furthermore, in electron microscopies, the images that can be viewed may be non-flat, tilted or three-dimensional thus providing clear imagery of the cylindrical-conic sections as has been shown previously on similarly-fabricated electrodes [23].

Overall, through this experience, it is hoped other undergraduate classes achieve hands-on training in the rapidly-evolving electrochemical sensing research space as our students have been, while enjoying their experience as well. As evidence, two of the authors (ZN and SS) on this publications have gone onto commencing higher degree research endeavors, with one in electrochemistry (SS).

5. Conclusion

We propose herein an undergraduate activity in three parts, involving the development of physically small

carbon electrodes with tips in the nanometer range, and their microscopic and electrochemical characterization. In the first part of the activity, students pulled capillary tips using a laser puller and develop these into working electrodes by imparting a conducting layer of highly oriented pyrolytic graphite, connected through powdered graphite and finished off with a wire connector. In the second part, the students examine the electrode tips using optical microscopes and make comparative assessment of tip size. In the final part, the students subject the electrodes to chemical characterization using the well-known $[Ru(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$ redox markers. These steps *vide supra* are of course only applicable to in-lab prepared electrodes, and can be eliminated altogether with commercially-procured electrodes. Electrode functioning can be determined by exploiting the $[Ru(NH_3)_6]^{3+}$ complex reduction at the electrode surface. This is followed by subjecting functioning electrodes to electrochemistry of the $[Fe(CN)_6]^{3-}$ complex, which yields useful information on the reversibility and thermodynamics of the electrode surface. For modification, students apply a controlled reduction potential to the electrode in a solution of gold chloride to deposit AuNPs onto the electrode surface and repeat the $[Fe(CN)_6]^{3-}$ characterization. Changes in the waveslope and half-wave potential of the $[Fe(CN)_6]^{3-}$ redox peaks can provide useful information on the altered electrode surface that the students need to explain as part of their learning. The experiment encompasses materials science, electrochemistry and chemical kinetics. It provides students an opportunity to integrate concepts from these chemistry themes and apply them in a manner reflecting current electrochemistry directions.

Supporting Information

Experimental details, Instructor Guide with sample results and Student Guide. (DOC)

Experimental details, Instructor Guide with sample results and Student Guide. (PDF).

Notes

The authors declare no competing financial interest.

Acknowledgments

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