Fabrication of Metal Nanoparticle-Modified Screen Printed Carbon Electrodes for the Evaluation of Hydrogen Peroxide Content in Teeth Whitening Strips

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S *Supporting Information*

ABSTRACT: A laboratory experiment in which students synthesize Ag, Au, and Pt nanoparticles (NPs) and use them to modify screen printed carbon electrodes for the electroanalysis of the hydrogen peroxide content in commercially available teeth whitening strips is described. This experiment is designed for two 3-h laboratory periods and can be adapted for upper-division undergraduate students in instrumental analysis, materials science, or physical chemistry laboratories. The experiment presented has already been used as a hands-on component in a Functional Nanomaterials Course, which exposed students to the analysis of the electrochemical properties of metal nanoparticles. Moreover, it allows for teaching the basics of nanoparticle synthesis and enables students to learn the fundamentals of electrochemical sensing with nanostructured materials.

KEYWORDS: *Upper-Division Undergraduate, Analytical Chemistry, Instrumental Methods, Physical Chemistry, Hands-On Learning/Manipulatives, Colloids, Electrochemistry, Nanotechnology*
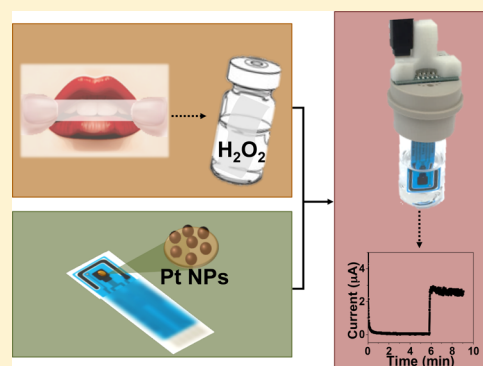
Nanomaterials are being explored for a wide range of applications in environmental,[1] biomedical,[2,3] and alternative energy technologies,[4] due to their unique physical, chemical, and electronic properties, which emerge from their nanoscale dimensions. In response to the continuous growth of nanotechnology, nanoscience concepts are being incorporated in the undergraduate curricula.[5−11] In addition to classes and seminar courses, several laboratory experiments have been developed with the intention of giving undergraduate students the opportunity of having hands-on experiences in the preparation and characterization of nanomaterials,[12−21] but only few undergraduate experiments have been developed that incorporate the use of nanomaterials for practical applications.[22−26] The aim of this laboratory experiment is to combine the teaching of the fundamentals of metal nanoparticle synthesis, electrochemistry concepts, and the use of metal nanoparticles in electrochemical sensing applications, such as the detection of hydrogen peroxide (H_2O_2).

H_2O_2 is an important analyte that is widely monitored in a diverse range of applications including disease diagnosis, environmental monitoring, food processing, and industrial manufacturing.[27−31] It is also involved in biological processes, intracellular pathways, and serves as an important oxidizing agent in organic synthesis and reactions.[32−34] Various analytical techniques for the determination of H_2O_2 like chromatography and chemiluminescence are costly, time-consuming, and may exhibit low sensitivity and selectivity.[35,36] It is therefore relevant to find alternative detection methods that are reliable, rapid, and cost-efficient.

The electroanalysis of H_2O_2 offers a simple, cost-efficient, rapid, and sensitive alternative technique. H_2O_2 is an electrochemically active species that can be oxidized or reduced at the surface of commonly adapted electrodes. However, the slow electrode kinetics on conventional electrode materials require large overpotentials, which place the detection window for H_2O_2 in the same potential range where interferences from electroactive compounds present in fluid samples, such as ascorbic and uric acid, are unavoidable. Recent advances in the development of electrochemical sensors revolve around the incorporation of nanomaterials in the electrode material in order to solve this problem. The nanostructuring of electrode materials provides a high active surface area that can significantly improve the electrocatalytic detection of bioactive molecules, such as H_2O_2.

Metal nanoparticles such as Ag, Au, and Pt have been widely studied for their use in the fabrication of electrochemical sensors for H_2O_2 detection.[37−40] In contrast to unmodified bulk carbon electrodes, the hybridization of metallic nanomaterials with carbon electrode materials has been shown to improve the detection of various electroactive analytes, as a result of the lowering of the overpotential of the redox species,

and in combination with the metal nanoparticles' high surface area.[37] In this regard, metal nanoparticle-modified carbon electrodes used in electroanalysis have been demonstrated to offer several advantages compared to unmodified carbon macroelectrodes: (a) large effective surface area, (b) high catalytic activity, (c) increased mass transport, and (d) improved control over the local environment at the electrode surface.[37,41]

A simple electroanalytical technique used for sensors is amperometry, in which a constant potential is applied to the working electrode and the current is measured as a function of time. Steady-state currents are achieved when amperometric measurements are performed under stirring conditions and Fick's first law of diffusion illustrates the relationship between the limiting current, i_{lim} (A), and analyte concentration, C (in mol/cm^3) according to the following equation:

$$i_{lim} = \frac{nFACD}{\delta} \qquad (1)$$

where n = number of electrons transferred, F = Faraday's constant (96 485 C/mol), A = area of the (planar) working electrode (cm^2), D = diffusion coefficient (cm^2/s), and δ = diffusion layer thickness (cm). The ratio D/δ is commonly referred to as the mass transport coefficient.

In this experiment, students will utilize metal nanoparticles that they will prepare in the laboratory for the electrochemical detection of H_2O_2 in commercially available teeth whitening strips, which typically contain 3−7% H_2O_2.

■ EXPERIMENTAL SECTION

The experiment is best divided between two 3-h laboratory periods with the Ag, Au, and Pt nanoparticle synthesis, electrode modification, and comparison of the electrochemical responses of the metal nanoparticle-modified electrodes to be conducted in the first laboratory period, and the analysis of the H_2O_2 concentration in commercially available teeth whitening strips in the second laboratory period.

Equipment and Materials

A portable potentiostat, compact cells (20 mL scintillation vials fitted with a custom cap), and screen printed carbon electrodes with 4 × 5 mm recessed rectangular working electrode, Ag/AgCl reference electrode and carbon reference electrodes are used for the electrochemical measurements. Different brands of commercially available teeth whitening strips are used for the hydrogen peroxide concentration determination.

Synthesis of Ag, Au, and Pt Nanoparticles (NPs)

A series of small sized Ag, Au, and Pt NPs are synthesized by reducing their respective metal salts with a strong reducing agent, followed by coating of the freshly formed NPs by a capping agent to prevent their agglomeration. Briefly, sodium borohydride is added to a solution of the metal salt (i.e., silver nitrate, $AgNO_3$, chloroauric acid, $HAuCl_4$, or chloroplatinic acid, H_2PtCl_6) and sodium citrate to generate the respective metal NPs (see Supporting Information for detailed experimental procedure). The formation of the metal NPs can be monitored by measuring the UV−vis absorption spectra of the synthesized nanomaterials, whereby both Ag and Au show characteristic absorption bands in the visible spectral range, while Pt does not exhibit an absorption peak in the monitored 300−1100 nm spectral wavelength range.

Modification of Screen Printed Electrodes

Different screen printed carbon electrodes (SPCEs) are separately modified with the previously prepared metal NPs by depositing 20 μL (with a micropipette) of the synthesized Ag, Au, or Pt NP solutions on the 4 × 5 mm working electrode pattern. The metal nanoparticle-modified SPCEs are then placed in an 80 °C oven for 10 min to allow the evaporation of the solvent. Careful transportation of the electrodes to the oven is necessary in order to ensure the solution remains solely in contact with the working electrode.

Whitening Strips Sample Preparation

Each whitening strip must be weighed before it is dissolved in 10 mL of deionized water and subsequently vortex mixed for approximately 1 min and allowed to rest for 4 min before testing.

Electrochemical Measurements

The electrolyte used for all electrochemical measurements is 10 mL of phosphate buffered saline solution (PBS, 1×, pH 7.4). The surface of the electrodes is cleaned in the buffer solution by cycling the electrode between −0.4 and 0.6 V (sweep rate of 200 mV/s, 25 cycles) to reduce the noise level during the amperometry measurements. The amperometric responses of the three types of modified SPCEs to the addition of increasing amounts of H_2O_2 at an applied potential of 0.345 V are recorded by the students and are used to obtain calibration curves.

■ HAZARDS

Standard procedures for safe handling of chemicals should be followed. Students must wear goggles, lab coats, and gloves at all times. Chloroauric and chloroplatinic acids are corrosive to the skin and must be handled with appropriate care as they may cause skin burns, eye damage, and irritation. Silver nitrate, chloroauric and chloroplatinic acids should be kept away from heat and light for extended periods of time. Sodium borohydride is hazardous in case of contact with skin, eyes, ingestion, or inhalation. In addition, H_2O_2 is irritating and corrosive in high concentrations (>10%) and can cause skin burns and ulceration. Inhalation of mist will cause irritation of lungs, throat, and nose that usually subsides after exposure has ended. Solutions of 3% or less may cause pain, but no damage. No waste generated during this lab experiment should be disposed down the drain. However, the supporting electrolyte buffer, spent electroanalysis solutions, and the remaining solution of the dissolved whitening strips could also be safely disposed down the drain.

## ■ RESULTS AND DISCUSSION

Synthesis of Ag, Au, and Pt NPs

The laboratory experiment described is suitable for undergraduate physical chemistry, instrumental analysis, or materials science courses, as it incorporates the synthesis, electrochemical analysis, and application of nanostructured materials. In addition to wet chemistry techniques (i.e., metal nanoparticle synthesis and analytical handling of chemical reagents), students are able to learn first-hand the changes in optical properties of metals when their size is reduced to the nanoscale regime, and the differences in optical properties of Ag, Au, and Pt nanoparticles, by measuring the UV−vis absorption spectra of the synthesized metal nanoparticles in solution. In addition, the students learn different electrochemical techniques (i.e.,
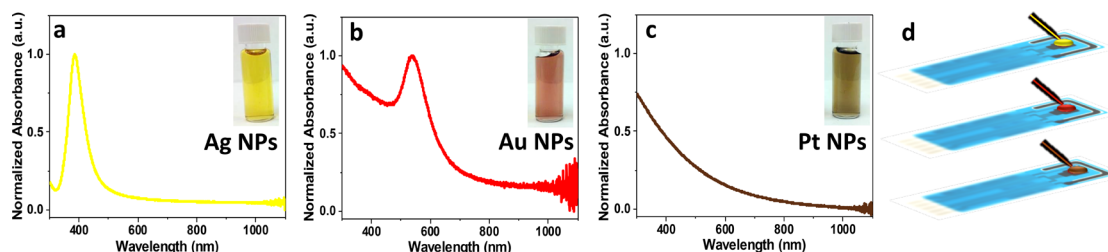
Figure 1. UV−vis absorption spectra and photographs of Ag, Au, and Pt NP solutions (a−c), respectively, and a schematic diagram of the corresponding modified screen printed carbon electrodes (d) used for the electrochemical detection of H_2O_2.
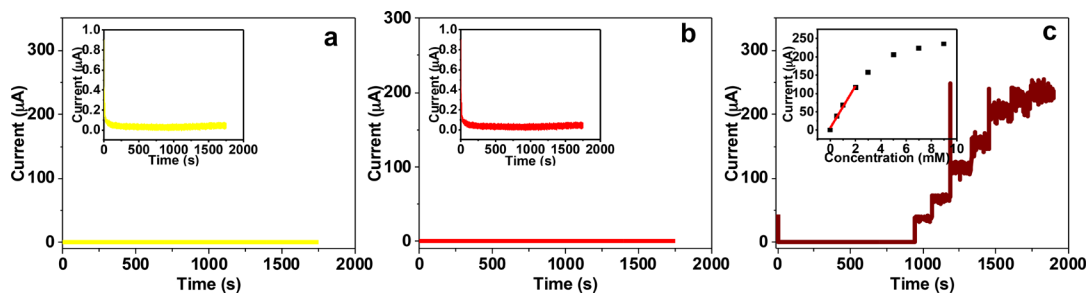
Figure 2. Amperometric responses of the Ag (a), Au (b), and Pt (c) NP-modified SPCEs upon the addition of increasing amounts of H_2O_2 into PBS (1×, pH 7.4) at an applied voltage of 0.345 V versus an internal Ag/AgCl reference electrode. The insets in (a) and (b) show a zoomed-in version of the electrochemical response curves for the corresponding modified SPCEs, while the inset in (c) shows the current vs concentration curve of the corresponding Pt NP-modified SPCE. The data presented were obtained by undergraduate students.
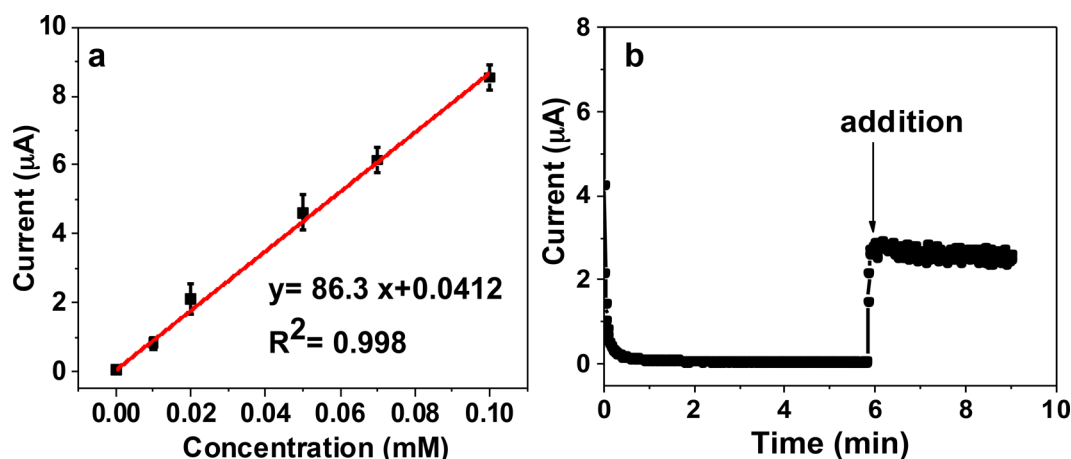
Figure 3. Calibration plot in the 0−0.1 mM H_2O_2 concentration range for Pt NP-modified SPCE with corresponding error bars obtained from five student trials (a), and typical Pt NP-modified SPCE response to the addition of 20 μL of a dissolved whitening strip solution (b).

fabrication of metal nanoparticle-modified carbon electrodes and amperometry electrochemical analysis) and data analysis methods (linear calibration and evaluation of sensor sensitivity, limit of detection, and limit of quantification).

Nanosized metal materials are formed at room temperature by the addition of sodium borohydride to a metal salt solution in the presence of sodium citrate. The sodium borohydride reduces the metal ions in solution and facilitates the formation of metal NPs that are stabilized by the sodium citrate surfactant. The success in the nanoparticle synthesis is indicated by the change in the resulting color of the reaction solutions, which can be monitored by evaluating the UV−vis absorption spectra of the resulting metal nanoparticle solutions (Figure 1a−c), where the Ag NPs show a strong absorption band at around 400 nm, the absorption band of Au appears around 520 nm, and Pt does not show an absorption peak in the 300−1100 nm spectral wavelength range. The nanoparticle solutions are then

used as-prepared for the modification of the screen printed carbon electrodes that will be used in the electrochemical detection of H_2O_2 (Figure 1d). In addition to the SPCEs used in this study, other common types of electrodes such as rotating disks electrodes (RDEs) can also be also be used and modified with metal NPs using the same drop cast method used in this study.

Detection of Hydrogen Peroxide

The modified SPCEs are then used for the electrochemical detection of H_2O_2 in solution. First, students explore the sensitivity of the different types of fabricated metal nanoparticle-modified electrodes to H_2O_2 detection using amperometric analysis. Amperometric measurements were performed while stirring the solutions in order to reach the steady-state current immediately. From eq 1, it is important to maintain the same stirring rate throughout the whole experiment since

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changes in stirring rate will modify δ and affect the current response.

Figure 2 shows typical amperometric responses of the modified SPCEs upon the addition of increasing amounts of H_2O_2 into PBS (1×, pH 7.4) at an applied voltage of 0.345 V versus an internal Ag/AgCl reference electrode. As H_2O_2 is added, the Pt NP-modified SPCEs respond rapidly to the analyte, achieving the maximum steady-state current response within a few seconds. On the other hand, no significant current responses are obtained from the Ag NP- and Au NP-modified SPCEs in the 0.5−9 mM H_2O_2 concentration range utilized in the experiment.

When the current measured versus the concentration of H_2O_2 from the amperometry measurements acquired using the Pt NP-modified SPCE is plotted, a curve as shown in the inset of Figure 2c is obtained (see Supporting Information for step-by-step guide to data analysis). The curvature indicates that the sensor linearity is limited to below 2 mM H_2O_2 concentrations.

Detection of Hydrogen Peroxide in Whitening Strips

During the second laboratory period, students work with Pt NP-modified SPCEs to obtain a calibration curve in the 0−0.1 mM H_2O_2 range, within which their unknown H_2O_2 sample concentration from the dissolved whitening strips is expected to fall. This procedure allows students to determine sensor parameters, such as sensitivity, limit of detection, and limit of quantification, as well as parameters such as relative standard deviation for each concentration, based on the analysis of different students in the class. Deviations among results from different students allow discussions about error sources and sensor reproducibility. Figure 3a shows a calibration plot in the 0−0.1 mM H_2O_2 concentration range with the evaluated error bars from an average of five student trials. The sensitivity of the Pt NP-modified SPCE was calculated from the averaged data to be 433 μA/mM cm^2 with a 6.60 × 10^{-6} M limit of detection. After the amperometric measurements required for the calibration plot are completed, students measure their assigned commercial sample (dissolved whitening strip), by adding 20 μL of the dissolved whitening strip solution to 10 mL of PBS (1×, pH 7.4). Figure 3b shows a typical amperometric response of the modified electrode to the whitening strip solution addition. With the use of the previously obtained calibration curve, students can determine the H_2O_2 concentration and % H_2O_2 in a strip.

Moreover, the collective data can be used to further engage students by comparing different brands of dissolving whitening strips, be it by percent of H_2O_2 per strip or amount of H_2O_2 per dollar.

CONCLUSIONS

This experiment provides higher level undergraduate students with the opportunity of first-hand experiences with nanomaterials, from synthesis to practical applications. Students learn several important concepts: (a) the fundamentals of metal nanoparticle synthesis, (b) the basics of electrochemical analysis, (c) the effect of nanomaterial modification on the electrode response, (d) the determination of analyte concentration using an electrochemical sensor, and (e) data analysis. In particular, the evaluation of the teeth whitening strips and their comparison by brand/price will draw student's interest to the practicality of this experiment. In addition, this experiment only requires a potentiostat, inexpensive single-use screen printed carbon electrodes, and microliter amounts of dilute

metal salt solutions of Ag, Au, and Pt. In addition, common laboratory reagents are utilized (PBS solution, citric acid surfactant, and sodium borohydride reducing agent). This experiment can be easily incorporated into an undergraduate physical chemistry, instrumental analysis, or materials science laboratory within two 3-h lab periods.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00096.

> Instructor notes, detailed procedures, CAS numbers, pre- and postlab assessments, and additional data(PDF, DOCX)

> Student handouts, detailed procedures, CAS numbers, pre- and postlab assessments, and additional data (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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