Concentration Effect on the Electron Transfer Between Ferricyanide and Ferroceneated Gold

Rachel Wampler, Chemistry

Mentor: Dr. Peng Sun

Kellogg Honors College Capstone Project

Abstract

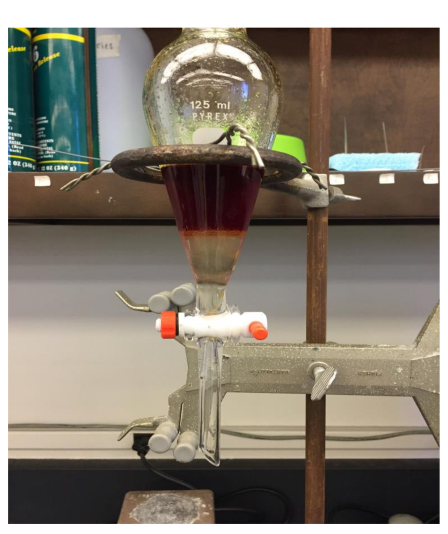
Nanomaterials have been widely used in electrochemical sensors[1]. This is because many nanomaterials are electroactive. To understand the sensing mechanism, one must understand how electrons are transferred between nanomaterials and analyte molecules. The voltammetry, an electroanalytical method, can be used to determine the electron transfer mechanism. This experiment uses cyclic voltammetry to study the mechanism of electron transfer between an electroactive gold nanoparticle[2] and ferricyanide. Using three different dilution ratios, 1:1, 1:2, and 1:5, the voltammograms of each plot, within the same scan rate, were overlaid. As the gold nanoparticle becomes more diluted, the current analyzed decreases proportionally, which means the concentration of electroactive gold nanoparticle is the current determining factor. This research is the first step toward a long-term goal of study the mechanism of electron transfer kinetics of nanomaterials.

Experimental

Synthesis of Nanoparticles

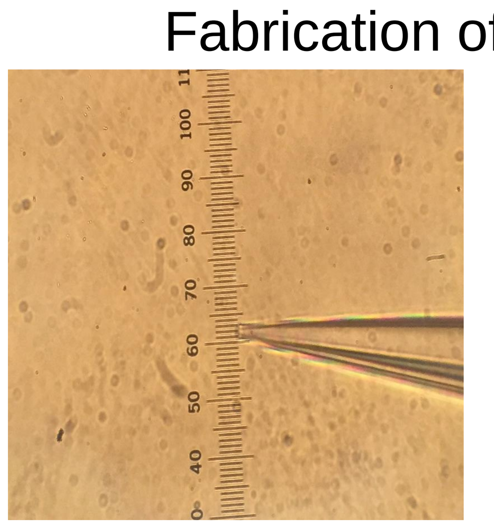
$$H^{+}AuCl_4^{-}(aq) + (R_8)_4N^{+}Br^{-}(org) \rightarrow (R_8)_4N^{+}AuX_4^{-}(org) + HX(aq)$$

Phase transfer of chloric acid → Addition of thiol → Addition of reducing agent



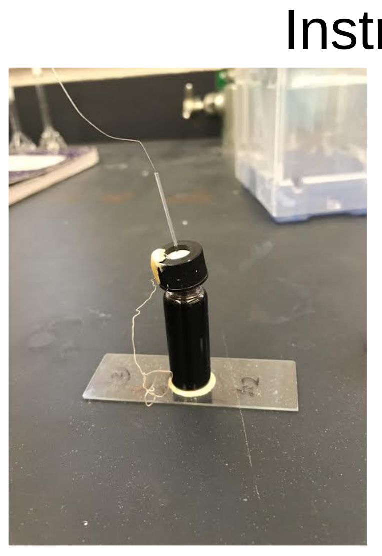
In this picture, the clear, light yellow layer defines the aqueous layer, while the non-aqueous layer is the clear, dark red solution on top. The aqueous layer was discarded while the non-aqueous layer was then placed in a suction pump apparatus.

Fabrication of Glass Pipets



In this figure, a 3-micrometer pipet is shown. This pipet was kept and was used for the voltammetric study of the gold nanoparticle.

Instrumentation



In this picture, the electrochemical cell is shown. The platinum wire was inserted into the measured glass pipet, which was filled with the 1-millimolar solution of Potassium Ferricyanide and Ferrorocyanide.

Results and Discussion

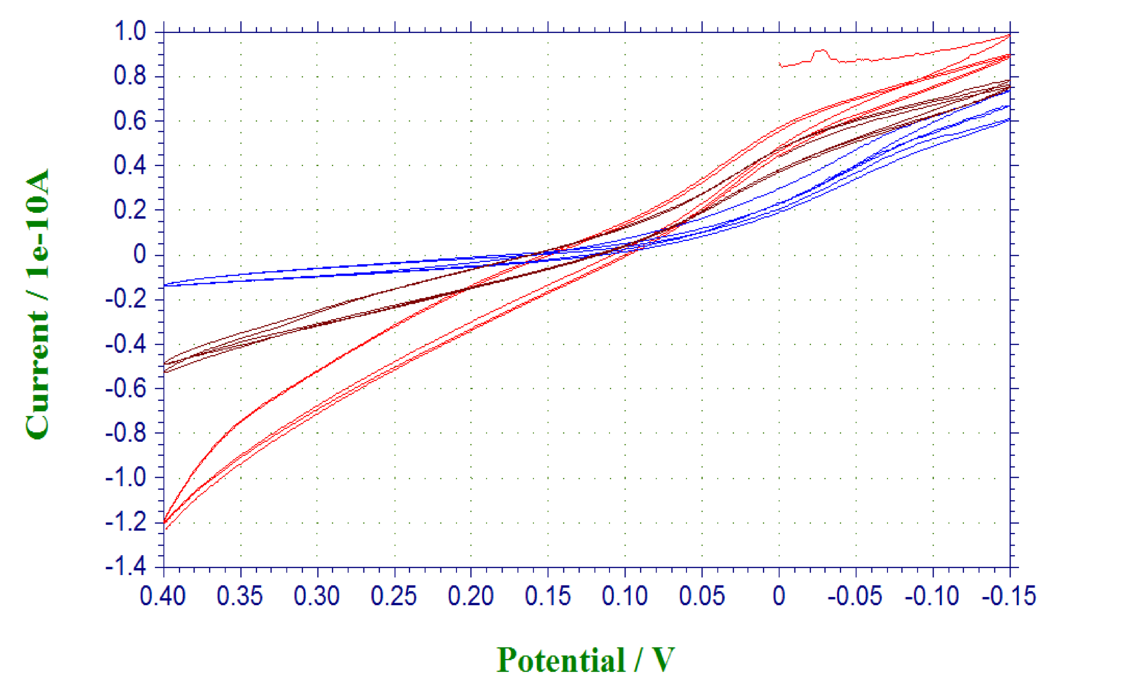


Figure 1: Overlay of cyclic voltammograms on the same pipette in solutions with different dilutions. The red curve represents the pure nanoparticle solution. The brown curve represents the 1:2 dilution, and the 1:5 dilution is represented by the blue curve. Each of these scans is at the 0.5 V/s. The switching potentials are -0.15 and 0.40.

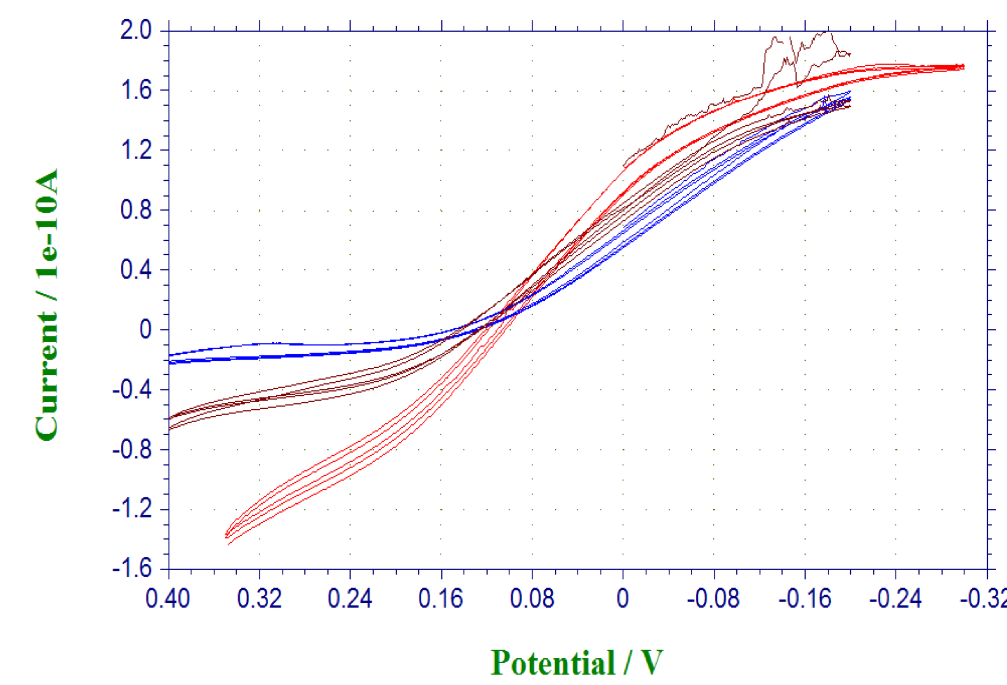


Figure 2: The cyclic voltammetric curves are analyzed an overlaid. The red curve represents the pure nanoparticle solution. The brown curve represents the 1:2 dilution, and the 1:5 dilution is represented by the blue curve. Each of these scans is at the 0.3 V/s. The switching potentials are -0.3 and 0.35.

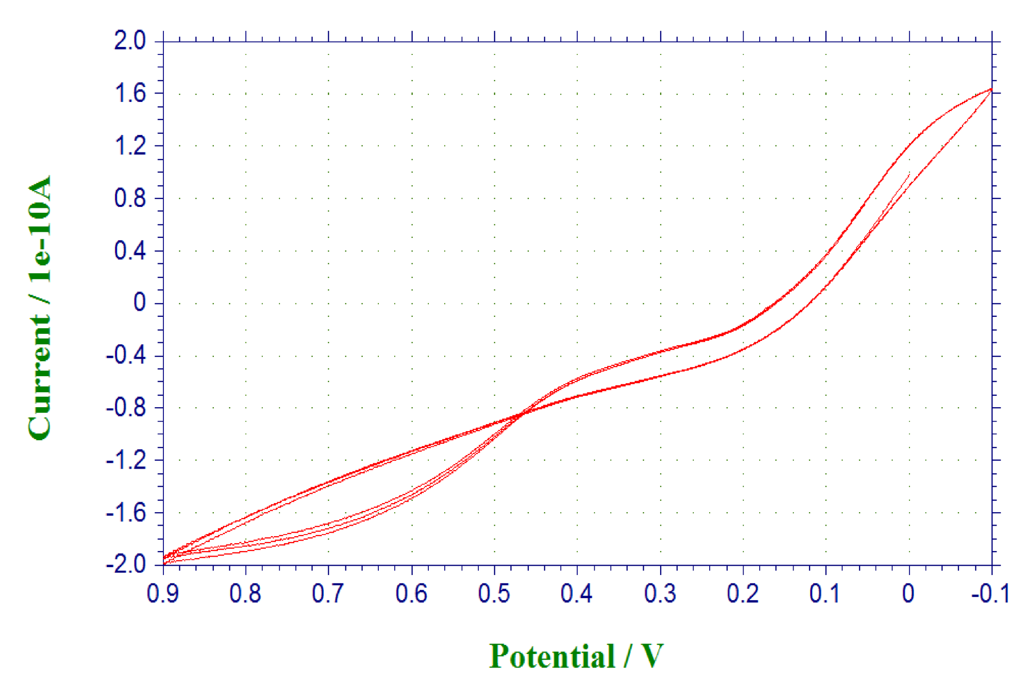
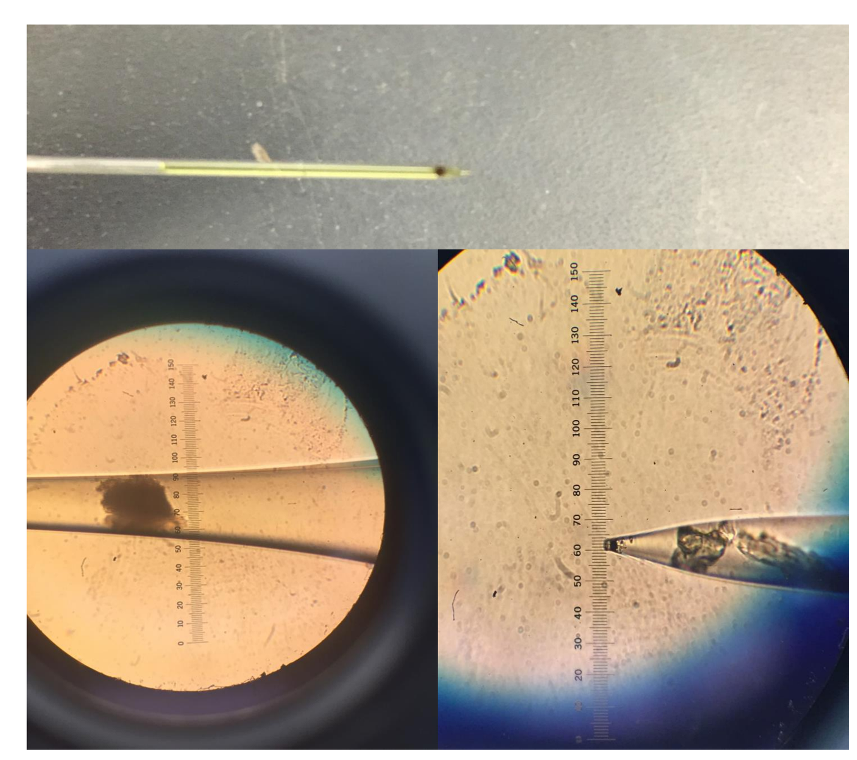
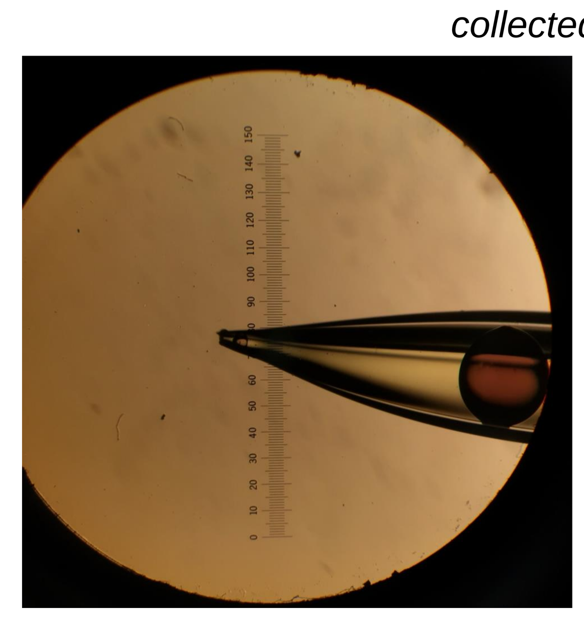


Figure 3: Voltammograms obtained on the following cell: Ag/1:5 dilution of the electroactive gold nanoparticle in DCM solution/1mM Ferrocyanide and Ferricyanide/Pt. Pipette radius: 5-micrometer; scan rate 0. 05 V/s. The irregular shape is shown above.



These pictures depict multiple pipets that have collected dust after the scanning process. This pipet has a large, bulky collection of dust particles at the tip. It leads to noisy voltammetric curves with extra intersections. The mass collected at the tip is visible without a microscope.



In this pipet a red bubble had appeared after the completion of the voltammetric set. The bubble is distinctly seen in the yellow Potassium Ferricyanide and Ferrorocyanide solution because of the noticeable color difference.

References

(1) Zhu, C.; Yang, G.; Li, H.; Du, D.; Lin, Y. *Anal. Chem.* **2015**, *87* (1), 230–249.

(1) Brust, M.; Fink, J.; Bethell, D.; Schiffrin, D. J.; Kiely, C. *J. Chem. Soc., Chem. Commun.* **1995**, No. 16, 1655–1656.