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Development and Application of Cu-Modified Carbon Electrodes from Pyrolyzed Paper Strips

Gema M. Durán
Clemson University

Tomás E. Benavidez
Clemson University

Jason Giuliani
Clemson University

Ángel Ríos
Clemson University

Carlos D. Garcia
Clemson University

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Gema M. Durán, Tomás E. Benavidez, Jason Giuliani, Ángel Ríos, and Carlos D. Garcia
Department of Chemistry, Clemson University | cdgarci@clemson.edu
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Abstract

A one-step approach for the synthesis and integration of copper nanoparticles (CuNPs) onto paper-based carbon electrodes is herein reported. The method is based on the pyrolysis (1000 ºC under a mixture of 95% Ar / 5% H_2 for 1 hour) of paper strips modified with a saturated solution of $CuSO_4$ and yields to the formation of abundant CuNPs on the surface of carbonized cellulose fibers. The resulting substrates were characterized by a combination of scanning electron microscopy, EDX, Raman spectroscopy as well as electrical and electrochemical techniques. Their potential application, as working electrodes for non-enzymatic amperometric determination of glucose, was then demonstrated (linear response up to 3 µM and a sensitivity of 460 ± 8 $\mu A \cdot cm^{-2} \cdot mM^{-1}$). Besides being a simple and inexpensive process for the development of electrochemically active substrates, this approach opens new possibilities for the in-situ synthesis of metallic nanoparticles without the traditional requirements of solutions and adjuvants.

Electrode Fabrication

- Paper strips (JP40 filter paper, 80 $g \cdot m^{-2}$) of 1.5 cm x 3.5 cm were soaked in a solution containing $CuSO_4$, were placed between two silicon wafers, dried in a convection oven (at 100 ºC for 2 h), and then transferred to a tube furnace (Type F21100, Barnstead-Thermolyne; Dubuque, IA, USA)
- Samples were pyrolyzed with forming gas (5% H_2 / 95% Ar, 1 $L \cdot min^{-1}$) at 1000 ºC during 1 h
- CuNPs@CE were patterned using a commercial CO_2 laser engraver (Mini24, Epilog Laser Systems; Golden, CO, USA) and then fixed to a Plexiglas substrate using double-sided tape, defining electrodes with a geometric area of 0.385 cm^2

Catalytic mechanism

Incipient Hydrous Oxide Adatom Mediator model: active metal atoms on the electrode surface that undergo a pre-monolayer oxidation step, and could mediate the oxidation of glucose at the electrode surface

$$Cu^{2+} + 2OH^- \rightarrow CuO + H_2O + 2e^-$$

$$CuO + OH^- \rightarrow CuOOH + e^-$$

$$CuO + H_2O + 2OH^- \rightarrow Cu(OH)_4^- + e^-$$

$$Cu_{(III)} + \text{glucose} \rightarrow gluconolactone + Cu_{(II)}$$

$$gluconolactone \xrightarrow{hydrolysis} gluconic\ acid$$

Electrode Characterization and Electrochemical Response

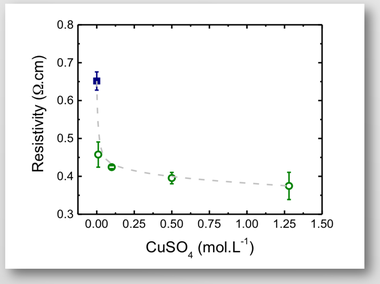

Figure 1: Effect of the concentration fo CuSO4. Resistivity of the pyrolyzed paper without CuNPs (■) and the CuNPs-modified carbonized paper (○)

Figure 2: Surface topography. SEM micrographs of pyrolyzed paper fibers modified with of CuNPs

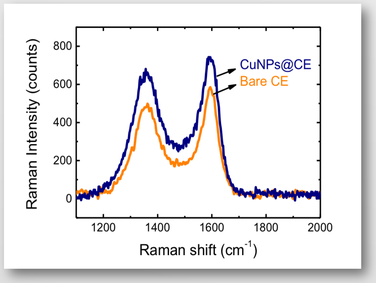

Figure 3: Substrate composition. Raman spectra obtained from pyrolyzed paper and CuNPs-modified pyrolyzed paper.

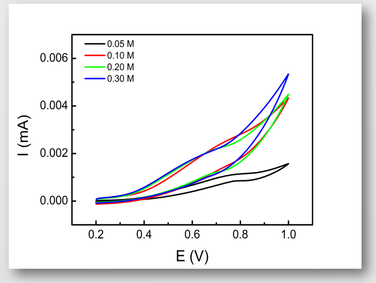

Figure 4: Effect of pH on the electrochemical response. Cyclic voltammetry of CuNPs@CE in NaOH solution at different concentrations containing 10 mM of glucose. Scan rate = 50 $mV \cdot s^{-1}$.

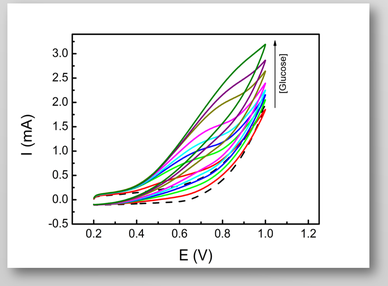

Figure 5: Effect of glucose concentration on the electrochemical response. Cyclic voltammetry of CuNPs@CE in absence (dash grey line) and presence of glucose at concentrations 1, 3, and 5 mM. Conditions: scan rate = 50 $mV \cdot s^{-1}$, 100 mM NaOH.

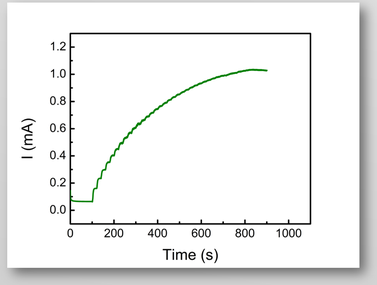

Figure 6: Chronoamperometric response of CuNPs@CE. Experiments carried out at +0.65 V (versus $Ag|AgCl|KCl_{(sat)}$) by adding known amounts of glucose into 100 mM NaOH solution under continuous stirring.

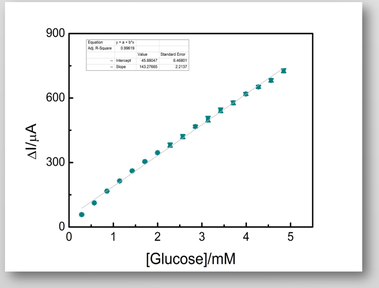

Figure 7: Calibration curve of glucose performed with the CuNPs@CE. Data points and error bars (contained within the data points) represent the average and standard deviation calculated by using four different electrodes

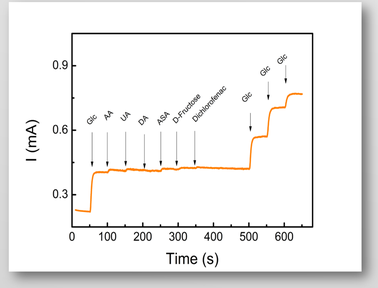

Figure 8: Response to interferences. Amperometric response of CuNPs@CE at +0.65 V upon addition of 1 mM Glu and selected interfering species as indicated. As control, two additions of 1 mM Glu and one addition of 0.5 mM Glu were performed under continuous stirring

Application to Real Samples

Reported value	610.6 mM	676.2 mM	0 mM	0 mM
CuNP	643.9 mM	686.2 mM	0 mM	0 mM
Agreement	105.5%	101.5%	100%	100%

Table 1. Determination of glucose in several beverage samples.

Conclusions

- Simple approach for the development and fabrication of CuNPs@CE
- Material was characterized by a combination of techniques (resistivity, microscopy, Raman spectroscopy, cyclic voltammetry, and electrochemical impedance)
- Electrodes succesfully applied for the analysis of glucose in beverages with adequate sensitivity and selectivity

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