COPPER-BASED MATERIALS - NEW "GREEN" ELECTROCHEMICAL SENSORS FOR HYDROGEN PEROXIDE

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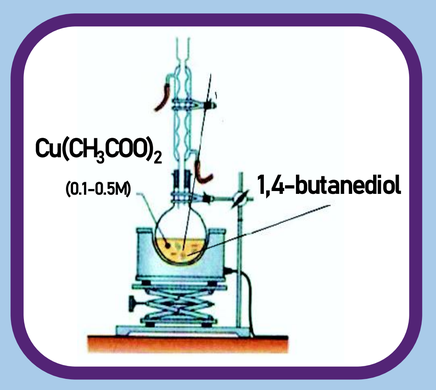
Introduction

The obtaining of new "green" and sustainable electrochemical sensors for physiologically relevant electro-active analytes is challenging and stimulating. Copper is well-suited for designing electrochemical sensors, being highly reactive in electrocatalytic reactions (one-two electron pathway) [1]. Polyols are the main source of oxygen for the formation of metal oxides, their specific properties (polarity, viscosity, and saturated vapour pressure) influencing the nucleation process, crystal growth, particle shapes, crystallite sizes and, therefore, their further aggregation into higher dimensional assemblies [2]. Herein, we report on four new copper-based compounds obtained through polyol-based approach. Depending on the reaction parameters (precursor concentration, time/temperature of reaction), $Cu^{II}O$, mixtures $Cu^{II}O/Cu_2^{I}O$ and $Cu_2^{I}O/Cu^{0}$ and metallic copper nanoparticles were obtained. Their optical, morpho-structural, textural and electrochemical properties will be discussed.

Synthesis



140°C/180°C
6-12h

Cu^{I}_2O — Cubic

$Cu^{II}O$ — Monoclinic

CuNPs

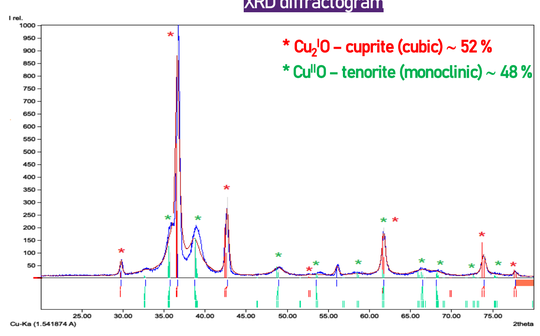
Results

1 $Cu^{II}O/Cu_2^{I}O$ — 0.25M/140°C/6h

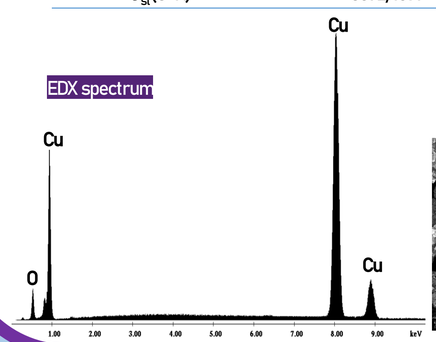
FTIR band assignments

Assigned vibrations	Wavenumber (cm^{-1})
$\upsilon(Cu^{II}-O)$	523/450
$\upsilon(Cu^{I}-O)$	633
$\upsilon(C-OH)$	1052
$\upsilon_{st}(COO)_{asym/sym}$	1736 /1411
$\upsilon_{st}(C-H)$	2935/2837
$\upsilon_{st}(O-H)$	3692/1677

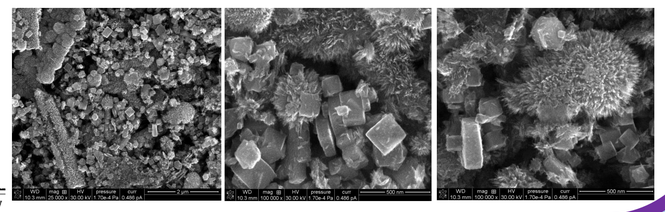
XRD diffractogram



EDX spectrum

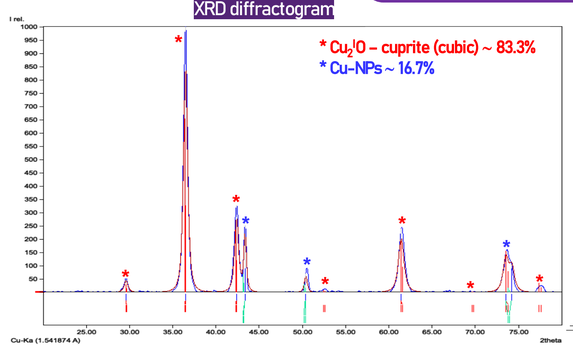


SEM micrographs

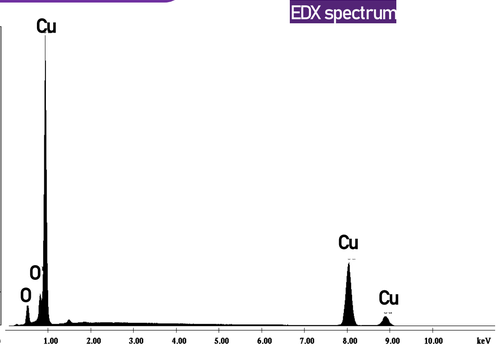


2 $Cu_2^{I}O/Cu^{0}$ — 0.25M/140°C/9h

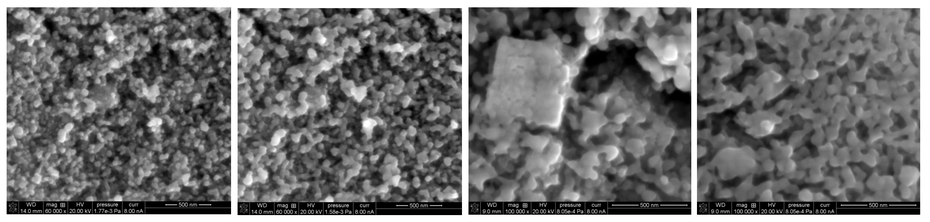
XRD diffractogram



EDX spectrum

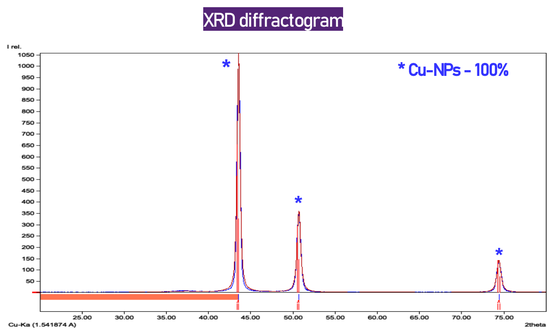


SEM micrographs

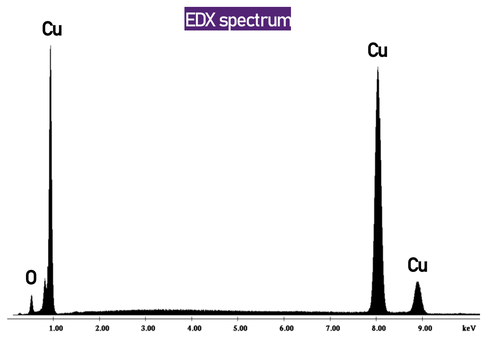


3 CuNPs — 0.1M/180°C/6h

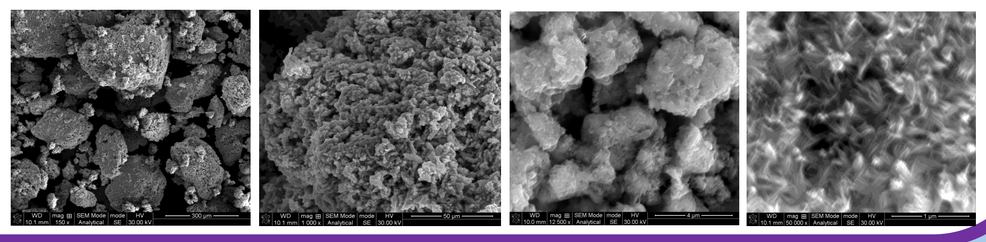
XRD diffractogram



EDX spectrum



SEM micrographs

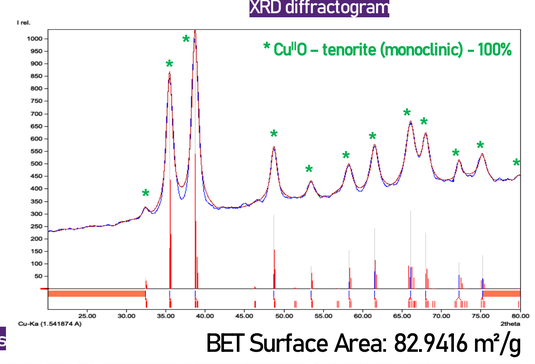


4 $Cu^{II}O$ — 0.5M/140°C/6h

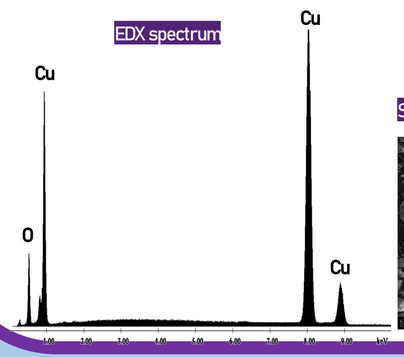
FTIR band assignments

Assigned vibrations	Wavenumber (cm^{-1})
$\upsilon(Cu^{II}-O)$	458/526/586
$\upsilon(C-OH)$	1051
$\upsilon_{st}(COO)_{asym/sym}$	1731 /1417
$\upsilon_{st}(C-H)$	2933/2870
$\upsilon_{st}(O-H)$	3419 /1633

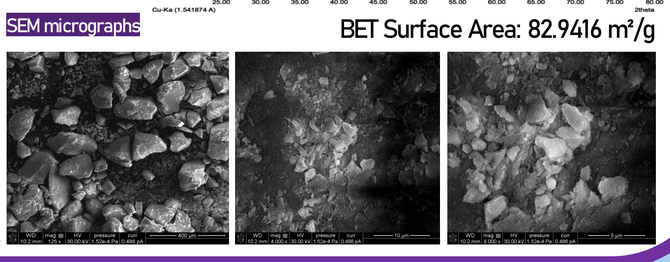
XRD diffractogram



EDX spectrum



SEM micrographs

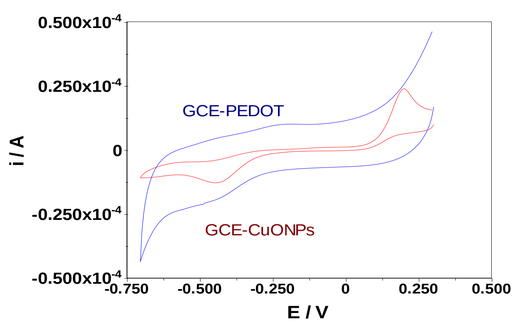


BET Surface Area: 82.9416 m^2/g

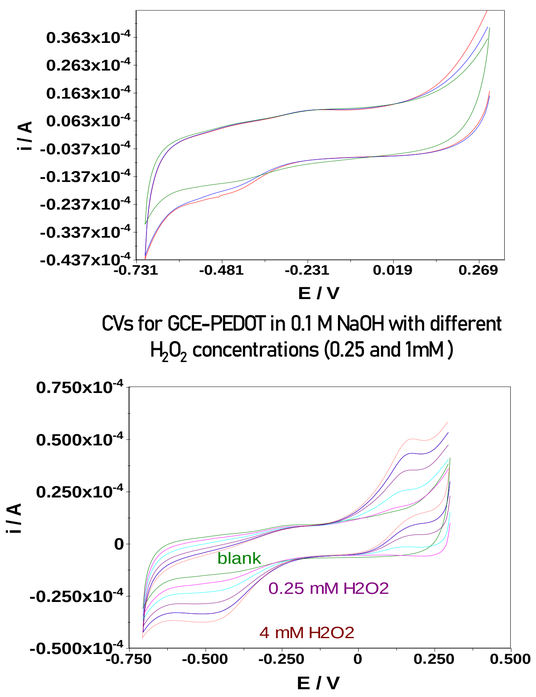
Electrochemical Study

Electrochemical measurements were performed with an Autolab PGSTAT 302N (Ecochemie) potentiostat controlled by GPES 4.9 electrochemical software from Eco-Chemie (The Netherlands) and connected to a three-electrode cell. All experiments were carried out at room temperature. Glassy Carbon electrodes (GCE) (Metrohm) with a 3-mm diameter were used as working electrodes, while a glassy carbon rod was used as a counter electrode. As reference it was employed a Ag/AgCl electrode.

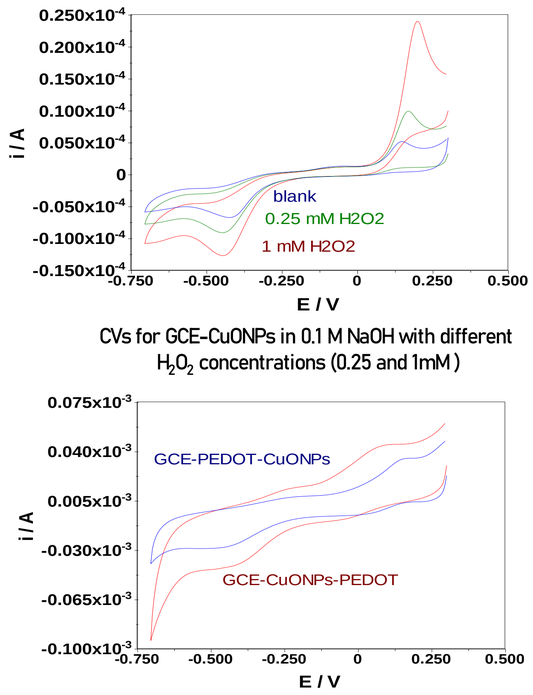
Electrochemical methods such as cyclic voltammetry (CV), differential pulse voltammetry and electrochemical impedance spectroscopy (EIS) were used in the development and characterization of the sensors.



CVs for GCE-CuONPs and GCE-PEDOT in 0.1 M NaOH with 1 mM H_2O_2

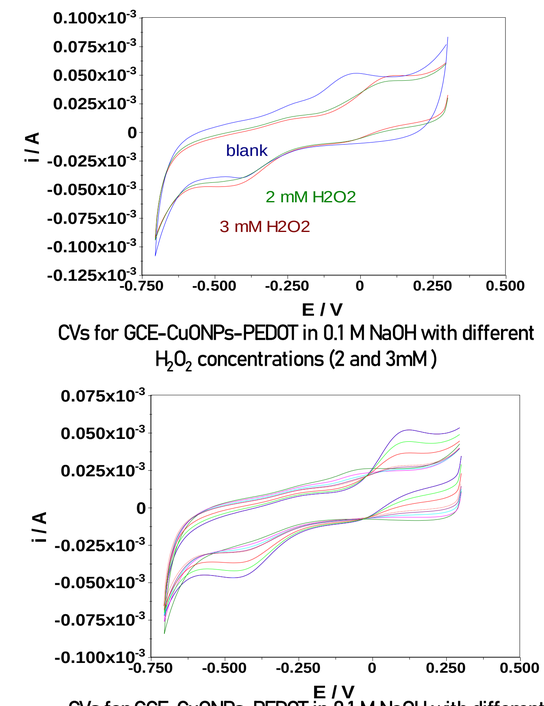


CVs for GCE-PEDOT-CuONPs in 0.1 M NaOH with 0.25, 1, 2, 3, and 4 mM H_2O_2



CVs for GCE-CuONPs in 0.1 M NaOH with different H_2O_2 concentrations (0.25 and 1mM)

CVs for GCE-PEDOT-CuONPs and GCE-CuONPs -PEDOT in 0.1 M NaOH containing 2 mM H_2O_2



CVs for GCE-CuONPs-PEDOT in 0.1 M NaOH with different H_2O_2 concentrations (2 and 3mM)

CVs for GCE-CuONPs-PEDOT in 0.1 M NaOH with different H_2O_2 concentrations (0.25, 0.5, 0.75, 1, 2, 3, and 4mM)

Conclusions

Copper-based particles were obtained through polyol-assisted method showing different compositions ($Cu^{II}O$, $Cu^{II}O/Cu_2^{I}O$, $Cu_2^{I}O/Cu^{0}$, CuNPs) and morpho-structural properties, depending on reaction parameters. CuO nanoparticles proved to be a stable and electrochemically active toward hydrogen peroxide reduction.

Acknowledgements

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References

[1] Verma, N., Kumar, N., ACS Biomater. Sci. Eng., 5 (2019), 1170.

[2] Dong, H., Chen, Y.-C., Feldmann, C., Green Chem., 17 (2015), 4107.