STUDY OF THE SELECTIVITY OF COPPER NANOPARTICLES IN THE ELECTROCATALYTIC REDUCTION OF CO_2 TOWARDS PRODUCTS OF BIOTECHNOLOGICAL INTEREST

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One of the greatest challenges facing humanity is climate change, which is mainly caused by anthropogenic CO_2 emissions. According to the World Meteorological Organization (WMO), United Nations, the average global temperature recorded in 2021 was 1.11 (±0.13) °C higher than pre-industrial levels (1850-1900). The 2021 was the seventh consecutive year, period 2015-2021, in which the global temperature was 1 °C higher than pre-industrial levels [1]. so innovative solutions are needed for sustainable development by converting a greenhouse gas into high-value and biologically compatible products, such as formic acid (FA), which is used as an additive in silage processes to improve its nutritional value, as an additive in feed, as a food preservative, and in flavor enhancer formulations. In the manufacturing industry, it is used as an acidulant in textile dyeing and finishing, leather tanning, wool dyeing, the preparation of organic esters, the manufacture of pesticides, electroplating, as an antiseptic in wine and beer making, and as a coagulant for rubber latex [2-3]. Due to the unique properties of nanomaterials, which offer a wide range of applications in the environmental, agricultural, food and energy sectors, it is possible to develop nanoparticles (NPs) that can be used as catalysts in the selective electrocatalytic conversion of CO_2. Copper nanoparticles (CuNPs) have emerged as promising electrocatalysts for the conversion of CO_2 into reusable C_1-C_2 products [4,5], and the synthesis process does not generate any polluting products to water bodies. In the following work we present some results of the electrochemical synthesis of copper NPs with sacrificial anode [6], using sodium dodecyl sulfate (SDS) and trisodium citrate dihydrate as stabilizers at 2.5% w/v in 40% EtOH/H2O at -0.5 mA. The obtained nanoparticles were characterized by Dynamic Light Scattering (DLS), UV-Visible and electrochemically using Cyclic Voltammetry (CV) [7]. The obtained NPs show average sizes around 10 nm according to DLS measurements and the UV-Visible results show the absorbances with a slight increase in the range of 400 - 650 nm which have been reported in the literature as signals corresponding to Cu^0, and around 200 nm the signals correspond to copper oxides, this is expected since the nanoparticles are obtained in an aqueous medium and therefore they tend to oxidize [8-9]. Through the study by Cyclic Voltammetry, using a 0.1M sodium nitrate solution and an Ag/AgCl electrode as a reference electrode, it is possible to observe that the nanoparticles stabilized with SDS, seem to favor the hydrogen evolution reaction (REH) and in turn the CO_2 reduction reaction ($RREHCO_3$) compared to the NPs synthesized with trisodium citrate dihydrate, in turn the characteristic peaks of the copper redox processes are shown. Once characterized, the copper nanoparticles were used for the electroreduction of CO_2, using a reduction potential of -1.25V in a 0.5 M $KHCO_3$ solution acidified with a phosphate buffer solution at pH 7, saturated with CO_2 for 30 min; Using Differential Pulse Voltammetry (DPV), the formation of formic acid—a key raw material for bioprocesses such as microbial fermentations and renewable hydrogen storage—was identified during the first 30 minutes of reaction. SDS-stabilized nanoparticles provided the highest conversion efficiency during this time period. The stability and selectivity of these nanoparticles under aqueous conditions highlight their potential for scalable bioelectrochemical systems, connecting CO_2 valorization with biotechnology.

References

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Figures

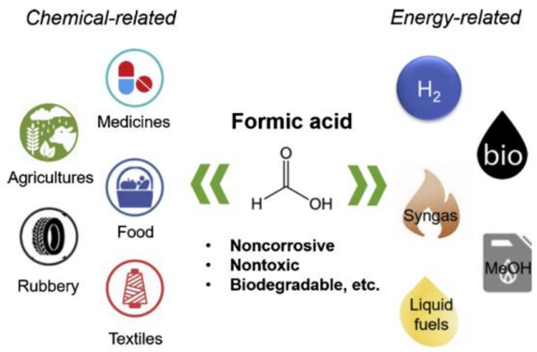

Figure 1. The wide applications of FA in chemical- and energy-related fields [3].

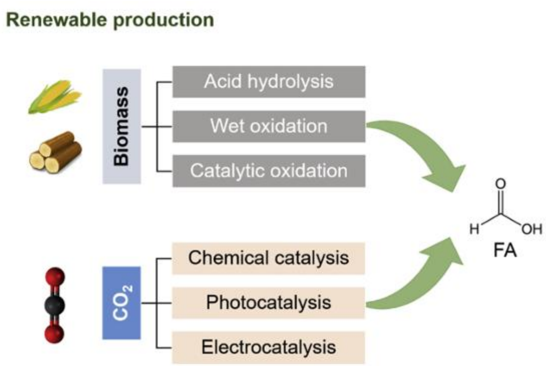

Figure 2. The current industrial production of FA from non-renewable feedstock (top) and the renewable production of FA from biomass and CO2 (bottom) [3].

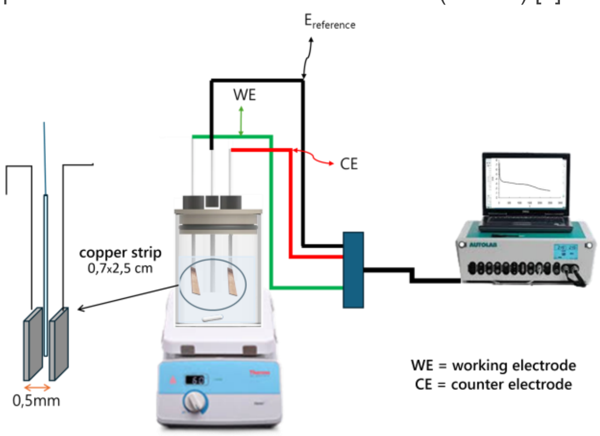

Figure 3. Diagram of the experimental setup for the electrochemical synthesis of copper nanoparticles.

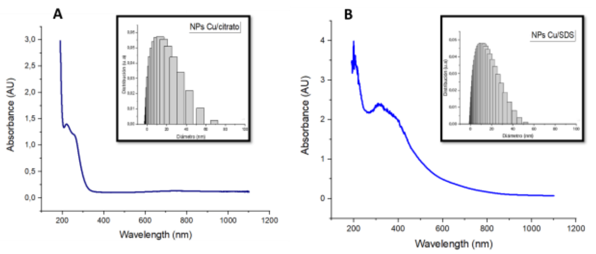

Figure 4. UV-Vis spectra and size distribution for the nanoparticles synthesized with different stabilizers: A) SDS and B) trisodium citrate dihydrate at 2.5% W/V EtOH/H_2O 40%.

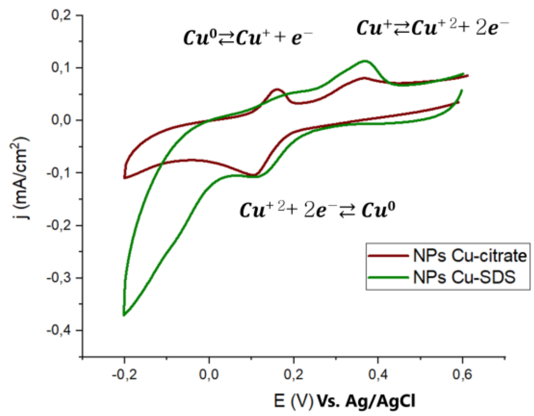

Figure 5. Cyclic voltammogram of Cu NPs synthesized with different stabilizers in 0.1M $NaNO_3$ at 20mV/s measured with an Ag/AgCl electrode as reference.

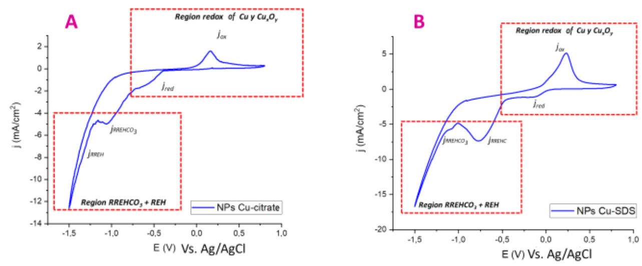

Figure 6. Cyclic voltammogram of: A) Cu-SDS NPs and B) Cu-citrate, for the reduction of CO_2 in a 0.5M $KHCO_3$ solution acidified with a pH 7 phosphate buffer and saturated with CO_2, at 20mV/s measured with an Ag/AgCl electrode as reference.

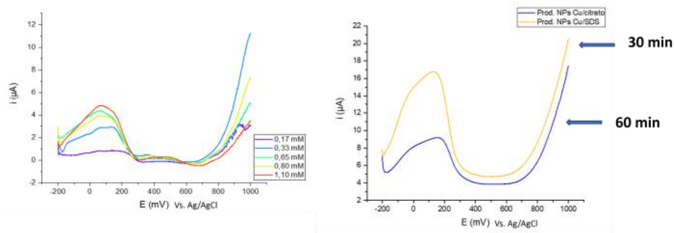

Figure 7. DPV obtained for the product of the CO_2 reduction reaction using Cu/citrate NPs and Cu/SDS NPs, in 0.5 M $KHCO_3$, acidified with phosphate buffer pH 7, purged with Ar and saturated with CO_2, measured with a Pt microelectrode.