

# SYNTHESIS OF NANOSTRUCTURED ELECTRODES FOR THE CATALYTIC ELECTROREDUCTION OF CO<sub>2</sub>

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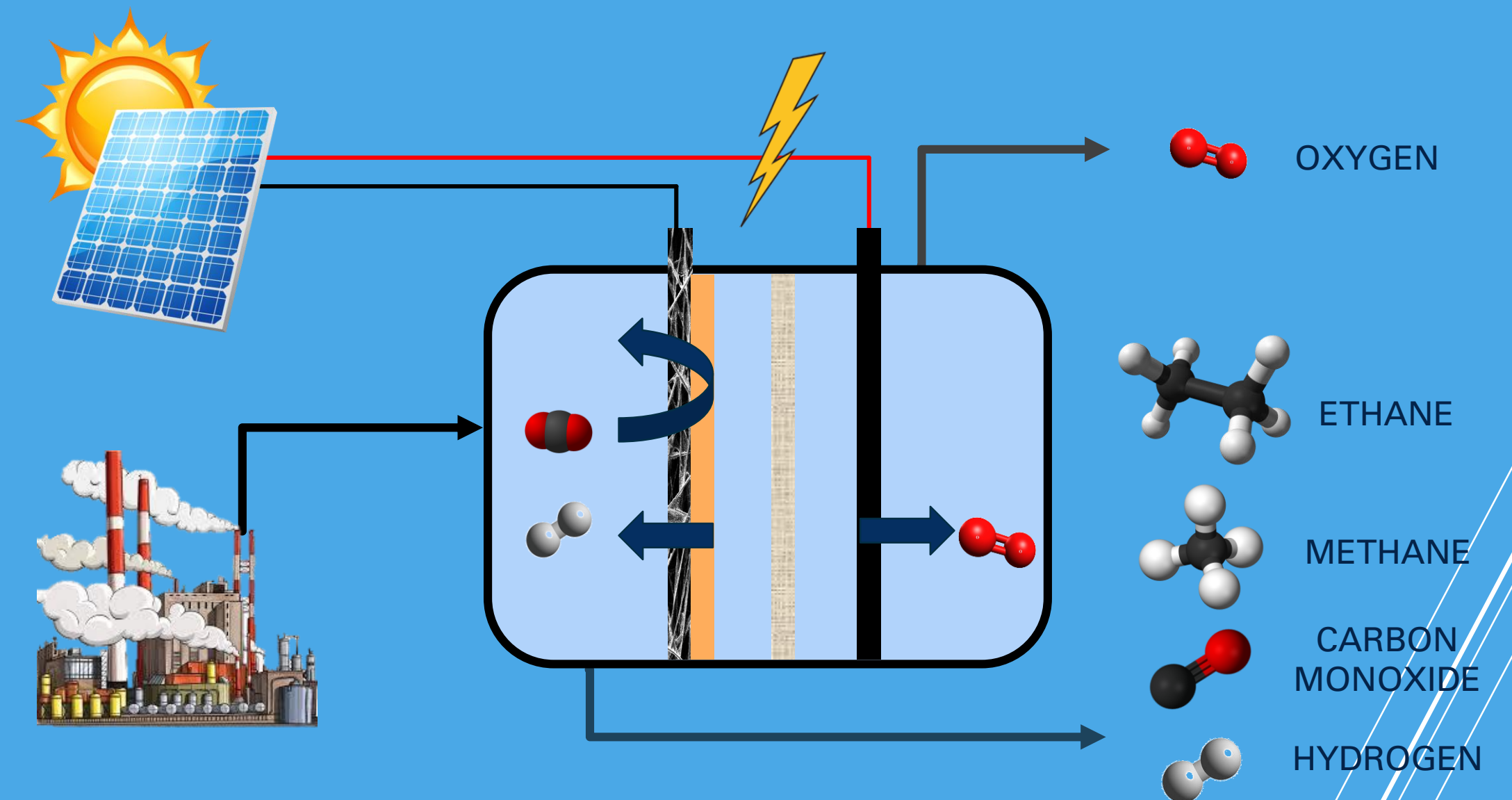
## INTRODUCTION

Environmental emissions caused by the combustion of fossil fuels had been widely linked to global warming processes. Renewable energy sources could be an effective alternative but, due to their intermittent nature, they require extensive and complex accumulation systems.

A promising solution is represented by the electroreduction of carbon dioxide (ERCO<sub>2</sub>), where CO<sub>2</sub> is electrochemically reduced to produce chemical products and fuels. This process could allow the simultaneous abatement of CO<sub>2</sub> emissions and the storage of renewable-based energy. ERCO<sub>2</sub> is characterized by the wide amount of possible products, mostly carbon monoxide (used as syngas) and C1-C3 hydrocarbons. In order to reach exploitable grades of conversion and selectivity, ERCO<sub>2</sub> requires catalytic electrodes.

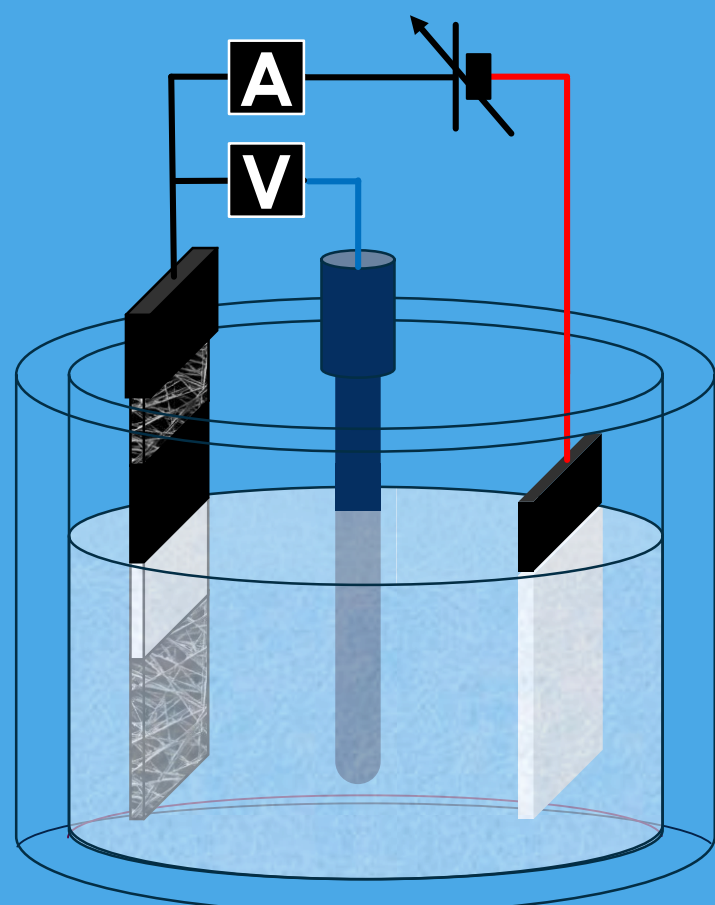
In this study, we evaluate the synthesis and the catalytic properties of nanostructured metallic electrodes. Our catalysts are composed of a micrometric layer of nanoengineered copper supported on a conductive, gas permeable surface made of carbon paper (Cpap).

The role of synthesis conditions was analyzed in order to tune the electrodes nanostructure and thus their catalytic activity.

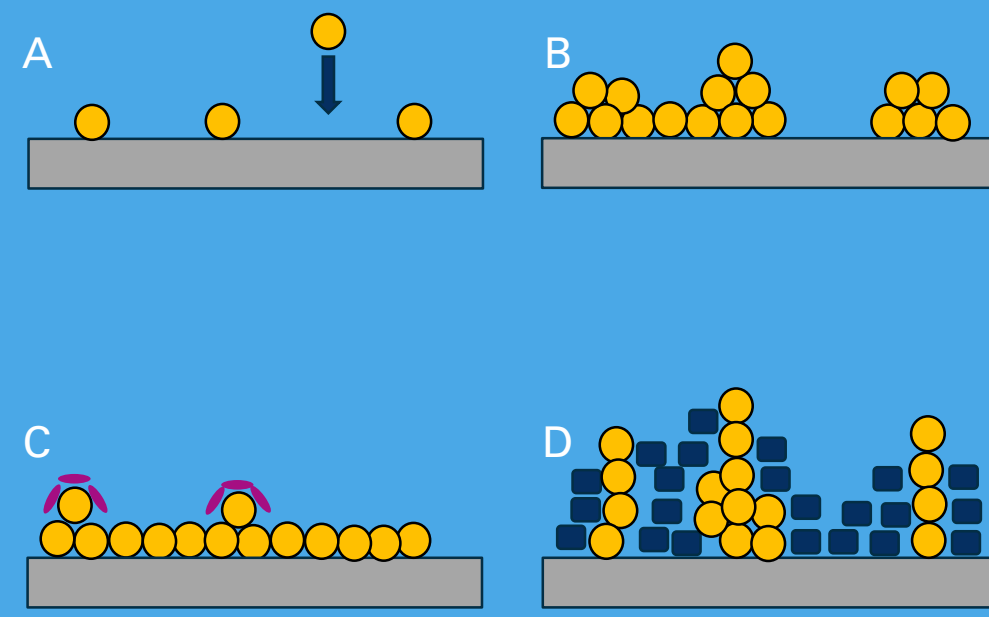


## SYNTHESIS

Catalysts are synthesized by galvanostatic electrodeposition of the copper from an aqueous plating bath. Deposition solutions contained copper sulphate, nanostructuring additives and sulphuric acid as pH regulator. Electrodeposition has been preferred to other kind of nanosynthesis in order to obtain a simple, inexpensive and scalable process. Synthesis conditions had been analyzed and linked to their nanostructuring effects. The effect of deposition parameters, such as current density, amount of charge, additives and pH were considered.



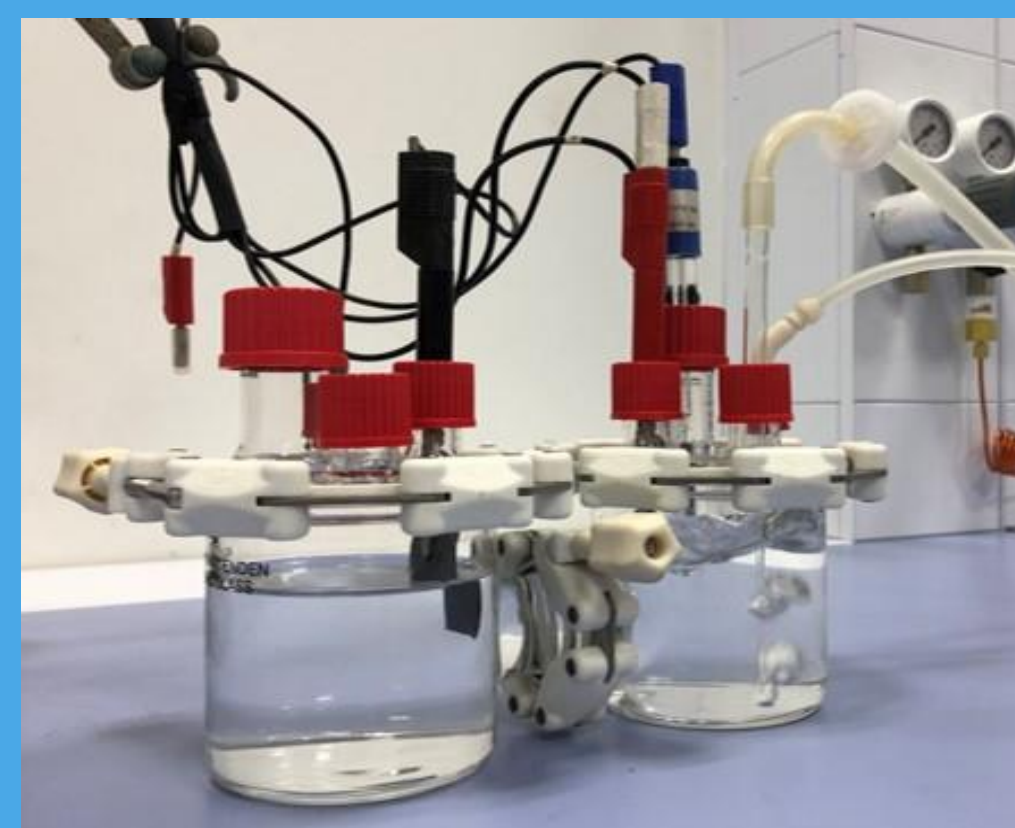
On the left, a diagram of the three-electrode deposition cell: the carbon paper support, a referent electrode and a graphite counter-electrode. Electrical parameters are regulated by a potentiostat. The cell is stirred and thermostated at 25°C.



Classic and assisted electrodeposition. The process is conceived in two phases: Nucleation (A) where few, isolated atoms are reduced on the deposition surface and Growth (B) where new atoms cover the previously reduced ones. Additives may alter this process. Some substances may be adsorbed mostly on isolated structures, enhancing the growth of flat metallic planes (C) or may be adsorbed on the support, enhancing a vertical growth (D).

## CHARACTERIZATION

Electrodeposited nanostructures were analyzed both by Scanning Electronic Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX). SEM images represent a double benefit: they allow us to make a qualitative organization of the nanostructures, an esteem of the structure distribution on the support and a quantitative comparison between the dimensions of various nanostructures. EDX mapping confirms the identification of the metallic nanostructures.

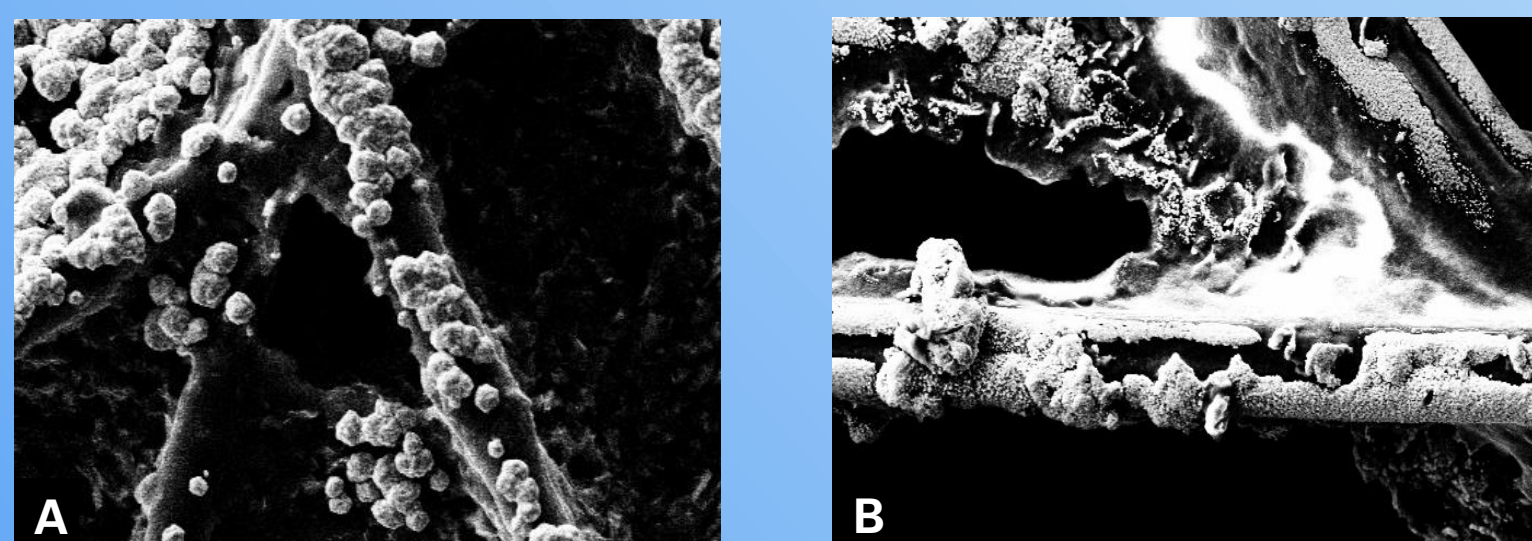


The test cell, divided into two compartments by a Nafion® membrane. The presence of CO<sub>2</sub> in the reaction environment is guaranteed by a bubbler and a magnetic stirrer.

Catalytic properties are tested in a double compartment, three-electrode cell. ERCO<sub>2</sub> is here tested in an aqueous electrolyte based on potassium hydrogencarbonate. Catalysts are subjected to Linear Sweep Voltammetry, an electrochemical analysis designed to evaluate redox reactions by applying a potential which increase or decrease at a constant ratio. Afterwards, electrodes were tested in a potentiostatic setup and gaseous products were analyzed by gas chromatography (GC).

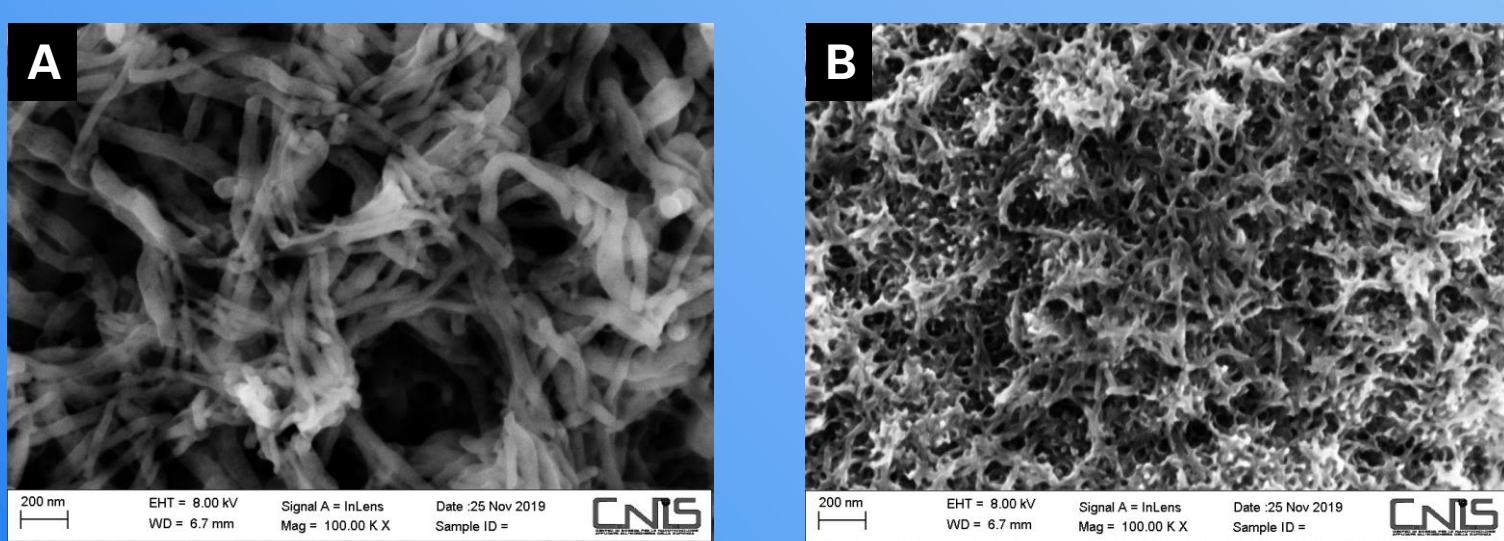
## REAGENTS EFFECT

Additives with surfactant proprieties, such as n-Dodecyltrimethylammonium Bromide (DTAB), allow the wetting of the hydrophobic surface of the carbon paper, increasing the deposition uniformity.

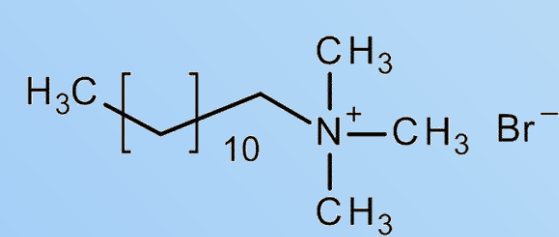


Comparison between simple copper deposition (A) and DTAB-assisted deposition (B). DTAB allows the formation of thinner layers and a wider covering of the sustaining structure.

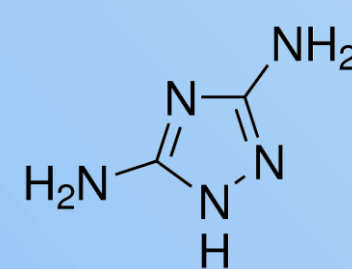
On the other side, compounds like 3,5-Diamino-1,2,4-Triazole (DAT), a copper complexant, act as nanostructuring agent: bounded to the depositing copper atoms, its molecule inhibit the lateral growth of the metallic structure, allowing the creation of a nanowires/nanogrid pattern. pH variation of the baths affect both dimension and distribution of the nanostructures.



Nanowires produced by DAT-assisted electrodeposition. Being the DAT complex stability linked to pH, the morphologic action of DAT may be tuned. (A) Bath pH 2.1 (B) Bath pH 1.0.



DTAB molecular structure. Being a long chain quaternary ammonium salt, this molecule shows the classic structure of a cationic surfactant.



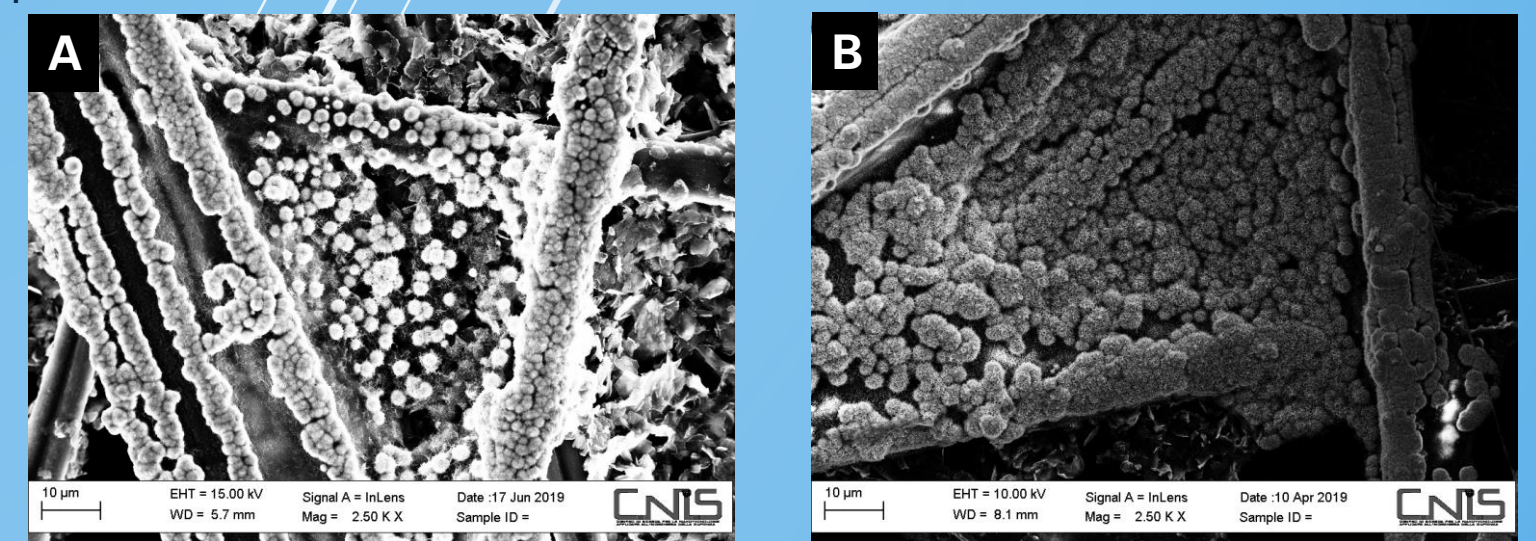
DAT molecular structure. It is a triazolic aromatic compound. Its behavior as deposition additive is still under investigation.



DAT-copper complex in an aqueous environment containing copper (II) sulphate.

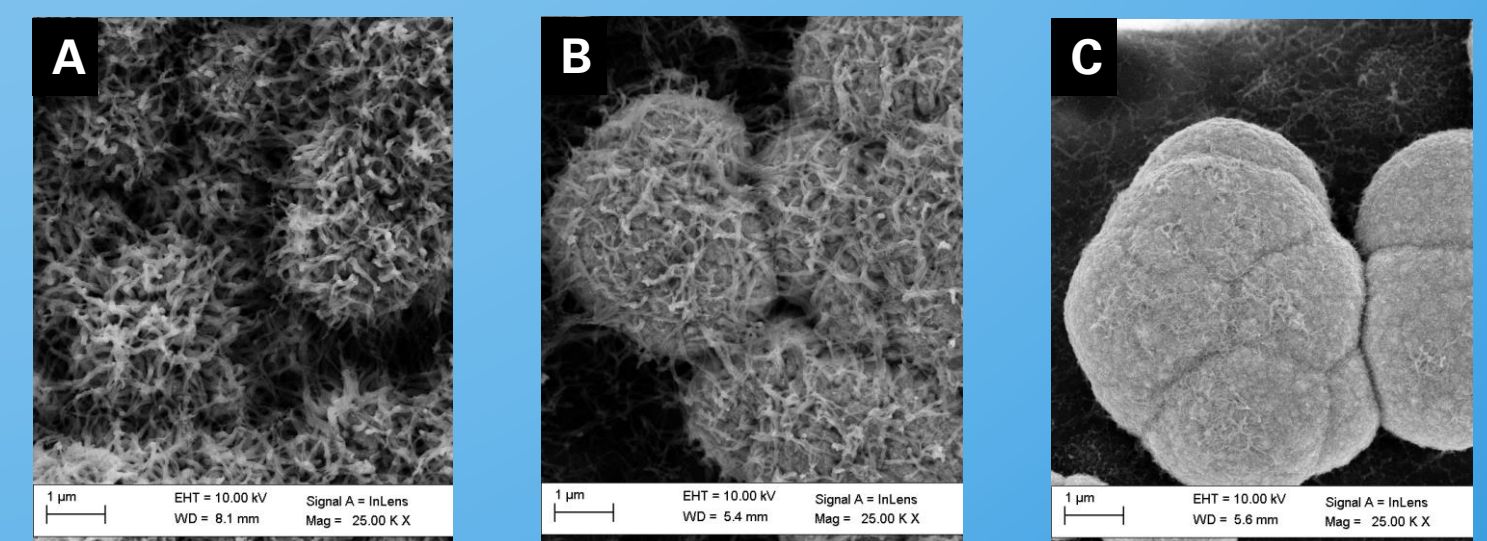
## CURRENT DENSITY AND CHARGE EFFECT

The amount of metal reduced during an electrodeposition is approximately proportional to the charge passing into the deposition cell. Our electrodes show no exception.

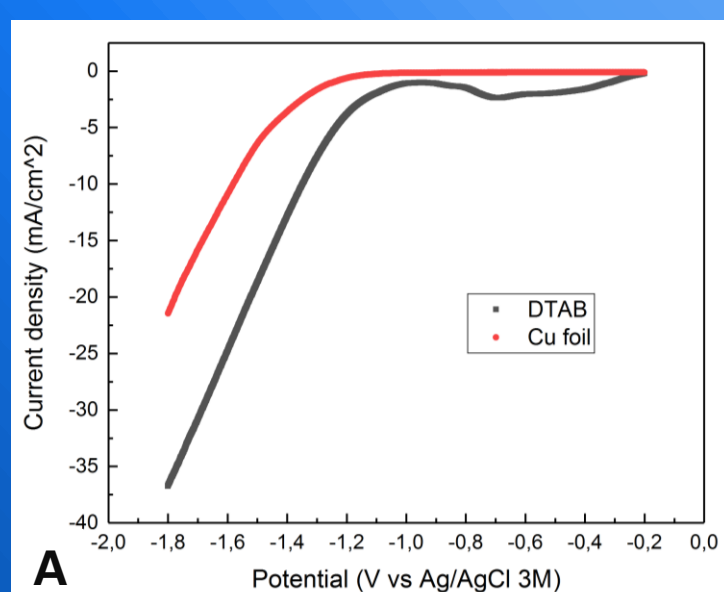


(A) DAT-assisted copper deposition after the application of 1 Coulomb per square centimeter of support. (B) 2 Coulomb deposition.

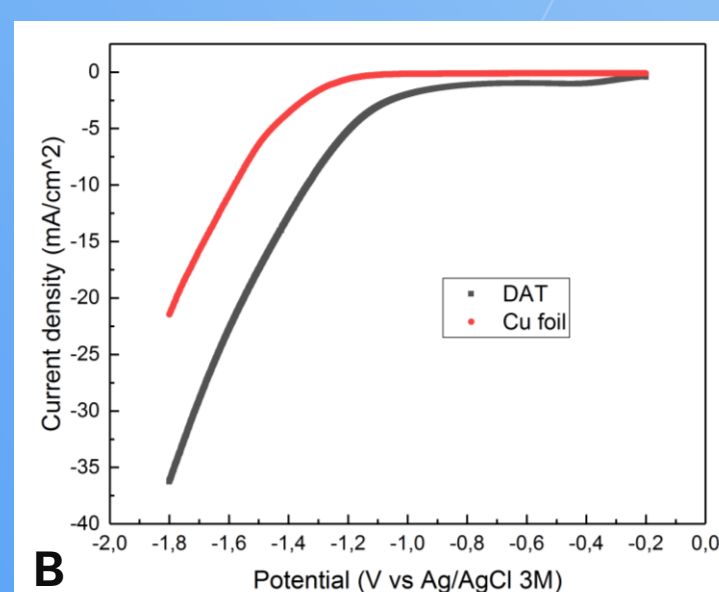
Current density may affect deposition morphology, selectivity and yield. This is due to the kinetic role of the current in the deposition process. Enhancing concentration gradients or modifying the interaction of the additives, a specific current density is essential in nano-electrosynthesis.



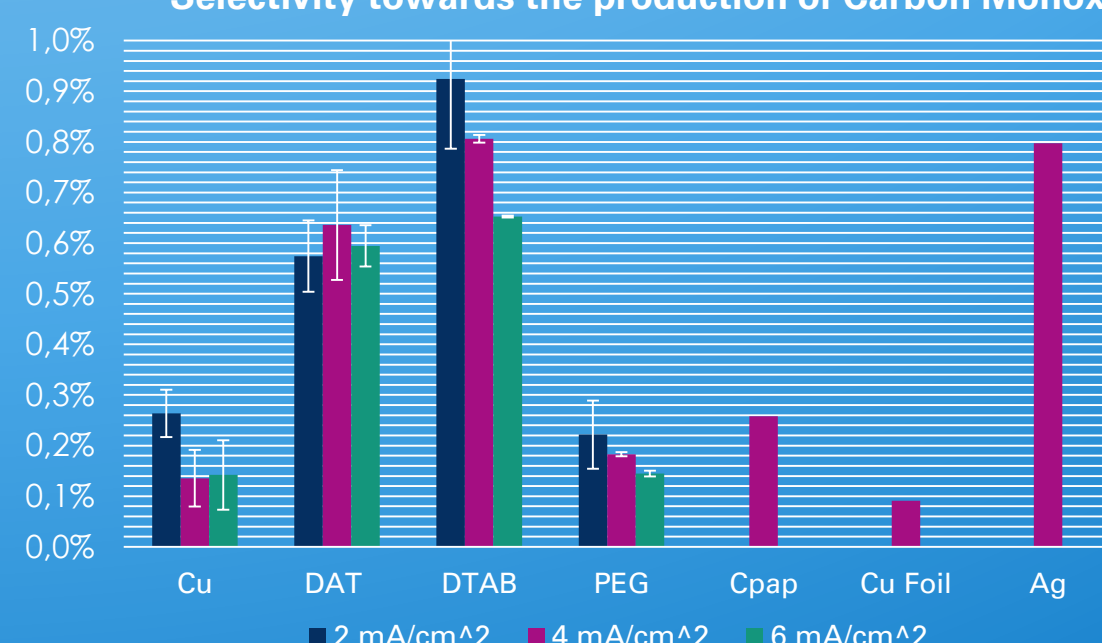
Nanowires production may be dramatically altered by variations in current density. Even if hemispherical microstructures are maintained, nanowires length and distribution are modified by the current density: (A) 2 mA/cm<sup>2</sup>; (B) 4 mA/cm<sup>2</sup>; (C) 6 mA/cm<sup>2</sup>.



Linear Sweep voltammograms obtained from electrodeposited electrodes. The catalytic behavior of the electrode (black line) is compared with a copper foil (red line) analyzed in the same kind of CO<sub>2</sub>-saturated electrolyte. (A) DTAB-assisted electrodes and copper foil; (B) DAT-assisted electrode and copper foil. Both DTAB and DAT electrodes show a greater reductive current than the copper foil.



## Selectivity towards the production of Carbon Monoxide (arbitrary GC units)



The histogram represents a comparison between different kind of electrodes in term of selectivity towards the production of carbon monoxide. Electrodes are compared to a plain carbon paper foil, a copper foil and a silver foil (silver is renowned as the best catalyst for this specific reaction). It is clearly visible how both deposition additives and current density may influence catalytic proprieties of the electrodes.