

Development and advanced characterization of Cu-based catalysts for the electro and photo-electrocatalytic CO₂ reduction

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Carbon dioxide (CO₂) emissions into the atmosphere are both natural, as a product of terrestrial biogeochemical cycles, and anthropogenic, mainly as the result of the combustion of fossil fuels. While the former ones are balanced by natural processes, CO₂ originating from anthropogenic activities remains into the atmosphere causing the entrapment of the radiation from the Earth and the consequent warming of the planet. The CO₂ concentration in the atmosphere is increasing every year from the 50s to now, until current levels exceeding 415 ppm. A renewable and green approach to CO₂ recovery is increasingly necessary to minimize the worrying impact of these emission to the environment. A growing research effort in the field of electrochemical and photo-electrochemical reduction of CO₂ is one of the current response from scientists and engineers. The implemented strategy is to introduce CO₂ as a raw material into a circular economy loop to synthesize high-added-value products, fulfilling at the same time the enduring growth in global fuel demand. The challenges to cope with in the catalytic conversion of CO₂ into fuels are huge. Thermodynamically, CO₂ is a fully oxidized, inert, and extremely stable molecule, thus its conversion to other C-based molecules results difficult without a substantial energy input. In this work the focus is on electrochemical and photo-electrochemical processes. The electricity can drive the water splitting reaction to generate protons (H⁺) necessary for CO₂ hydrogenation. The process of electrocatalytic CO₂ reduction implies the usage of an external electric field as the main energy source to induce redox reaction on electrodes. The photons-assisted process, instead, refers to the generation of electrons by photo-excitation of a semiconductor photoelectrode by a light source, and the consequent migration of these photo-excited electrons to the electrode surface under the guidance of external applied potential to accomplish the catalytic reduction of CO₂. The possibility to conduct the reaction under mild conditions, and the simple control on the reaction via the tuneable external bias, are common to both techniques, making them more suitable than other methods since can directly exploit renewable energy sources such as sunlight. Currently, the selective production of desired chemicals is a challenging topic, because the redox potentials are similar for different reaction pathways. The CO₂ reduction reaction (CO₂RR) path is mainly focused on the production of molecules like CO (the syngas production is also taken into consideration) and formic acid, for which the transfer of 2e⁻ is required. The ability to obtain, among others, the aforementioned products with a high activity belongs to the Cu and Cu-based compounds reactivity, which are the ones investigated during this work. Various catalysts for electro and photo-electrocatalytic CO₂RR have been designed, synthesised, characterised and tested in different setup in order to choose the best for carrying out the reaction and maintaining its stability over time. Working within Italian regional (SATURNO-Bioeconomy) and European (SunCoChem) Projects has meant that the effort was always direct to the more scalable synthetic route for the catalysts (*i.e.*, standardization of synthesis). In [Chapter 3](#), a bimetallic PdCu aerogel was studied in electrocatalytic systems. Particular care in the choice of the more suitable synthesis path was taken,

then the obtained catalyst showed a good syngas production ($\text{CO}:\text{H}_2 \sim 1$) with Faradaic Efficiency (FE) values of 38 and 42% respectively, and a FE = 3.5% for Ethanol. Then the scale-up of the cell for the CO_2RR was accomplished and by applying higher potentials the selectivity of C-compounds raised up to 40%. In [Chapter 4](#), the investigation on Sn as a protective agent on Cu_2O started, focusing on making an efficient and stable photo-electrocatalyst. The first synthesis attempt was performed via co-precipitation, having in mind its ease and scalability. The role of light in the formation of C-compounds and H_2 hindering was observed at different current density values applied. Then, the study on Cu_2O and SnO_2 proceeded and [Chapter 5](#) deals with another synthetic approach, namely the creation of core-shell nanoparticles. Photo-electrocatalytic characterization confirmed the enhancement in performance with respect to the previous catalyst design, with improved photo-activity and better results in terms of Formic acid FEs. Given the raising interest in long-term stability, the Cu:Sn ratio was varied in order to accomplish a thicker protective layer onto the Cu_2O core. A deep characterization of the new set of catalysts was carried out at the Helmholtz-Zentrum Berlin facilities. In particular, carriers mobility was studied via Time Resolving Microwave Conductivity (TRMC) analysis, and the lifetime of electrons at the surface photoelectrode-electrolyte was evaluated thanks to a novel approach for CO_2RR such as IMVS (Intensity-Modulated Photovoltage Spectroscopy). Insights of these advanced characterization methods are discussed in [Chapter 6](#), and finally resulted in a tendency of mainly producing C_1 compounds with the increasing amount of Sn. The rationalization of this effect led to the application of a very low Cu:Sn ratio in the standardization of the synthesis of core-shell $\text{Cu}_2\text{O}-\text{SnO}_2$ catalyst. After assessing the stability of the CO and H_2 production after a 5-hour lasting chronoamperometric test, the metallic catalyst was functionalised with supramolecular Ru/Re complexes developed by partners of the Suncochem Project. The modified catalyst was tested in the same conditions and the comparison of the performance (in terms of photo-activity and FE) are shown in [Chapter 7](#).