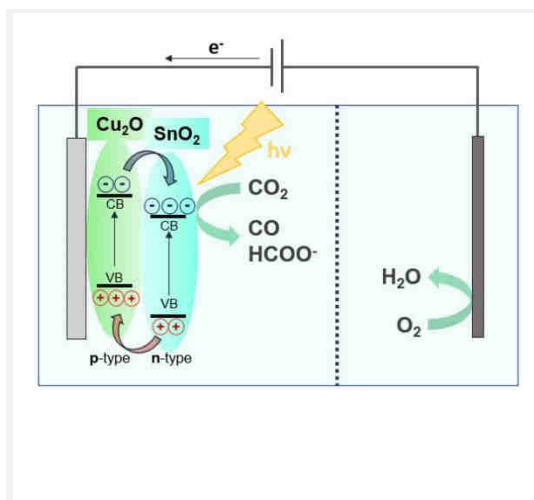


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The CO₂ conversion into high value-added products is becoming increasingly attractive to found substitutes to fossil-fuel-based products and tackle the environmental crisis. Herein, a simple, reproducible and scalable novel photo-electrocatalyst was synthesised and characterized. The strategy of coupling cuprous oxide with tin oxide allowed to protect the instable Cu(I) species from photo-corrosion. Evidences of the SnO₂ stabilization role were found via XPS and chronoamperometry test. An optimised catalytic ink was used to prepare the photocathodes. The CO₂ photo-electroreduction tests demonstrated a prevalent production of CO and Formate with Faradaic efficiencies of 18.5% and 53.5%, respectively, under 2-hours of chronopotentiometry. Moreover, light conditions were demonstrated to play a major role in hindering H₂ and promoting C-products formation.

CO₂ concentration in the atmosphere is increasing every year from the 50s, at the beginning of industrial acceleration, up to now, when it exceeds 410 ppm. Since natural CO₂ sink cannot keep up with the constant anthropogenic emissions, a renewable and green approach to CO₂ recovery is increasingly necessary to minimize its worrying impact on the environment. Within the depicted scenario, electrochemical and photoelectrochemical CO₂ reduction processes have been widely investigated as promising methods to transform CO₂, under mild reaction conditions, into useful chemicals or fuels [1,2]. The first challenge of such processes is to find suitable catalysts with a high activity, good charges separation and improved solar conversion efficiency. Within this work, we focused on the CO₂ reduction reaction (CO₂RR) path directed towards products like CO (the syngas production is also taken into consideration) and formic acid, for which the transfer of 2 electrons is required. Cu₂O is a cheap, abundant, and intrinsically p-type semiconductor. Due to its narrow band gap (~ 2.1 eV) and the suitable positioning of conduction and valence bands, Cu₂O is an ideal photocatalyst for CO₂RR. Despite these promising features, Cu₂O is limited by its instability and continuous decrease of photoactivity under operative conditions [3]. The coupling cuprous oxide with a n-type wide bandgap semiconductor is here investigated as an effective way to prevent its self-photoreduction or oxidation. A noticeable electron mobility together with a good intrinsic stability have driven the choice towards tin oxide (SnO₂), which is also able to form a p-n junction with the Cu₂O photocatalyst.

In this work we target the development of a facile and scalable synthesis method for the Cu₂O-SnO₂ catalyst. A particular focus is given to the preparation of photoelectrodes for the photo-electrocatalytic CO₂ reduction process and, finally, the evaluation of the catalyst performances in terms of stability and faradaic efficiencies of the target products.

The synthesis of photoactive copper-tin-oxide-based catalyst was optimized by an ultrasound assisted co-precipitation method. The significant advantages of the sonochemical synthesis approach [4] guided the choice of coupling these two methods. In addition, the reproducibility of the synthesis is boosted by using a completely automatized set-up made of peristaltic pumps, as shown in Fig. 1.

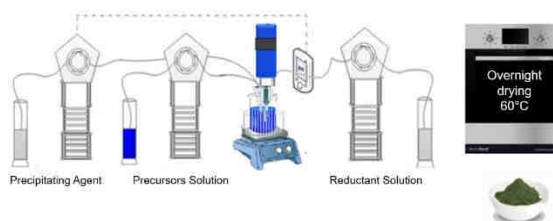


Fig. 1 Schematic setup designed for the automatized Cu₂O-SnO₂ synthesis.

The characterization steps included several techniques: Transmission Electron Microscopy (TEM), Field Emission Scanning Electron Microscopy (FESEM), X-ray photoelectron spectroscopy (XPS) X-rays Diffraction Analysis (XRD), among others, and