Facile and scalable synthesis of Cu_2O-SnO_2 catalyst for the photoelectrochemical CO_2 conversion

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Since natural CO_2 sink cannot keep up with the constant anthropogenic emission, a renewable and green approach to CO_2 recovery is increasingly necessary to minimize the worrying impact of its emission to the environment. Within the depicted scenario, electrochemical and photoelectrochemical CO_2 reduction are being widely investigated as promising methods to transform CO_2, under mild reaction conditions, into useful chemicals or fuels. [1,2] Cu_2O 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, Cu_2O is an ideal photocatalyst for CO_2RR. Simultaneously, SnO_2 is an n-type direct band-gap semiconductor with noticeable electron mobility together with an intrinsic stability. The role of SnO_2 coupled with Cu_2O as catalyst for syngas production was recently investigated [3], therefore it follows the stabilization mechanism induced by Sn(IV) onto the Cu(I) oxidation state, by acting as a barrier for further reduction of copper species, avoiding photoactivity losses. 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 of the two methods. The characterization steps included Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray (EDX), UV-Visible Spectroscopy, X-ray photoelectron spectroscopy (XPS) analyses and X-rays Diffraction (XRD), allowing the morphological assessment, the crystalline phase evaluation and the composition of the surface species. The cubic crystalline phase (cuprite) of Cu_2O was noticed in the XRD pattern, which is evident from the most intense peak (111) at 2θ values of 36.52°. No traces of other phases related to Copper were observed in the diffraction pattern, which points out the suitability of the chosen synthesis methods and that the reduction process has been successfully carried out towards the cubic phase of Cu_2O. The study on specific surface area and porosimetry of the material, measured from N_2 adsorption/desorption isotherms, revealed a mesoporous structure with a BET surface area value of 142 m^2/g, a pore volume of 0.12 cm^3/g and an average pore width of 5.9 nm, which were detected via BJH method. The high surface area and pore volume of the compound is beneficial for the photocatalytic activity. From UV-Visible Spectroscopy analysis, the band gap energy value of 2.5 eV was calculated via Tauc plot method. The composition of a catalyst-based ink was optimized to avoid the Cu(I) oxidation during the electrodes preparation and preserve the catalyst photoactivity, which was assessed for the photo-electrocatalytic CO_2 reduction in an H-cell system, leading to the formation of value-added C-compounds like syngas and Formate, among others.

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Acknowledgment: The research leading to these results has received funding from the EU's Horizon 2020 Research and Innovation Action under the SunCoChem project (Grant Agreement No 862192).