INFLUENCE OF SEMICONDUCTORS MATERIALS IN THE PHOTOELECTROCATALYTIC CO_2 REDUCTION IN LIQUID PHASE FOR ALCOHOLS PRODUCTION

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Photoelectrocatalysis has being shown to be a good technique in CO_2 reduction contributing with a great concern that is hearth climate [1,2]. Thus, the present work compares the performance of the p-type Cu/Cu_2O semiconductor, and the p-n junction semiconductors $Si/TiO_2/Pt$ and $Ti/TiO_2/CuO$ on the photoelectrocatalytic CO_2 reduction under liquid phase and compares its contribution on the different kind of generated products, aim the alcohol production. Cu/Cu_2O semiconductor was prepared by electrodeposition [2], while the $Si/TiO_2/Pt$ was constructed by sputtering and e-beam deposition [3] and the $Ti/TiO_2/CuO$ was prepared by dip-coating [4]. The morphological and structural characterization of all synthesized semiconductors were carried out by XRD, EDS and FEG-SEM analysis. The photocurrent response was evaluated by LSV in $NaHCO_3$ 0.1 $molL^{-1}$ with and without CO_2 using similar geometric areas. The photoelectrochemical experiments were performed in a two-compartment reactor, where the semiconductor was irradiated by UV-Vis light (125 W) and submitted to controlled-potential and the samples were collected during the reaction time. Pt gauze was used as counter electrode and an Ag/AgCl (KCl sat) as reference. The possible products formed by photoelectrocatalytic reduction of CO_2: methanol, ethanol, acetaldehyde, formaldehyde, acetone, formic acid and acetic acid were analyzed and quantified by CG-FID (CP-3800 Varian) and HPLC-DAD (Shimadzu 10AVP). All the semiconductor studied presented activation (photocurrent) just under light and potential effects, current generation was not observed without light incidence. The photocurrent response for the entire semiconductors in presence of CO_2 and UV–Vis light presented a high photocathodic currents attributed to CO_2 photoreduction. The phototelectrocatalytic CO_2 reduction performance on Cu/CuO, $Si/TiO_2/Pt$ and $Ti/TiO_2/CuO$ semiconductors were accomplished evaluating the applied potential, supporting electrolyte type, pH and concentration of supporting electrolyte. In the case of Cu/Cu_2O semiconductor was possible to observe the formation of the products methanol, ethanol, formaldehyde, acetaldehyde and acetone. Under 0.1 mol L^{-1} sodium carbonate/bicarbonate buffer solution at pH 8 was yield 89% of faradaic efficiency for methanol formation (5.60 mmol L^{-1}), however a small useful life of the electrode was observed [2]. The products methanol (0.29 mmol L^{-1}), ethanol (0.025 mmol L^{-1}) and acetone (0.004 mmol L^{-1}) were quantified applying $Ti/TiO_2/CuO$ with a long life of the semiconductor, but only 10% of faradaic efficiency was achieved [5]. The $Si/TiO_2/Pt$ semiconductor presented a preferential ethanol formation (2.60 mmol L^{-1}) while the products methanol (0.88 mmol L^{-1}) and acetone (0.049 mmol L^{-1}) were also identified [3]. The faradaic efficiency for all the products formation in this case reached 96%, while a stable and long life time of the semiconductor. The mechanism of product formation is discussed for each case.

References

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