Influence of Semiconductors Materials in the Photoelectrocatalytic CO\textsubscript{2} Reduction in Liquid Phase for Alcohols Production

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Photoelectrocatalysis has being shown to be a good technique in CO\textsubscript{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\textsubscript{2}O semiconductor, and the p-n junction semiconductors Si/TiO\textsubscript{2}/Pt and Ti/TiO\textsubscript{2}/CuO on the photoelectrocatalytic CO\textsubscript{2} reduction under liquid phase and compares its contribution on the different kind of generated products, aim the alcohol production. Cu/Cu\textsubscript{2}O semiconductor was prepared by electrodeposition [2], while the Si/TiO\textsubscript{2}/Pt was constructed by sputtering and e-beam deposition [3] and the Ti/TiO\textsubscript{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\textsubscript{3} 0.1 molL\textsuperscript{-1} with and without CO\textsubscript{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\textsubscript{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\textsubscript{2} and UV–Vis light presented a high photocathodic currents attributed to CO\textsubscript{2} photoreduction. The phototelectrocatalytic CO\textsubscript{2} reduction performance on Cu/Cu\textsubscript{2}O, Si/TiO\textsubscript{2}/Pt and Ti/TiO\textsubscript{2}/CuO semiconductors were accomplished evaluating the applied potential, supporting electrolyte type, pH and concentration of supporting electrolyte. In the case of Cu/Cu\textsubscript{2}O semiconductor was possible to observe the formation of the products methanol, ethanol, formaldehyde, acetaldehyde and acetone. Under 0.1 mol L\textsuperscript{-1} sodium carbonate/bicarbonate buffer solution at pH 8 was yield 89% of faradaic efficiency for methanol formation (5.60 mmol L\textsuperscript{-1}), however a small useful life of the electrode was observed [2]. The products methanol (0.29 mmol L\textsuperscript{-1}), ethanol (0.025 mmol L\textsuperscript{-1}) and acetone (0.004 mmol L\textsuperscript{-1}) were quantified applying Ti/TiO\textsubscript{2}/CuO with a long life of the semiconductor, but only 10% of faradaic efficiency was achieved [5]. The Si/TiO\textsubscript{2}/Pt semiconductor presented a preferential ethanol formation (2.60 mmol L\textsuperscript{-1}) while the products methanol (0.88 mmol L\textsuperscript{-1}) and acetone (0.049 mmol L\textsuperscript{-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