Photoelectrochemical production of formic acid and methanol from carbon dioxide on metal-decorated CuO/Cu_2O-layered thin films under visible light irradiation

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As a cathode material for fuel generation from CO_2 reduction in a photoelectrochemical system, layered CuO/Cu_2O films were developed and their surfaces were decorated with transition metals (*i.e.* Ag, Au, Cd, Cu, Pb, and Sn). Deposition of the transition metals effectively enhanced CO_2 conversion to fuel in terms of faradaic efficiency. In particular, $Pb/CuO/Cu_2O$ demonstrated outstanding performance among the transition metals: 40.45% of total faradaic efficiency at -0.16 V (*vs.* SHE), which was a higher potential than standard redox potentials of formic acid and methanol formation from CO_2. Moreover, electrochemical impedance spectroscopy showed that the deposition of the deposition of the transition metals onto CuO/Cu_2O electrode effectively generated photo-induced electron-hole pairs under visible light irradiation. However, fast performance degradations of the prepared electrodes were observed during the reactions as well as the disappearances of the photocurrents. X-ray photoelectron spectroscopy results revealed that the outer CuO layer was readily reduced to Cu_2O/Cu, and this compositional destruction was responsible for the degradation of the photocurrent by prohibiting transfers of the electrons (or holes) to the active sites.