Mechanistic elucidation on the stability of SnO$_2$ NPs under electrochemical CO$_2$ reduction condition: An in operando Raman Spectroscopy study

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In this present study we demonstrate degradation effects on the basis of a direct electro-reduction process of CO$_2$ taking place on a SnO$_2$ NP catalyst supported on reduced graphene oxide (rGO). The field of CO$_2$ electro-catalysis is rapidly growing due to the global demand for new technologies which allow for the reduction of CO$_2$ in the atmosphere and to store at the same time excesses of electric energy from wind and solar sources in form of a reduced carbon compound. In this respect, an electrochemical approach towards the conversion of CO$_2$ into more valuable products seems to be highly promising. The SnO$_2$ NP catalyst supported on reduced graphene oxide (rGO) shows a superior activity and selectivity towards the formation of formate with Faradaic efficiencies (FEs) above 80%. However, our study also demonstrates that the Faradaic efficiencies crucially depend on the applied electrode potential and the pH of the electrolyte. The SnO$_2$ NPs themselves undergo at cathodic potentials an electro-reduction reaction transforming the SnO$_2$ (Sn$^{IV}$) into metallic tin (Sn$^{0}$). This chemical transition can be monitored potential and time dependent by in operando (this is, during an ongoing CO$_2$ electroreduction) Raman spectroscopy (Fig.1). This catalyst degradation is accompanied by a significant drop down of the Faradaic efficiency of formate formation. Highest efficiencies are actually obtained under conditions where the NP is neither fully oxidized nor fully reduced and consist of a Sn/SnO$_2$ composite. The post-electrolysis characterization of the catalyst material reveals a full recovery of the SnO$_2$. This result emphasizes once more the importance of an in operando identification of the catalytically active species as basis for the elucidation of reaction mechanisms.

![Fig.1](image-url) In operando Raman studies at varied potential (A) The relative intensities of the Sn$^{IV}$-related A1g Raman peaks (B). In the three distinct potential regions represented by the shaded background, the catalyst is in the form of fully oxidized SnO$_2$ (I), a partially reduced compound of mixed oxidation state (II) and completely reduced metallic Sn (III), as illustrated by the scheme of (C).