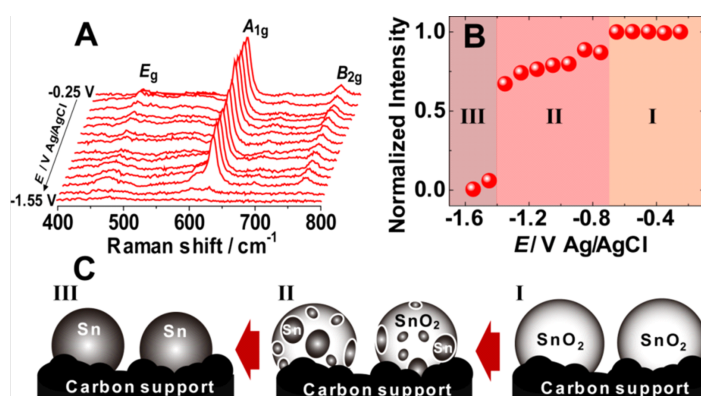


## Mechanistic elucidation on the stability of SnO<sub>2</sub> NPs under electrochemical CO<sub>2</sub> reduction condition: An *in operando* Raman Spectroscopy study

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In this present study we demonstrate degradation effects on the basis of a direct electro-reduction process of CO<sub>2</sub> taking place on a SnO<sub>2</sub> NP catalyst supported on reduced graphene oxide (rGO). The field of CO<sub>2</sub> electro-catalysis is rapidly growing due to the global demand for new technologies which allow for the reduction of CO<sub>2</sub> 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<sub>2</sub> into more valuable products seems to be highly promising. The SnO<sub>2</sub> 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<sub>2</sub> NPs themselves undergo at cathodic potentials an electro-reduction reaction transforming the SnO<sub>2</sub> (Sn<sup>IV</sup>) into metallic tin (Sn<sup>0</sup>). This chemical transition can be monitored potential and time dependent by *in operando* (this is, during an ongoing CO<sub>2</sub> 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<sub>2</sub> composite. The post-electrolysis characterization of the catalyst material reveals a full recovery of the SnO<sub>2</sub>. 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** *In operando* Raman studies at varied potential (A) The relative intensities of the Sn<sup>IV</sup>-related A<sub>1g</sub> Raman peaks (B). In the three distinct potential regions represented by the shaded background, the catalyst is in the form of fully oxidized SnO<sub>2</sub> (I), a partially reduced compound of mixed oxidation state (II) and completely reduced metallic Sn (III), as illustrated by the scheme of (C).

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