

Mechanistic elucidation on the stability of SnO₂ NPs under electrochemical CO₂ 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 CO₂ taking place on a SnO₂ NP catalyst supported on reduced graphene oxide (rGO). The field of CO₂ electro-catalysis is rapidly growing due to the global demand for new technologies which allow for the reduction of CO₂ 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 CO₂ into more valuable products seems to be highly promising. The SnO₂ 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 SnO₂ NPs themselves undergo at cathodic potentials an electro-reduction reaction transforming the SnO₂ (Sn^{IV}) into metallic tin (Sn⁰). This chemical transition can be monitored potential and time dependent by *in operando* (this is, during an ongoing CO₂ 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/SnO₂ composite. The post-electrolysis characterization of the catalyst material reveals a full recovery of the SnO₂. 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.

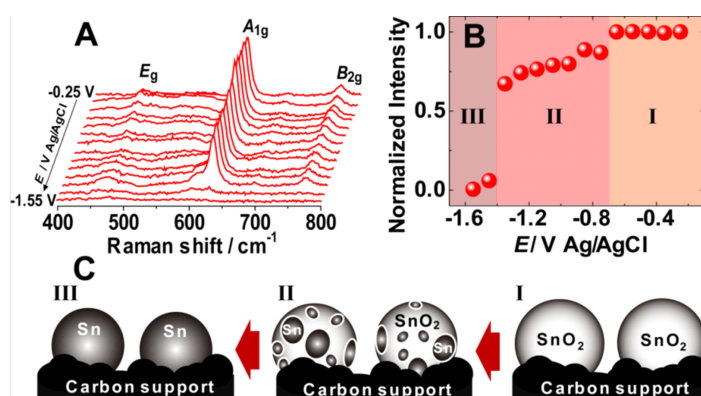


Fig.1 *In operando* Raman studies at varied potential (A) The relative intensities of the SnIV-related A1g Raman peaks (B). In the three distinct potential regions represented by the shaded background, the catalyst is in the form of fully oxidized SnO₂ (I), a partially reduced compound of mixed oxidation state (II) and completely reduced metallic Sn (III), as illustrated by the scheme of (C).

[1] A.Dutta, A. Kuzume, M. Rahaman, S.Vesztergom, P. Broekmann, *ACS Catal.* **2015**, 5 (12), 7498–7502

[2] M. Sackmann, A. Materny *J. Raman Spectrosc.* **2006**, 37, 305–310

[3] I. E. Wachs, C. A. Roberts *Chem. Soc. Rev.*, **2010**, 39, 5002–5017