

Transient IR Spectroscopy as a Novel Approach to Unravel the Active Surface Species of Chemoresistive Gas Sensors

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Summary:

Transient IR spectroscopy was used as a novel method for the mechanistic investigation of sensor materials for chemoresistive metal oxide gas sensors. Taking unloaded and gold-loaded tin oxide as an example, it was shown that *in situ* modulation-excitation spectroscopy (MES) combined with phase sensitive detection (PSD) allows the identification of the active species of the sensor reactions towards ethanol and CO, as well as the observation of new surface adsorbates such as CO adsorbed on partially negatively charged gold nanoparticles (CO-Au^{δ-}) not accessible under steady state conditions.

Keywords: Chemiresistors, tin oxide, IR spectroscopy, transient methods, mechanistic investigation

1 Introduction

To enable a rational design based on new and established chemoresistive sensor materials, a deep understanding of the underlying sensor mechanism is of great importance. Various approaches based on *in situ* and *operando* spectroscopy are available for the investigation of chemoresistive gas sensors based on metal oxides as a sensor material [1-3]. Using these methods, new and important insights into the sensing mechanism of unloaded and loaded sensor materials such as SnO₂ [1-3] could be obtained, as previous studies based on IR, Raman and UV-VIS spectroscopy have shown [1-3].

Despite the great potential of established *operando* spectroscopic methods, it is often difficult to clearly identify the active surface species that are involved in the primary sensor response based on their vibrational bands in the IR and Raman spectra. These vibrational bands of active species are often masked by spectator species that accumulate at the surface but do not participate in the sensor response. However, already established *in situ* spectroscopic approaches for the investigation of chemoresistive gas sensors can be complemented by transient spectroscopic methods, such as MES based on diffuse reflectance infrared Fourier transform spectroscopy (ME-DRIFTS), to isolate these hidden active surface species and obtain further information about the underlying sensor mechanism [4]. Unraveling these interactions of the gas phase with the sensor surface (reception) is integral for improving sensor properties such as

sensitivity, reversibility and selectivity towards the specific analyte gas to be detected.

2 Experimental

Commercial tin(IV) oxide SnO₂ (Sigma Aldrich) was used for the IR measurements in this work. Gold was loaded by wet impregnation using a 1 mM aqueous HAuCl₄ solution and a 30 mM aqueous ammonia solution [4]. IR spectra were recorded on a Vertex 70 IR spectrometer (Bruker) and an Invenio R IR spectrometer (Bruker), each equipped with a built-in liquid nitrogen cooled MCT and a heatable Praying Mantis gas cell (Praying Mantis High Temperature, Harrick Scientific Products). During the ME-DRIFTS periodic measurements (period length: $T_{t,EtOH} = 133.33$ s; $T_{t,CO} = 366.35$ s), the sensor material is first exposed to 500 ppm of the corresponding analyte ethanol or CO, each in synthetic air as carrier gas, and then to synthetic air without the analyte, by switching the gas feed with a 4-way-valve controlled by the IR-spectrometer. The raw spectra recorded are subjected to a background subtraction and afterwards demodulated using PSD and thus transferred from the time to the phase domain by using a Fourier transformation.

3 Results and Discussions

Fig. 1a) shows PSD spectra obtained during ethanol gas sensing over Au/SnO₂ at 150 °C. In the first half period during ethanol exposure, vibrational bands for ethanol (~22 s), as well as formate and acetate species (~24 s) can be observed, as well as some terminal hydroxyl-groups (~19 s). Other terminal, as well as

bridged hydroxyl-groups are also observed in the second half period (~95-107 s), where no ethanol is present, showing their consumption on the time scale of ethanol exposure and formate/acetate formation. At around 2030 cm^{-1} , two overlapping vibrational bands can be observed (~100 s), which cannot be observed under stationary conditions, but under the periodically changing conditions used here. They can be assigned to CO adsorbed on partially negatively charged gold nanoparticles ($\text{CO-Au}^{\delta-}$) [4] and represent a surface adsorbate that was not previously observed during ethanol gas sensing. Carbonates and carboxylates can also be observed in the second half period (~91 s). Due to their time values in the second half period, they are not formed directly during the sensor reaction with ethanol, but by decomposition of formate and acetate-species as well as readsorption of CO_2 from the gas phase.

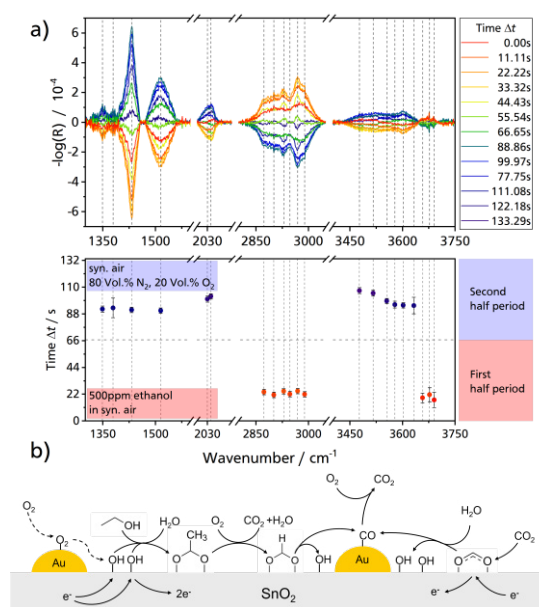


Fig. 1: a): PSD spectra for 0.58 wt.% Au/SnO₂ during pulsing of 500 ppm ethanol in synthetic air at 150 °C (Top) with assigned time values Δt (Bottom); b): Proposed mechanism for ethanol gas sensing over gold-loaded tin oxide.

Based on these spectroscopic results, we propose the mechanism for ethanol gas sensing over gold-loaded shown in Fig. 1b), involving an oxygen-spillover from gold on the surface of tin oxide [3]. In the course of the sensor reaction, hydroxyl-species are consumed during the adsorption of ethanol and stepwise oxidation to formate and acetate species, releasing electrons into the conduction band. These surface species formed can decompose in vicinity to gold, forming hydroxyl-species as well as CO, which adsorbs on gold and is oxidized to CO_2 before desorbing into the gas phase. CO_2 can then readsorb, binding electrons from the conduction band [4].

Tin oxide and gold-loaded tin oxide were also recently investigated during CO gas sensing using *in situ* modulation excitation DRIFT spectroscopy. New insights into the proposed sensor mechanism [2,3] including the temporal evolution of reaction intermediates were obtained, which are not available under stationary conditions. Our results show that carbonates are not directly involved in the primary sensor response to CO exposure and the formation of CO_2 from CO with the participation of lattice oxygen. Carbonates are mainly formed after the surface reaction by readsorption of CO_2 from the gas phase, where they can impair the regeneration of the sensor material after the end of the CO exposure by remaining on the sensor surface, similar to the behavior observed during ethanol gas sensing.

Based on the presented results we can conclude that the sensing mechanism of ethanol gas sensing is characterized by the formation and consumption of hydroxyl groups, as well as the formation of formate and acetate as surface adsorbates [4], while the mechanism of CO gas sensing is primarily based on a redox mechanism involving the consumption of surface lattice oxygen atoms and the formation of CO_2 .

Our results show the great potential of transient *in situ* spectroscopic methods for investigating the surface reaction of chemoresistive gas sensors in presence of different analytes to gain new insights in presence of intermediary surface species and their temporal evolution. Therefore, this transient approach can strongly facilitate the rational design of chemoresistive gas sensors with improved sensing properties.

References

- [1] A.-K. Elger, C. Hess, Elucidating the Mechanism of Working SnO₂ Gas Sensors Using Combined Operando UV/Vis, Raman, and IR Spectroscopy, *Angewandte Chemie International Edition*, 58, 15057 (2019); doi: 10.1002/anie.201908871
- [2] D. Degler, S. Wicker, U. Weimar, N. Barsan, Identifying the Active Oxygen Species in SnO₂ Based Gas Sensing Materials: An Operando IR Spectroscopy Study, *Journal of Physical Chemistry C*, 119, 21 (2015); doi: 10.1021/acs.jpcc.5b04082
- [3] D. Degler, S. Rank, S. Müller, H. W. Pereira de Carvalho, J.-D. Grunwaldt, U. Weimar, N. Barsan, Gold-Loaded Tin Dioxide Gas Sensing Materials: Mechanistic Insights and the Role of Gold Dispersion, *ACS Sensors*, 1, 1322-1329 (2016); doi: 10.1021/acssensors.6b00477
- [4] M. Pfeiffer, C. Hess, Application of Transient Infrared Spectroscopy To Investigate the Role of Gold in Ethanol Gas Sensing over Au/SnO₂, *Journal of Physical Chemistry C*, 126, 8, 3980-3992 (2022); doi: 10.1021/acs.jpcc.1c10384