

**Proposal  
Code**

**MA- 911**

Proposal Title Operando high-energy resolution fluorescence XAS measurements on Pt-doped SnO<sub>2</sub>-sensors

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Semiconducting metal oxide based gas sensors play a tremendous role in various applications spanning from comfort, safety to process monitoring. The material of choice for reducing gases is SnO<sub>2</sub>, which dominates not only the present academic research but also the commercial sensors <sup>[1]</sup>. In order to improve sensitivity, selectivity and stability and to decrease the operation temperature, SnO<sub>2</sub> is mostly doped with noble metals like Pd, Pt or Au <sup>[2]</sup>.

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Although many efforts have been undertaken to understand the structure of these promoters, their interaction with the background and target gases, and the sensing, the understanding of the role of the noble metals and their structure under operating conditions is still a matter of strong discussion <sup>[3]</sup>. This requires studies under real operating conditions, as especially reported for catalytic studies <sup>[4]</sup>. Recent studies on the role of Pd in realistic sensors have further questioned the often anticipated mechanism like spillover and Fermi-control <sup>[5]</sup>. One of the most often used dopants is - especially in commercial sensors - platinum and despite several studies have focused on the oxidation state of platinum <sup>[2b, 6]</sup>, none of them have focused on realistic Pt-doped SnO<sub>2</sub>-sensors under operating conditions allowing structure-property relationships. This is due to the following challenges: (i) platinum is only present in very low concentrations (0.2-1 wt% Pt in SnO<sub>2</sub>), (ii) the layer is highly porous and only 50 μm in thickness, (iii) platinum in much higher concentration is usually present in the heater and the electrodes, and (iv) characterization techniques that allow the identification of the structure (oxidation state, particle size, Pt composites) also in its amorphous state (short range order structural information) are required. XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) spectroscopy are well established element specific methods for this purpose, but so far, only structural characterizations before and after the reaction of the powder itself (no “operando” conditions) or idealized materials have been reported in those studies <sup>[2b, 6]</sup>. Hence, this requires a completely new approach concerning the design of the sensors and the X-ray spectroscopic approach.

In order to decouple the XAS signal for the minute amounts of Pt (<<1 wt. %) in the SnO<sub>2</sub> matrix from the Pt-containing electrodes and heater they were replaced by metals/alloys

with similar electrical/resistive properties. Au instead of Pt was used for the electrodes and Ag/Pd alloy for the heater as shown in Fig. 1A. The performance of the modified sensors was verified and was very similar to the conventional systems. Furthermore, the so-called HERFD-XANES (high energy resolution fluorescence detection XANES <sup>[7]</sup>) method using an X-ray emission spectrometer was used to isolate the Pt L<sub>3</sub> XAS signal from the underlying signals of the Au electrodes (fluorescence lines are at 9.442 and 9.713 keV, respectively). In fact, this combination of design and new spectroscopic methods allows not only to uncover element specifically the Pt-dopant structure but also to record high resolution XANES data due to minimization of core-hole lifetime-broadening <sup>[8]</sup>, which is necessary to detect subtle structural changes of the Pt-centers. In addition, this approach paves the way to collect “range-extended” EXAFS data <sup>[7]</sup> which is important for the structural analysis of the Pt centers on a molecular level.

The advantage of this approach compared to conventional fluorescence EXAFS is demonstrated in Figure 1B. The absorption at the Pt L<sub>3</sub> edge is very low in comparison to the absorption at Au L<sub>3</sub> edge from the underlying electrodes (spectrum b). Detection of the Pt L<sub>3</sub> X-ray absorption spectrum by monitoring the Pt L $\alpha_1$  emission line using crystal analyzers (details, *cf.* electronic supplementary information) suppressed the influence of undesired Au L<sub>3</sub> absorption edge in the EXAFS region. In Fig. 1B furthermore the high energy resolved fluorescence detected (HERFD) XANES spectra at the Pt L<sub>3</sub> edge of the 0.2 wt %Pt:SnO<sub>2</sub> sensor, equipped with the Au electrodes as well as the Ag/Pd heater (spectrum a), is compared with those of a 25  $\mu$ m thick Pt foil (spectrum d) and a SnO<sub>2</sub> sensor based on the conventional substrates with Pt electrodes/heater (spectrum c). The Pt L<sub>3</sub>-spectrum of the sensor equipped with Pt electrodes/heater, where the average of both

the sensor-Pt in SnO<sub>2</sub> and the electrodes are detected, is almost identical with the Pt foil. However, they differ significantly from the spectrum of the 0.2% wt Pt:SnO<sub>2</sub> sensor with Au and Ag/Pd electrodes and heaters respectively, i.e. *only* the sensor-Pt in SnO<sub>2</sub> is detected (Fig. 1B inset). Consequently, one can say that the Pt from the electrodes is in mainly metallic state which is in contrast to conclusions presented previously<sup>[9]</sup>. The whiteline intensity, which is the first resonance after the edge jump, of the Pt-foil and also of the Pt-electrodes is twice higher than in conventional spectra since the lifetime broadening is suppressed in the HERFD-XANES spectra<sup>[10]</sup>. A rise in the whiteline is observed with increasing oxidation state of platinum due to an increase of unoccupied 5d<sub>5/2</sub> states, to which the 2p<sub>3/2</sub> core level electron is excited<sup>[8]</sup>. Therefore, if the whiteline intensity decreases, the density of unoccupied d states is lower, which corresponds to the lower oxidation/less ionic state of Pt. The whiteline feature at 11.569 keV with peak intensity higher than 4 is characteristic for oxidized platinum with rather strong empty d-states<sup>[11]</sup>. In fact, the comparison with PtO<sub>2</sub> reference spectra showing lower whiteline intensity than the Pt incorporated in the SnO<sub>2</sub> matrix (Fig. 2A) demonstrates that Pt in the SnO<sub>2</sub> has more empty states, i.e. is more oxidic than Pt in PtO<sub>2</sub> and more electron are transferred from the Pt to the SnO<sub>2</sub>.

These findings from the XANES data in Fig. 2A are further supported by full extended X-ray absorption fine structure (EXAFS) data. The corresponding Fourier transformed EXAFS spectra of the Pt sensors with special heater and electrode (spectrum a and b) and the conventional one (spectrum c) are given in Fig. 2B. Whereas the conventional design only elucidates metallic Pt (from the electrode, backscattering amplitude at 2.8 Å) the main contribution in the radial distribution functions of the Fourier transformed EXAFS

of the specially designed 0.2 wt % Pt:SnO<sub>2</sub> based sensors is due to backscattering by the oxygen neighbors, located roughly at 2.03 Å (for details of the EXAFS analysis, cf. table SI-1 of the ESI). This and the absence of a Pt-Pt contribution characteristic for metallic platinum or small platinum clusters (Fig. 2B c and ref. <sup>[12]</sup>) support that Pt is fully oxidized. Note further that two additional tin shells could be fitted at about 2.90 and 3.68 Å (cf. ESI, table SI-1). The obtained Pt-O and Pt-Sn distances are in good agreement with the Sn-O and Sn-Sn distances of SnO<sub>2</sub> (see ESI). Hence, most probably the doping of the metal oxide leads to substitution of Sn ions by Pt ions in the SnO<sub>2</sub> lattice. The high stability of the ionic platinum species in the lattice of the oxide was further enlightened by reduction experiments of the sensor in 2 vol % H<sub>2</sub> in He at 600°C. FT-EXAFS spectra of 0.2 wt % Pt:SnO<sub>2</sub> sensors before and after reduction - compared with the spectrum of the Pt electrodes - still show the lack of Pt-Pt contributions (Fig. 2B).

For catching the state of the Pt under the working conditions of the sensors, the XAS spectra and resistance changes of 0.2 wt % Pt: SnO<sub>2</sub> sensors were simultaneously recorded during target gas exposure (Fig. 3). Although the HERFD-XANES mode is very sensitive to subtle variations of the oxidation state, the electronic structure or the local environment of Pt, only minor changes during the exposure to CO or H<sub>2</sub> in air were observed (Fig. 3A), whereas huge changes in the resistance were detected (Fig. 3B). This is further supported by EXAFS analysis where the surrounding of Pt remains unchanged (see e.g. Fig. 2B). The slight decrease of the whiteline intensity indicates the changes of the electronic structure induced by adsorbed CO or H<sub>2</sub> species, which is well known also by conventional XAS <sup>[13]</sup>. Obviously, metallic Pt particles or clusters can be excluded as a reason for improved sensor activity in Pt doped SnO<sub>2</sub> sensors. In fact, even in rather

strong reducing conditions no metallic Pt is observed which is in line with HRTEM investigations that neither showed Pt particles before and after reduction (ESI). Hence, platinum seems either to influence the electronic structure as a whole and/or offers new adsorption sites in the SnO<sub>2</sub> lattice that leads to higher selectivity and activity. The strong whiteness of the Pt L<sub>3</sub>-edge and its incorporation into the lattice indicate that electrons are donated from the d-band into SnO<sub>2</sub> changing the Fermi level and the electronic properties of SnO<sub>2</sub>. This means that the role played by Pt in gas sensing is more complex than anticipated: On the one hand, we still have, like in the case of Pd<sup>[5]</sup>, the atomic/molecular adsorption sites generation for the Pt atoms dispersed at the surface. Here, we are providing direct experimental proof for this molecular dispersion and its consequences for the understanding of sensing. On the other hand there is an astonishing bulk effect, in fact a Pt bulk doping, which results in more electrons in the conduction band of SnO<sub>2</sub>. They are essential for sensing because the ionosorption of oxygen at the surface of the tin dioxide requires electrons from the bulk; the formed species are the reaction partners for the reaction with reducing gases, such as H<sub>2</sub> and CO, and, consequently, their more extensive availability contributes to the increased sensor signals. In conclusion, new insight into the structure of the Pt constituent of SnO<sub>2</sub>-based sensors has been achieved by high energy resolved fluorescence detected X-ray absorption spectroscopy at dopant levels down to 0.2 wt % Pt and in a thin highly porous layer. For this purpose, a novel approach for identification of the sensing mechanism under working conditions at the high-flux beamline ID26 at ESRF has been presented. Firstly, the sensor was successfully modified in a way that platinum was only present in the sensing layer. Secondly, the gold fluorescence was efficiently eliminated by using the high energy

resolved fluorescence detection mode. This did not only result in proper XANES but even in range-extended EXAFS data since the sensor layer is located on top of the gold electrode. In this way, the study demonstrates the potential of using new synchrotron-based techniques in solid state chemistry and materials science together with sample design and structure-function relationships. The whiteline intensity of  $\gg 6$  uncovered that platinum is in a highly oxidized state. Platinum is furthermore very difficult to reduce, which shows that it is strongly incorporated into the matrix as also supported by detailed EXAFS analysis. These results are surprising because in many cases metallic Pt particles or clusters have been ascribed to the improved properties. The present results however uncover that, in addition to the appearance of surface adsorption sites associated to the Pt atoms incorporated into the surface lattice of  $\text{SnO}_2$ , there is also a possible bulk sensitization effect linked to the increase of the free charge carriers concentrations due to the Pt d-electrons transferred to  $\text{SnO}_2$ . These conclusions on the role of Pt in Pt- $\text{SnO}_2$  based sensors in gas detection mechanism go in a similar direction as in the case of Pd in Pd- $\text{SnO}_2$  based sensors. Note, however, that Pd species in  $\text{SnO}_2$  are easier to reduce than the corresponding Pt species, incorporated in the  $\text{SnO}_2$  lattice. In future, it will be rewarding applying this technique for differently prepared Pt-based sensors to shed even more insight into the role of surface and bulk doping as well as the importance of the kind of noble metal.

### *Experimental Section*

The investigated material was synthesized by conventional wet chemistry sol-gel procedure. The doping was achieved via gel impregnation in the intentional concentration

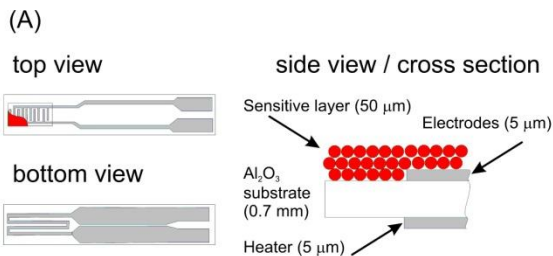
of Pt chloride. The sensors were prepared by screen printing of a paste onto an alumina substrate. Detailed description is given in <sup>[14]</sup>. High-energy-resolution fluorescence detection experiments were performed at beamline ID26 at the European Synchrotron Radiation Facility <sup>[15]</sup>. The incident energy was selected using the <111> reflection from a double Si crystal monochromator. Rejection of higher harmonics was achieved by two Si mirrors with a Pd and Cr layers working at 2.5 mrad angle relative to the incident beam under total reflection. The energy calibration was performed on Pt foil. The incident X-ray beam had a flux of app.  $2 \times 10^{13}$  photons·s<sup>-1</sup> on the sample position. HERFD-XANES spectra were measured with an X-ray emission spectrometer in horizontal plane <sup>[8]</sup>. Sample, analyzer crystal and photon detector (avalanche photodiode) were arranged in a vertical Rowland geometry <sup>[16]</sup>. The Pt HERFD-XANES spectra at the L<sub>3</sub>-edge were obtained by recording the intensity of the Pt L $\alpha_1$  emission line (9442 eV) as a function of the incident energy. The emission energy was selected using the <660> reflection of a spherically bent four Ge crystal analyzers (with  $R = 1\text{m}$ ) aligned at 80° Bragg angle. A combined (incident convoluted with emitted) energy resolution of 1.8 eV was obtained as determined by measuring the elastic peak (ESI). The sensor chamber for simultaneous XAS and resistance measurements and gas mixing set-up are described in <sup>[5]</sup>.



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## Figures



(B)

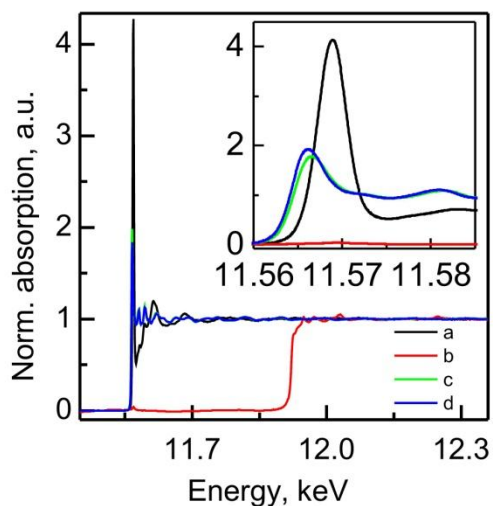


Figure 1: (A) Schematic view of the cross section of the  $\text{SnO}_2$  based sensor equipped with electrodes and heaters. In order to obtain structural information of the Pt dopants on an atomic level the conventional Pt electrodes and heater were exchanged with Au and Ag/Pd. (B) Pt  $L_3$  edge EXAFS spectra of 0.2 wt % Pt: $\text{SnO}_2$  sensor with Au electrodes measured by (a) high-energy resolved fluorescence detection and (b) traditional detection mode; for comparison HERFD-XANES reference spectra of sensors with Pt electrodes (c) and Pt foil (d). Note the increased whiteline intensity compared to conventional XANES due to the HERFD-detection mode.

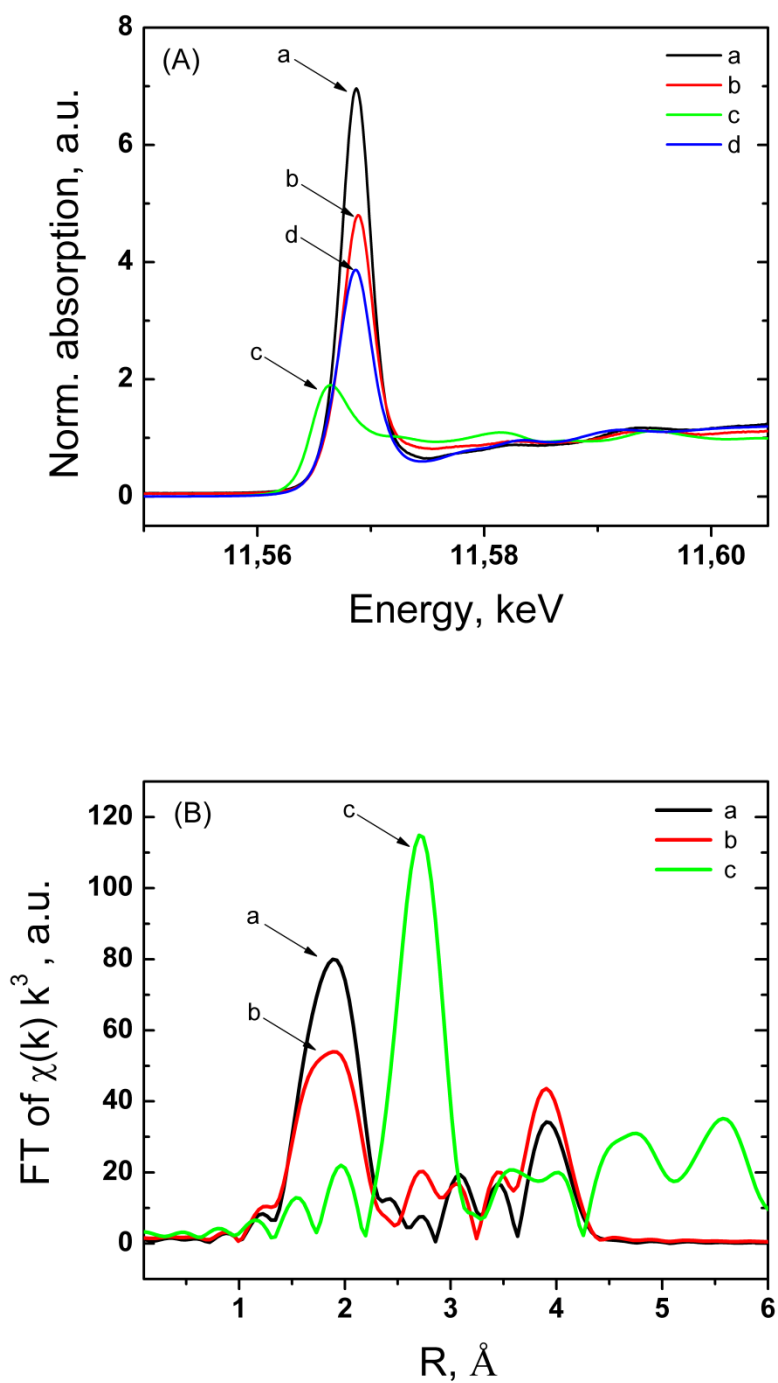


Figure 2 (A) XANES of 0.2 wt % Pt:SnO<sub>2</sub> sensor with (a) Au electrodes in dry air at 300°C, (b) after reducing conditions (2 Vol. % H<sub>2</sub>/He at 600°C), (c) SnO<sub>2</sub> with Pt-electrodes at 300°C in air and (d) PtO<sub>2</sub>-powder. (B) Corresponding Fourier Transformed EXAFS.

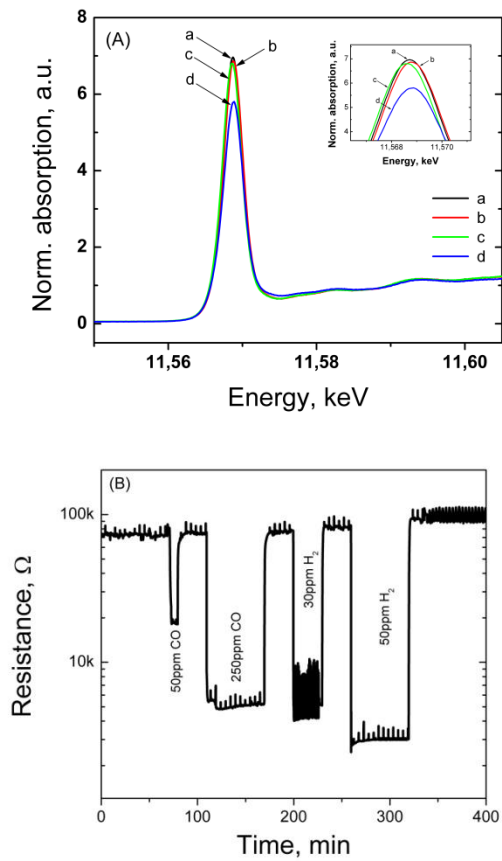
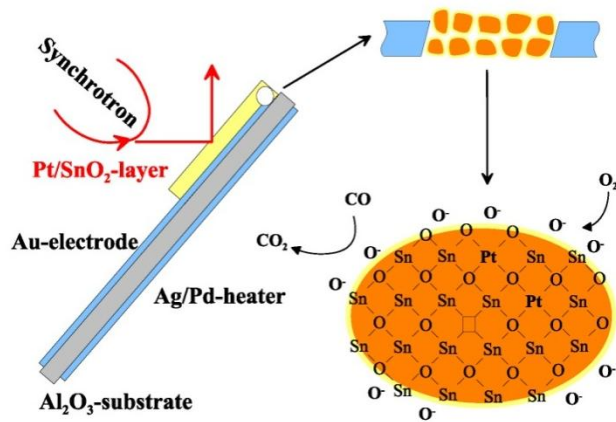


Figure 3 (A) XANES of 0.2 wt. % Pt:SnO<sub>2</sub> sensor with Au electrodes at (a) 300°C in dry air, (b) exposure to 50 ppm H<sub>2</sub> and (c) exposure to 250 ppm CO; (d) as comparison the spectra in 2 vol. % H<sub>2</sub> in He at 400°C. (B) Resistance change of 0.2 wt. % Pt:SnO<sub>2</sub> sensor upon exposure to 50 and 250 ppm CO and 30 and 50 ppm H<sub>2</sub> in dry air at 300°C during simultaneous XANES measurements.

Table of Contents "Catching the state of Pt in SnO<sub>2</sub>-based sensors under working conditions"



**Sensor at work:** The structure of platinum in a 50 micrometer thin SnO<sub>2</sub> layer is monitored by the combination of a specially designed experimental sensor setup with high energy resolution fluorescence detected X-ray absorption spectroscopy as well as "range-extended" EXAFS to gain new insights into the local structure of the platinum dopant.