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A novel SnO₂ sensor and its selectivity improvement with catalytic filters

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Summary

We have developed a new organometallic approach for the preparation of SnO₂ gas sensitive layer. The investigated sensor has shown to be very sensitive to CO at 500°C and to NO₂ at 350°C. Additionally, an improvement of the sensor selectivity was achieved by the use of catalytic filter materials directly integrated into the device. The filters are made of zinc oxide and titanium dioxide supported gold nanoparticles (Au@ZnO, Au@TiO₂), which were prepared by deposition-precipitation by urea (DPU) method. This catalytic filters, operated at room temperatures and under humid atmosphere (HR 50%), allowed to fully eliminate 100 ppm CO response, whereas the sensor always responds to 100 ppm C₃H₈.

Motivation and results

Despite the intense research work in the field of metal oxide semi-conductor sensors, the need for selective gas sensing devices remains a challenge. One strategy to improve the selectivity is to integrate catalytic filters into the device. Few years ago, gold nanoparticles (< 5 nm) based on reducible metal oxides supports (e.g. TiO₂, CeO₂ and MgO) have been investigated in several oxidation reactions [1, 2]. Such gold catalysts, prepared by a method initially developed by C. Louis and co-workers [3], exhibit a very high catalytic activity for CO even at room temperature [4]. Drawing on that pioneer work, we synthesized the Au@ZnO and Au@TiO₂ nano-composites. The catalytic activity towards CO for both materials was then evaluated as catalytic filters (i.e. at room temperature under 50% of humidity).

Concerning the SnO₂ sensor, a new sensitive layer was developed in our team by an organometallic approach. The pristine nanoparticles are made of Sn₃O₂(OH)₂. They were deposited on miniaturized silicon gas sensor substrates by an ink-jet method. Upon *in situ* heating, the layer was transformed into SnO₂. The sensor exhibited extremely high response to 1 ppm NO₂, especially at low temperatures (S=66% at 350°C) (Fig. 1a), while the other tested gases (i.e. CO, C₃H₈, and NH₃) were almost non-detected in these conditions. Such device allows therefore to selectively detect NO₂ gas at low temperature. At high temperatures, the sensor exhibited good CO sensitivity (Fig. 1b) with a detection limit below 2 ppm (S=9.8% at 500°C). However, other reducing gases were also well detectable at this temperature. The catalytic filters were therefore integrated into the device in order to increase the selectivity. The device is presented on Figure 2. The sensor was tightly connected with a holder containing 100 mg of Au@ZnO or Au@TiO₂ powders, forcing the gas mixture to pass through the filter before it reaches the SnO₂ sensitive layer. Figure 3a presents the sensor response to 100 ppm CO and C₃H₈ in the presence or in the absence of the catalytic filter. A complete removal of 100 ppm CO from the gas mixture was observed, whereas the C₃H₈ always passed through the filter. Superior reactivity towards CO at the applied conditions was obtained for Au@ZnO (Fig. 3b). These results open the way towards improved arrays of selective gas sensors.

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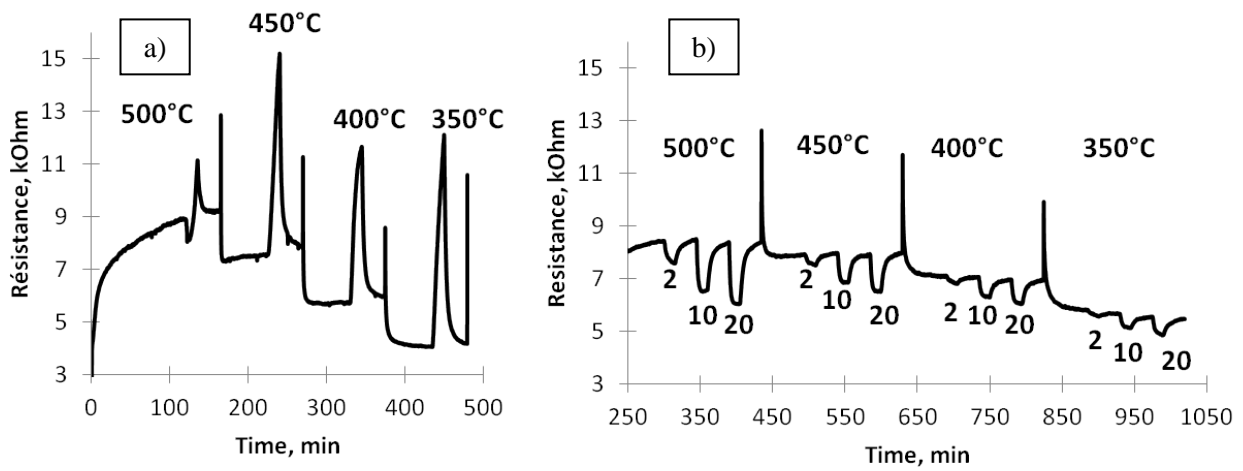


Figure 1. Sensor response to (a) NO₂ (1 ppm) and (b) CO (2, 10, 20 ppm) at different temperatures.

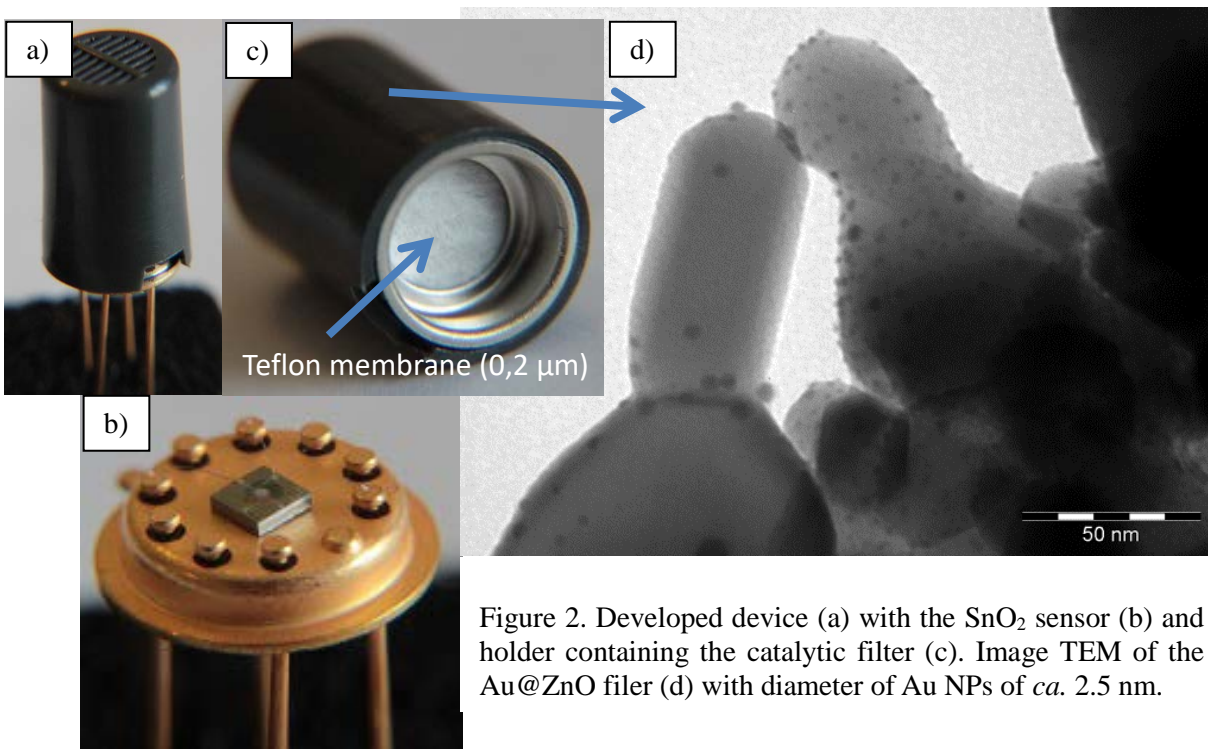


Figure 2. Developed device (a) with the SnO₂ sensor (b) and holder containing the catalytic filter (c). Image TEM of the Au@ZnO filter (d) with diameter of Au NPs of *ca.* 2.5 nm.

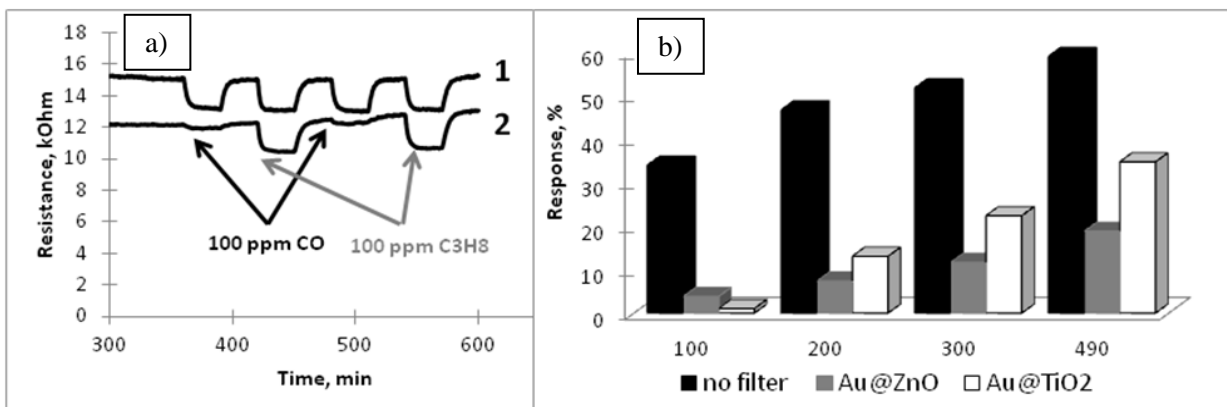


Figure 3. a) SnO₂ sensor response towards 100 ppm CO and C₃H₈ in the absence (1) and presence (2) of Au@ZnO filter, b) comparison of sensor response towards CO at different concentrations in the presence of Au@ZnO or Au@TiO₂ filters.