A Novel SnO2 Sensor and its Selectivity Improvement with Catalytic Filter

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Summary

We have developed a new organometallic approach for the preparation of SnO_2 gas sensitive layer. The investigated sensor has shown to be very sensitive to CO at 500°C and to NO_2 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 filers are made of zinc oxide and titanium dioxide supported gold nanopatricles (Au@ZnO, Au@TiO_2), 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 C_3H_8.

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. TiO_2, CeO_2 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 synthetized the Au@ZnO and Au@TiO_2 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 SnO_2 sensor, a new sensitive layer was developed in our team by an organometallic approach. The pristine nanoparticles are made of $Sn_3O_2(OH)_2$. They were deposited on miniaturized silicon gas sensor substrates by an ink-jet method. Upon *in situ* heating, the layer was transformed into SnO_2. The sensor exhibited extremely high response to 1 ppm NO_2, especially at low temperatures (S=66% at 350°C) (Fig. 1a), while the other tested gases (i.e. CO, C_3H_8, and NH_3) were almost non-detected in these conditions. Such device allows therefore to selectively detect NO_2 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@TiO_2 powders, forcing the gas mixture to pass through the filter before it reaches the SnO_2 sensitive layer. Figure 3a presents the sensor response to 100 ppm CO and C_3H_8 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 C_3H_8 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.

References

[1] M. Haruta, T. Kabayashi, H. Sano, N. Yamada, *Novel gold catalysts for the oxidation of carbon monoxide at a temperature far below 0°C,* Chem. Lett. 16, 2 (1987) 405

[2] L. Delannoy, K. Fajerwerg, P. Lakshmanan, C. Potvin, C. Methivier, C. Louis, *Supported gold catalysts for the decomposition of VOC : Total oxidation of propene in low concentration as model reaction***,** App. Cat. B: 94 (2010) 117

[3] R. Zanella, L. Delannoy and C. Louis, *Mechanism of deposition of gold precursors onto TiO_2 during the precipitation by cation absorption and deposition-precipitation with NaOH and urea,* App. Cat. : A, 291, 1-2 (2005) 62

[4] C. Milone, M. Trapani, R. Zanella, E. Piperopolulos, S. Galvagno, *Deposition–precipitation with urea to prepare Au/Mg(OH)$_2$ catalysts: Influence of the preparation conditions on metal size and load*, Mat. Res. Bull., 45, 12 (2010) 1928

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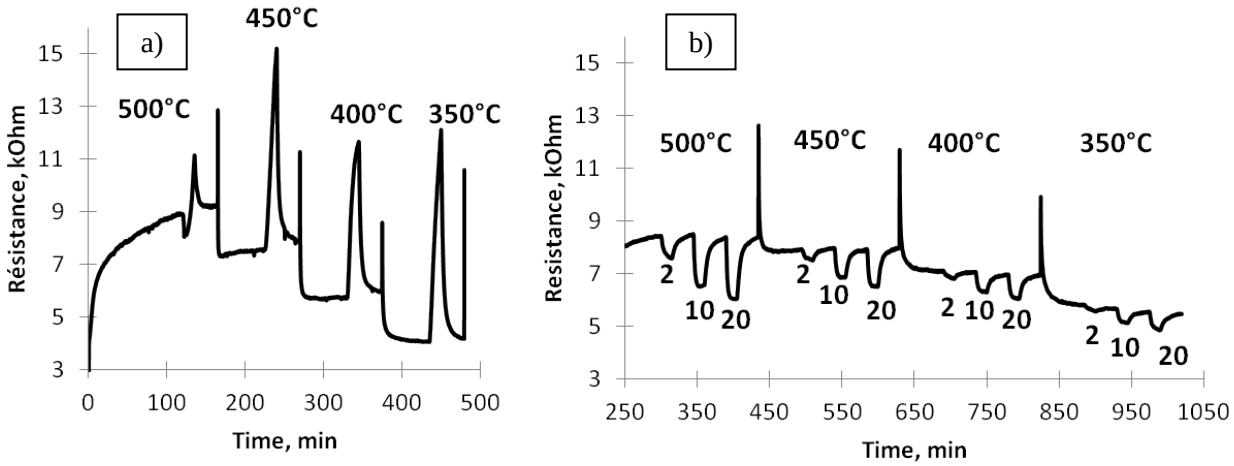

Figure 1. Sensor response to (a) NO_2 (1 ppm) and (b) CO (2, 10, 20 ppm) at different temperatures.

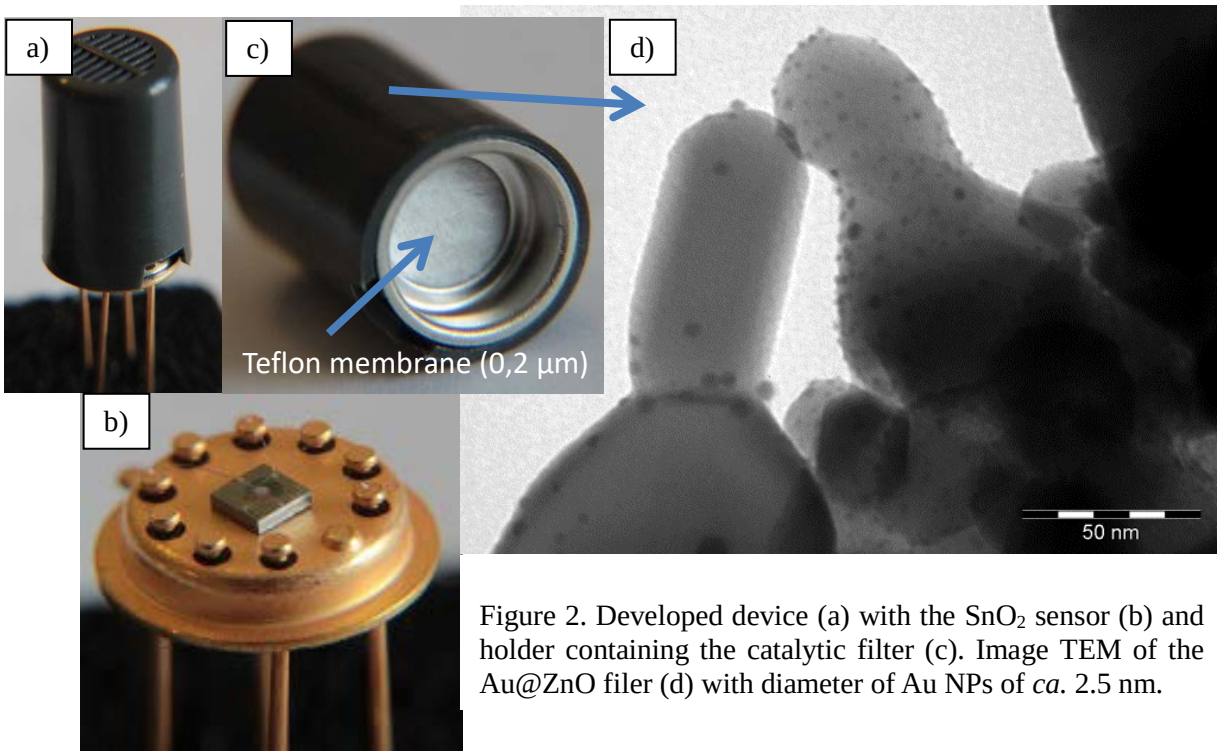

Figure 2. Developed device (a) with the SnO_2 sensor (b) and holder containing the catalytic filter (c). Image TEM of the Au@ZnO filer (d) with diameter of Au NPs of *ca.* 2.5 nm.

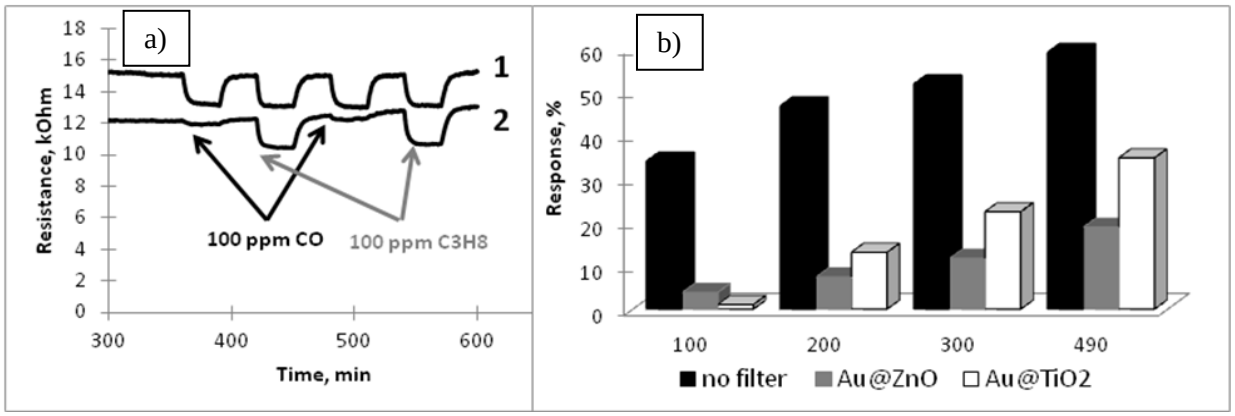

Figure 3. a) SnO_2 sensor response towards 100 ppm CO and C_3H_8 in the absence (1) and presence (2) of Au@ZnO filter, b) comparison of sensor response towards CO at different concentrations in the presence of Au@ZnO or Au@TiO_2 filters.