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*Extended Abstract*

# Light—Assisted Low Temperature Formaldehyde Detection at Sub-ppm Level Using Metal Oxide Semiconductor Gas Sensors †

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## Introduction

Formaldehyde HCOH is a toxic compound that, in trace concentrations, causes serious diseases of the respiratory tract, gastrointestinal tract and eyes. The biochemical oxidation of HCOH in human tissues occurs with the formation of $CO_2$ and formic acid, which with prolonged exposure is the cause of asthma, pulmonary edema, and cancer. The main problem in the HCOH detection is the need to determine very low concentrations: 0.5 mg/m$^3$ (0.4 ppm) and 0.1 mg/m$^3$ (81 ppb) in the air of the working and living area, respectively. A promising alternative for the HCOH quantification is the development of gas analyzers based on an array of metal oxide semiconductor sensors that exhibit the specific temperature dependence of the sensor signal when detecting different gases. It is currently shown that the use of such sensor arrays allows the detection of trace concentrations of individual substances, including various VOCs, in gas mixtures, as well as the recognition of gas mixture components. Such an analysis is relevant not only for environmental control and safety systems, but also promising for the development of new express methods for analyzing food quality, water purity, and medical diagnostics. However, the use of a dynamic temperature regime implies cyclic heating up to 500 °C, which leads to a significant increase in energy consumption and degradation of the sensitive layer. An alternative to dynamic thermal heating can be periodic photoactivation by UV or visible light with subsequent analysis of the photoconductivity rise and fall curves using a mathematical algorithm. This becomes possible when nanocomposites based on nanocrystalline semiconductor metal oxides and photocatalysts providing low-temperature decomposition/oxidation of target gas molecules are used as sensitive materials.

## Experimental

Nanocomposites $SnO_2/TiO_2$ modified with Pt, Ag and Au nanoparticles were obtained by wet chemical synthesis. $SnO_2$ $xH_2O$ xerogel was precipitated from $H_2SnCl_6$ solution. To obtain the $SnO_2/TiO_2$ composites, the $SnO_2$ $xH_2O$ xerogel and $Ti(OPr)_4$ alcohol solution were stirred at RT till full hydrolysis of titanium precursor. The resulting solid phase was impregnated with $Pt(acac)_2$, $AgNO_3$ and previously formed Au sol and then annealed at 300 °C for 24 h. The composition and microstructure of the samples were characterized by EDX, XRD, HRTEM and single-point BET methods. The surface sites were investigated using thermal analysis, FTIR and XPS. The sensor measurements were carried out in the temperature range 50–300 °C in the flow cell shielded from the background light. DC measurements were carried out to monitor the electrical conductance of the sample during exposure to HCOH/air gas mixtures (0.06–0.6 ppm HCOH in dry air) in dark

conditions and under constant and periodic lighting. Miniature LEDs with $\lambda_{max}$ = 365 nm (UV), $\lambda_{max}$ = 470 nm (blue), $\lambda_{max}$ = 535 nm (green) and $\lambda_{max}$ = 630 nm (red) inserted into the cell were used as illumination sources.

## Results

Figure 1a shows the change in the samples resistance at periodic changing the composition of the gas phase: "dry air—0.6 ppm HCHO in dry air", in the temperature range 300–50 °C in dark conditions. From the obtained data the values of the sensor response S were calculated as $S = R_{air}/R_{gas}$, where $R_{air}$ and $R_{gas}$ are the values of the nanocomposite resistance in pure air and in the presence of HCHO, respectively (Figure 1b). The best sensor response in dark conditions was obtained for Au@$SnO_2$/$TiO_2$ sample at 100 °C. The constant illumination of the samples during the measurements at 100 °C leads to a decrease in the sensor response (Figure 1c), and this decrease in the signal value growths with increasing radiation energy from red to UV light. However, the use of periodic illumination (Figure 1d) makes it possible to obtain the dependences of photoconductivity on the concentration of HCOH for their further description using a mathematical signal processing algorithm. Such a replacement of the dynamic temperature regime with periodic illumination will allow the quantitative determination of HCOH in gas mixtures with a significant reduction in energy consumption.

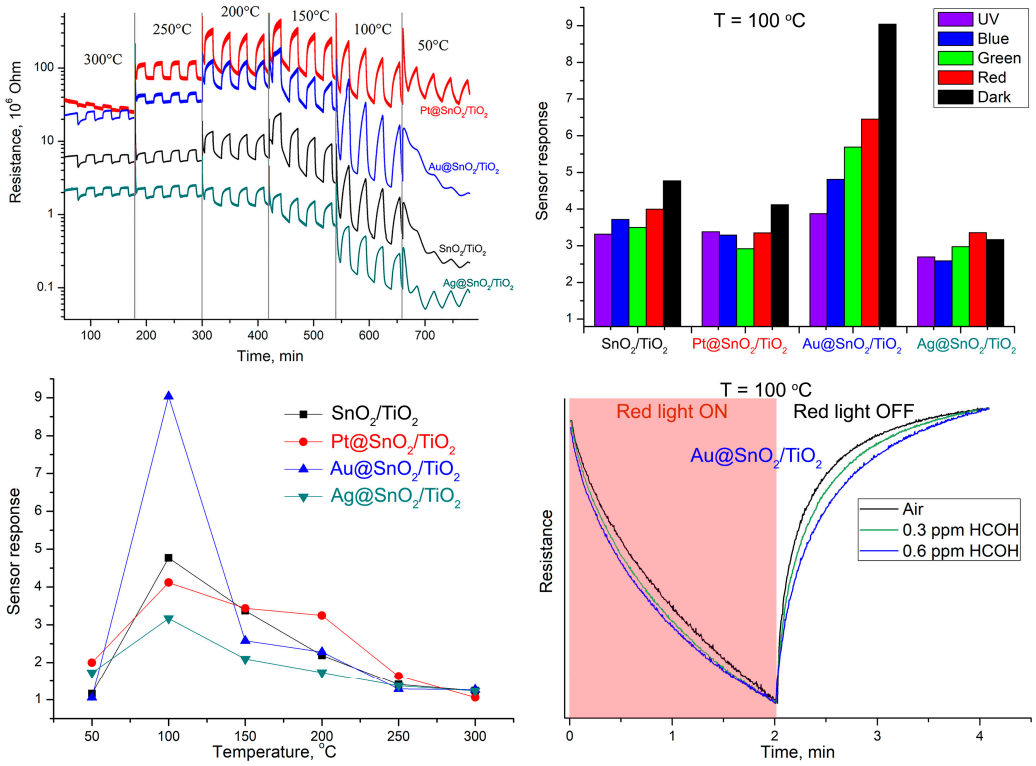


**Figure 1.** (**a**) Change in the samples resistance at periodic changing the composition of the gas phase; (**b**) Temperature dependences of sensor response to 0.6 ppm HCOH in dark conditions; (**c**) Influence of constant illumination on sensor response to 0.6 ppm HCOH at 100 °C; (**d**) Change in the resistance of Au@$SnO_2$/$TiO_2$ nanocomposites at 100 °C during one "Light ON/OFF" cycle in dry air containing 0, 0.3 or 0.6 ppm HCOH.

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