ROOM TEMPERATURE ETHANOL SENSOR WITH SUB-PPM DETECTION LIMIT: IMPROVING THE OPTICAL RESPONSE BY USING MESOPOROUS SILICA FOAM

Dániel Sebők[1,*], László Janovák[1], András Sápi[2], Dorina G. Dobó[2,3], Ákos Kukovecz[2,3], Zoltán Kónya[2,4], Imre Dékány[1,5]

[1]Department of Physical Chemistry and Materials Science, University of Szeged, 1 Rerrich square, H-6720 Szeged, Hungary
[2]Department of Applied and Environmental Chemistry, University of Szeged, 1 Rerrich square, H-6720 Szeged, Hungary
[3]MTA-SZTE "Lendület" Porous Nanocomposites Research Group, University of Szeged, 1 Rerrich square, H-6720 Szeged, Hungary
[4]MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, 1 Rerrich square, H-6720 Szeged, Hungary
[5]MTA-SZTE Supramolecular and Nanostructured Materials Research Group, University of Szeged, 8 Dóm square, H-6720 Szeged, Hungary
e-mail: sebokd@chem.u-szeged.hu.hu

Abstract

In this paper a low ppm-range ethanol sensor - operating at room temperature - is presented. The three types of ZnO_2 based hybrid thin films as sensor surfaces consist of semiconductor nanoparticles, polyelectrolyte (polyacrylic acid, PAA) and/or mesoporous silica. The thin films were prepared by Layer-by-Layer (LbL) self-assembly method and were subjected to reflectometric interference measurements (RIfS) for testing sensorial application. The sensor investigation showed that the detection limit of the thin films is in the sub-ppm range. Applying mesoporous silica as surface coating or interlayers in the sandwich-structured thin film (ZnO/SF) improved the optical response, but the sensitivity showed non-linear characteristic. The thin film with mixed structure (ZnO/PAA/ZnO/SF) showed linear response in the 0.5-12 ppm range with 0.6 nm /ppm sensitivity and acceptable selectivity.

Introduction

Sensors for volatile organic compounds (VOCs) play an important role in everyday life and industrial safety. These chemical agents are harmful and unhealthy, so the detection of these molecules has a great importance in environmental and health protection, such as in air and water quality control, food industry or – especially in the case of ethanol – the "driving under influence" (DUI) control. The principles, technical solutions, the materials used, the operating temperature ranges and concentration levels are fairly diversified. The studies can be divided into two major groups: room temperature (RT) and high temperature (around 200 and 300 °C) applications. However, it has to be noted that VOC pollutants easily evaporate at room temperature and can be very harmful and carcinogenic already at low concentration, but the most of the RT technical solutions are able to detect ethanol vapour only above 10 ppm concentration.
In this work, we made an attempt to combine the beneficial sensing properties of mesoporous materials and reflectometric interference technique [1-3] to construct a highly sensitive ethanol sensor operating at room temperature.

Experimental

Zinc peroxide nanoparticles with an average diameter of 80 nm were synthesized by the photolysis of zinc acetate dehydrate ($C_4H_6O_4Zn \cdot 2H_2O$, Fluka, a.r.) described in [2]. Poly(acrylic acid) (PAA, M_W = 100000, Sigma, a.r.) was used as a negatively charged polyelectrolyte. Furthermore, SBA-15 and silica foam were used as coatings or negatively charged interlayer materials. Five types of hybrid thin films were prepared by using the ZnO_2 nanoparticles, negatively charged PAA polyelectrolyte and the mesoporous silica samples (see Figure 1.) by the LbL deposition method.

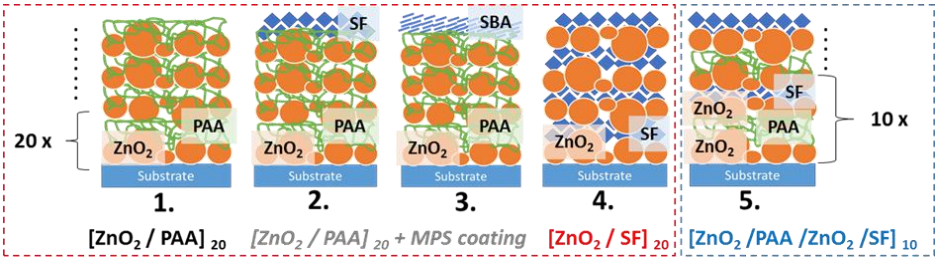

Figure 1. The schematic view of the prepared and applied hybrid thin films.

The specific surface area (BET method) and the total pore volume were determined by the BJH method using a Quantachrome NOVA 2200 gas sorption analyzer by N_2 gas adsorption/desorption at 77 K. SAXS technique was used to investigate the fractal properties and structural parameters of the mesoporous silica components. SAXS curves were recorded with a slit-collimated Kratky compact small-angle system (KCEC/3 Anton-Paar KG, Graz, Austria) equipped with a position-sensitive detector (PSD 50M from M. Braun AG Munich, Germany) containing 1024 channels 55 μm in width. CuK_α radiation ($\lambda_{CuK\alpha}$=0.1542 nm) was generated by a Philips PW1830 X-ray generator operating at 40 kV and 30 mA. The optical and sensorial properties of the thin films were studied by a Nanocalc 2000 spectrophotometer with ADC1000-USB A/Dconverter (Ocean Optics) (see Figure 2.).

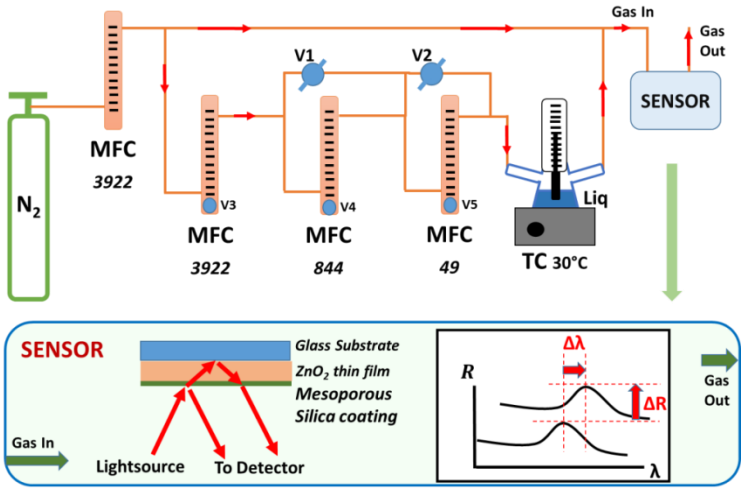

Figure 2. Scheme of the used experimental setup (gas flow system and reflectometric test cell) and the measurement principle.

The sensor responses, Δλ (nm) and ΔR (a.u.) were defined as the wavelength shift of the given extreme of the reflection spectra and the change of the reflection value corresponding to this extreme, respectively.

Results and discussion

The porosity, pore system characteristic and specific surface area are of great importance in the case of mesoporous adsorbents used in sensorial applications, therefore several structural parameters were determined and calculated by using SAXS technique. The double logarithmic plot of the scattering curve is suitable for determining the fractal properties of the material. In the case of SBA-15 the slope is approximately -2 in the higher *h*-range, which indicates a frame-like mass fractal structure, as well as, p = -3.5 for SF sample is characteristic for the surface fractal nature of the mesocellular foam structure. The N_2 adsorption/desorption studies of the silica samples show isotherms with hysteresis loop and pore size distributions between 3 and 10 nm characteristic for mesoporous materials. The specific surface areas and average pore diameters are 798 m^2g^{-1}, 4.2 nm and 666 m^2g^{-1}, 4.6 nm for SBA-15 and SF, respectively. The overall conclusion is that although the structural and fractal nature of these mesoporous materials are significantly different, but the average pore diameters and specific surface areas are similar, and these values appear to be sufficiently high for considerable adsorption capacity and sensorial applications.

The thin films were subjected to reflectometric interference measurements for testing sensorial applications. The measurements were carried out by measuring the shift of the local minimum of reflected intensity near λ=500 nm wavelength. It is λ_{min}=457 nm in the case of $[ZnO_2/PAA]_{20}$, and λ_{min}=507 nm and 568 nm for $[ZnO_2/PAA/ZnO_2/SF]_{10}$ and $[ZnO_2/SF]_{20}$, respectively (these values are valid in the *t=0* measurement point). The raw results (sensorgrams), i.e., the *Δλ vs. t* curves are presented in Figure3 (left side).In the case of *Δλ* curves the responses are positive because of the optical thickness increases due to the vapour adsorption. Significant signal drift can be observed in the case of ZnO_2/PAA, ZnO_2/PAA+coating and ZnO/SF thin films, which is rather disturbing phenomenon: should be drift compensation applied? In this case, not in general. If compensation is used then the responses become nearly independent of concentration; if it is ignored then each measurement step (at the same concentration) results in higher response than the previous one and this fact makes impossible to accurately determine unknown concentrations. As it can be seen on the *Δλ* calibration (response vs. concentration) curves (Figure 3., right side), we did not apply compensation, the responses increase with concentration, even if not linearly. However, in the case of $[ZnO_2/PAA/ZnO_2/SF]_{10}$ hybrid thin film response drift was not observed which resulted a linear Δλ calibration curve (0.586 nm/ppm). In summary, it was found that applying $[ZnO_2/PAA]$, $[ZnO_2/PAA]$+MPS coating or $[ZnO_2/SF]$ structured thin layers mostly failed due to the signal drift and nonlinear sensitivity. The mixed structure of $[ZnO_2/PAA/ZnO_2/SF]$ was devoid of drift and showed linear calibration curves, so this type of hybrid (nanoparticle/polyelectrolyte/mesoporous silica) multilayer is an appropriate structure to apply as sensing surface in reflectometric interference sensor in gas phase.

Based on the presented results the $[ZnO_2/PAA/ZnO_2/SF]_{10}$ thin film was selected for further experiments, such as reproducibility, response time analysis and selectivity. It can be stated that the sensors signal is well reproducible, the sensors response reaches the 90 % of maximum value within 40 s and it is relaxed to 10 % within 80 s. Selectivity test was carried out by using methanol, ethanol, *n*-hexane, toluene and xylene. It was established that in the case of ZnO_2/PAA/SF mixed structure 2-3 times higher response was observed for ethanol than for the

other volatile organic compounds (VOC), although also the affinity to aromatic molecules increased compared to ZnO_2/PAA structure.

Next the $[ZnO_2/PAA/ZnO_2/SF]_{10}$ thin film was subjected to sensorial test in a higher, c=2.46-37 (±0.68) ppm range. The concentration steps (0-50 min) were repeated after a 50 min long baseline stability test. The statement was that the sensor has a fairly stable baseline (without drift), but the Δλ calibration curve showed a slight quadratic deviation from linear behavior.

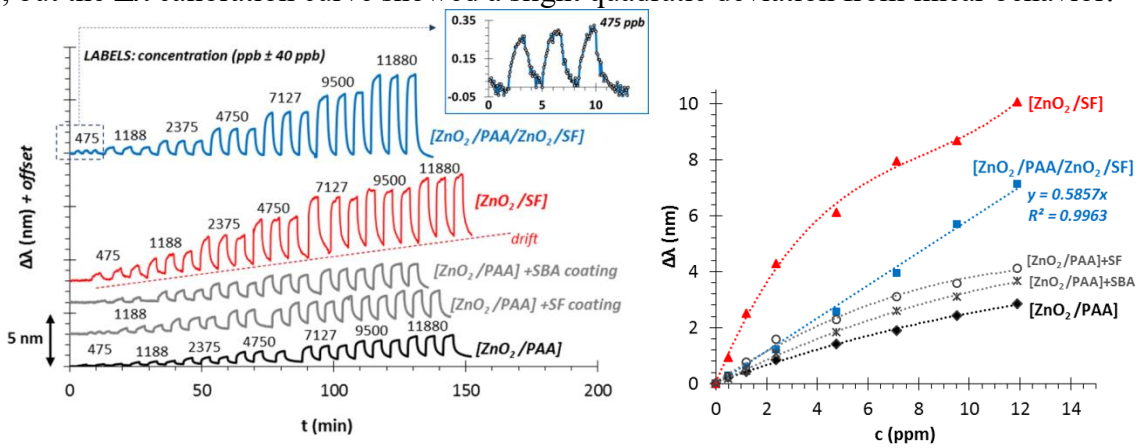

Figure 3. Ethanol sensing tests: *Δλ vs. t* curves for the tested thin films; inset: response of $[ZnO_2/PAA/ZnO_2/SF]_{10}$ mixed structure for c=475 ppb EtOH (left) and ethanol sensing *Δλ(nm) vs. c(ppm)* calibration curves for the prepared thin layers (right) (labels: structure of the thin films and calibration equation for $[ZnO_2/PAA/ZnO_2/SF]_{10}$ mixed structure).

Conclusions

In this work we successfully combined the beneficial sensing properties of mesoporous silica materials and reflectometric interference technique to construct a highly sensitive ethanol sensor operating at room temperature. The structural parameters and fractal properties of the silica samples (SBA-15 and silica foam) were studied by TEM, BET and SAXS techniques: latter methods showed that the specific surface area of the MPSs is over 650 m^2/g. The three types of hybrid thin films, namely ZnO_2/polyelectrolyte (PAA), ZnO_2/mesoporous silica foam (SF) and a mixed, ZnO_2/PAA/ZnO_2/SF structures were subjected to sensorial tests in the gas phase. We showed that the detection limit of the sensor is sub-ppm (< 500 ppb), but only the mixed (ZnO_2/PAA/ZnO_2/SF) nanostructure showed linear sensitivity in the 0.5-11.9 ppm range without response drift, while both the response time and selectivity remain reasonable good. Testing the sensor in extended (up to 40 ppm) concentration range showed a slight quadratic deviation from linear behavior.

Acknowledgements

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