Enhanced Nitroderivates Detection with Si Microcantilevers by using Sorption Heat on Microporous Materials as Additional Discriminating Tool

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Abstract (Arial 10)

This work deals with the vapor detection of explosives by easy to operate, low-cost, accurate and fast chemical sensors based on Si microcantilevers provied with internal heating and modified with nanoporous solids as chemical receptors. As a rough rule of thumb a method that is suitable for direct explosive detection should be able to detect explosives concentrations down to less than 1 ng/L. The progress achieved in the field of chemical sensors during the last decade has been truly outstanding, leading to a continuous lowering of sensitivity limits. This has been driven in large part by the development of cantilever-based sensors [1], and particularly by the advances in three main areas: smaller mechanical resonators, higher resonant frequencies and improved readout techniques to detect the motion. Regarding sensor selectivity, i.e., the ability of a sensor to discriminate among different analytes, advances have generally been achieved on an ad hoc basis, when a specific target has been identified for a certain analyte. However, this work puts forward a more realistic situation involving nanoporous solids [2-4], as chemical receptors that respond, at least partly, to more than one species. To this end, zeolite type materials with tunable sorption properties have been deployed as isolated crystalline entities on the top surface of the mechanical transducers. Consequently, the strategy follows a biomimetic approach with the so-called artificial "nose" consisting of a chemical sensor array and a pattern recognition system. It is clear that a workable electronic nose requires miniaturization of its components, for economic as well as for practical (fast detection, regeneration times for efficient operation and system integration) reasons; a distinguished feature of the Si microcantilever array platforms herein used. The cantilevers chips have been fabricated from n-type SOI (silicon on insulator) wafers by using standard optical lithography and bulk micromachining technologies with five-levels of masks. A multisensing platform comprising 8 micro-cantilevers per chip (Figure 1) with self-heating elements on the cantilever tips, and electromagnetic actuation and piezoresistive detection is proposed in this study for reproducible and reliable explosives detection. The use of meander shaped resistor (see Figure 1.b) is clearly beneficial for zeolite sorption capability refreshment with time on stream. The resonant frequency changes have been analyzed in presence of different concentration of toluene (13.5 mg/L- 3500 ppmV), water (2.1 mg/L- 2800 ppmV), and 2-nitrotoluene (0.14 mg/L- 25 ppmV), vapors in dry N_2. Detailed results obtained for two types of zeolite BEA (acid form denoted as HBEA & Fe exchanged type denoted as BEA-Fe) are depicted in Figure 2 and Figure 3 respectively. By using integrated heater, identical experiments have been performed at different temperatures on the cantilever tip (30ºC & 55ºC). Thus, additional finger prints of the same sample are obtained fulfilling time requirements. Unlike previous publications on explosives detection by following thermal signatures on microcalorimeter type cantilever sensors without chemical receptors [5], our sensing approach goes a step further in terms of reliability by using mass sensing as a function of temperature. The as calculated sorption heat values (Table 1), a distinguished feature of sorbate-sorbant interactions, could be used as additional key parameter for each of the Si coated cantilevers to improve false positive rates during explosives identification in complex environment.

References
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Figures
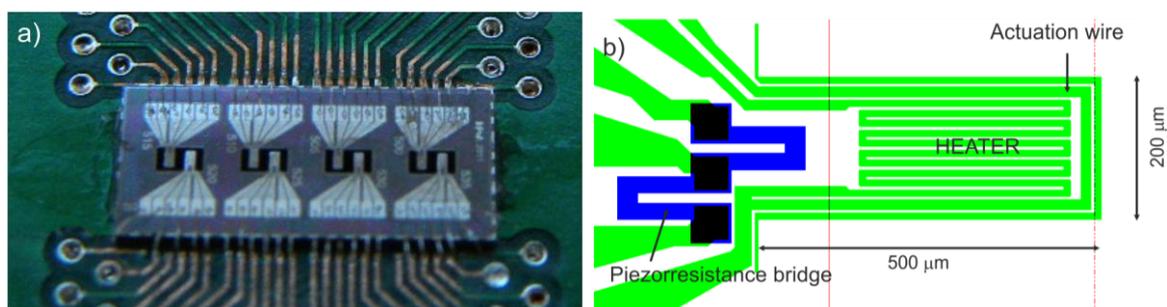
Figure 1: a) Chip with 8 microcantilevers (f_0~72 KHz), and b) connection scheme of one microcantilever with electromagnetic actuation, piezo-resistive detection and integrated heater.
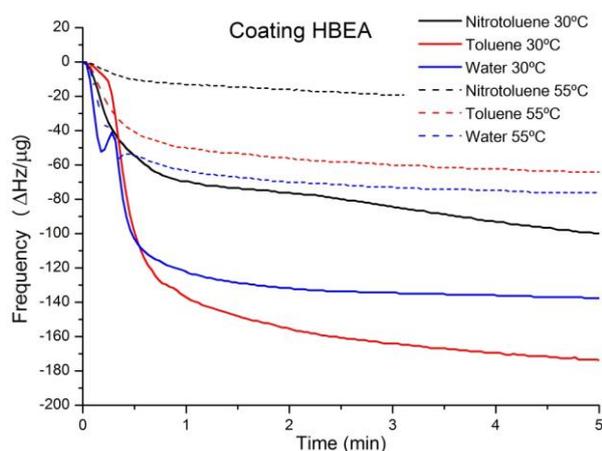
Figure 2: Resonant frequency changes per μg of zeolite HBEA in presence of different concentration of toluene (13.5 mg/L- 3500 ppmV), water (2.1 mg/L- 2800 ppmV), and o-nitrotoluene (0.14 mg/L- 25 ppmV) at 30°C and 55°C.
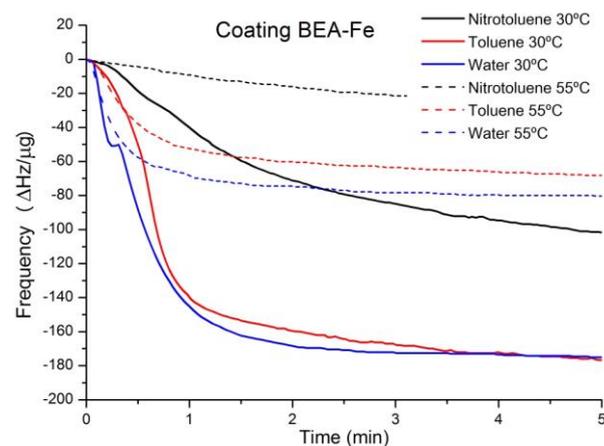
Figure 3: Resonant frequency changes per μg of zeolite BEA-Fe in presence of different concentration of toluene (13.5 mg/L- 3500 ppmV), water (2.1 mg/L- 2800 ppmV), and o-nitrotoluene (0.14 mg/L- 25 ppmV) at 30°C and 55°C.

Table 1: Detection results at 30°C and 55°C of 2-nitrotoluene, toluene and water by using zeolite HBEA and BEA-Fe.

	HBEA			BEA-Fe		
	Nitrotoluene	Toluene	Water	Nitrotoluene	Toluene	Water
*Sensitivity (30°C) mHz/ppm/ng	4.852	0.051	0.049	4.925	0.052	0.063
*Sensitivity (55°C) mHz/ppm/ng	1.211	0.019	0.026	1.502	0.020	0.028
*Time constant (30°C) (min^{-1})	2.25	0.80	0.44	2.69	3.64	0.65
*Time constant (55°C) (min^{-1})	3.12	0.76	0.42	0.92	0.77	0.45
**Sorption Heat -ΔG_{ads} (kJ/mol)	45.87	32.53	20.08	39.26	31.86	26.22

* Calculated from following fitting expression: $Y = Y_{inf}\left(1 - e^{-\frac{t}{t_1}}\right)$ where Y_{inf} [Hz/μg] represent the analyte adsorption per μg of zeolite in equilibrium and t_1 is the time constant.

** Calculated from: $\dfrac{-\Delta G_{ads}}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right) = ln\left(\dfrac{Y_{infT1}}{Y_{infT2}}\right)$ being R = 8,314 J·mol^{-1}·K^{-1} and T_1 and T_2 expressed in K.