

Explosives Detection by array of Si μ -cantilevers coated with titanosilicate type nanoporous materials

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Abstract— An array comprising 4 Si microcantilevers coated with nanoporous ETS-10 crystals sub-micrometric in size has been deployed as a multisensing platform for 2-nitrotoluene (an explosive related molecule) recognition. For such purposes, the adsorption properties of synthetic microporous ETS-10 titanosilicate type materials have been tailored by means of the Si/Ti ratio, and surface grafting with organic groups (amine, imidazol). Our general strategy for vapor detection of explosives involves the combination of Si based nanoporous solids as sensing materials and resonating Si cantilevers provided with self-heating elements as tiny microbalances (mass sensitivity factors ~ 18 Hz/ng). Particularly for this work, ETS-10 type titanosilicates with promoted basic properties (Si/Ti=4, $-\text{NH}_2$ anchored on the external surface) exhibit the higher affinity towards nitroaromatic derivatives as electron deficient molecules. A high remarkable hydrophilic character is shown by titanosilicates modified by covalent linkage with imidazole based organosilane (above 17% wt. water uptake at room temperature). Accounting from such versatile sorption behavior, the family of nanoporous ETS-10 crystals has been deployed by microdropping technique over the 8 Si-microcantilevers chip. By means of a portable low-power electronic interface capable of the simultaneous excitation and measurement of 4 sensor output signals, such multisensing platform has been successfully applied for 2-nitrotoluene detection at trace level.

Keywords— *microcantilevers; gas sensing; ETS-10; nanoporous coating; explosives; portable lock-in amplifier; actuation and detection; low-power consumption*

I. INTRODUCTION (*Heading 1*)

Identification and quantification of explosives has gained importance among emerging topics of research. In situ detection of explosives is of major importance in several applications related to civil security and environmental monitoring. Accordingly, extensive efforts have been devoted to the development of innovative and effective detectors, capable of monitoring explosives both in time and location. However, low-cost and easy to operate chemical sensors which can mimic the olfaction of dogs to ensure accurate, fast and economical detection of explosives are yet not commercial available [1]. 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 (below 1

ppb). The progress achieved in the field of chemical sensors during the last decades 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 [2], and particularly by the advances in three main areas: smaller mechanical resonators, higher resonant frequencies and improved readout techniques to detect the motion. In general, microcantilever sensors are configured to work as tiny microbalances with theoretical mass detection limits around 50 fg for standard fabricated micro-cantilevers. Working in dynamic mode operation, based on the cantilever excitation in its fundamental vibration mode, mass change (Δm) can be calculated from the following equation measuring changes of resonance frequency (Δf),

$$\Delta m = S^{-1} \Delta f = \left(-r_n^{-1} \cdot L^3 w \sqrt{\frac{\rho^3}{E}} \right) \Delta f \quad (1)$$

Where S is the theoretical mass sensitivity, which depends on cantilever dimensions (L length and w width) and material properties (ρ density and E young modulus); and frequency mode parameter ($r_n=0.1615$ for fundamental vibration mode).

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. Zeolite type nanoporous materials have been already deployed as sensing coatings on cantilevers due to their molecular recognition and highly tunable adsorption properties [3,4,5]. The potential of novel nanoporous framework materials, such as mixed tetrahedral-octahedral silicates (OPT) containing different transition metals, has been scarcely explored for selective chemical detection [6,7]. Owing to its wide-pore nature and thermal stability ETS-10 is arguably the most important OPT microporous titanosilicate (SiO_4 , TiO_6). The pore structure of ETS-10 has 12-rings in all three dimensions; these are straight along [100] and [010] (pore opening 0.49 nm x 0.76 nm) and crooked along the direction of disorder; and in this respect ETS-10 has excellent diffusion characteristics. It should be noted the topological similarities with BEA type zeolite with a three dimensional microporous channel system defined by 12-rings (0.76 nm x 0.64 nm and 0.55 nm x 0.55 nm along [001] and [100] respectively. Unlike zeolites, the framework charge

centres at the octahedral Ti^{IV} site carry an overall two-minus charge. Consequently, ETS-10 presents interesting

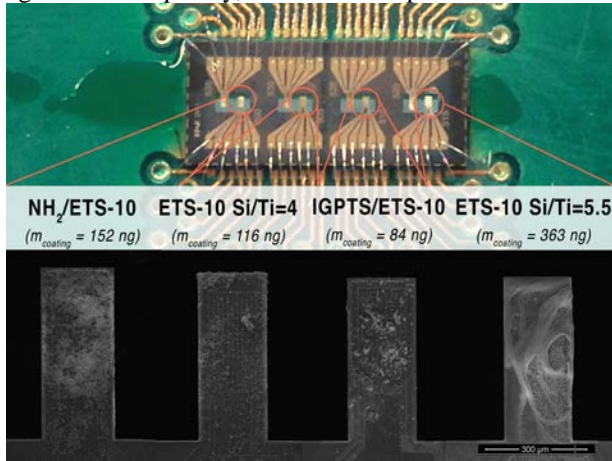


Fig. 1. Top view of the Si μ -cantilever array. Detail of ETS-10 coatings.

opportunities to exploit on the basis on its ion exchange capability, and low acidity.

In view of the molecular recognition properties that nanoporous solids can afford, our general strategy for reproducible and reliable vapor detection of explosives involves the combination of nanoporous sorbents as sensing materials and Si cantilevers provided with self-heating elements as tiny microbalances. The herein presented vapor phase detection results are those obtained with ad-hoc synthesized ETS-10 type titanasilicates deployed over resonating Si microcantilevers by evaporative microdropping technique. Special emphasis has been devoted to the study of post-synthesis treatments, i.e. surface functionalization and Ti enrichment, on the sorption properties and sensor performance. Fig. 1 shows the top surface of the Si-microcantilevers chip after ETS-10 coating.

II. EXPERIMENTAL

A. Microfabrication of Si cantilevers

The micromechanical structures presented were fabricated from n-type SOI (silicon on insulator) wafers by using standard optical lithography and bulk micromachining technologies with five-levels of masks [8]. Cantilevers are 200 μm wide, 15 μm

thick and from 500 to 535 μm in length. With this dimensions, theoretical mass sensitivity (S) values ranging from 16 to 20 Hz/ng are obtained (by using 1).

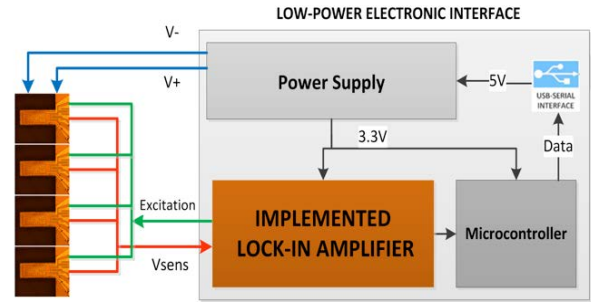
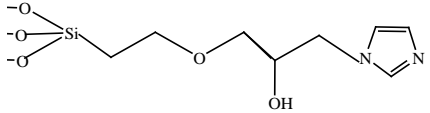
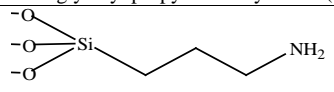


Fig. 2. Block diagram of the implemented low-power electronic interface for the actuation and read-out of 4 microcantilevers.

With the final aim of miniaturization and integration, individual heating wires, actuation of the cantilever and mechanical resonance detection are integrated on each cantilever. The actuation is based on the induced Laplace electromagnetic force due to the coupling between the perpendicular magnetic field created by the magnet allocated on the chip basis and the electrical current passing through the conducting strip printed on the top surface of the microcantilever. In order to detect the cantilever oscillation, semiconductor strain gauges are implanted at the surface of the microstructures which are arranged in half Wheatstone bridge configuration: a first gauge is localized where the stresses are maximum (the clamped-end of the beam), the other one is on the rigid substrate.

To exploit the truly benefits of the microcantilever's platform in terms of portability, reduced size and energy consumption, a portable low-power electronic interface [9] capable of creating the excitation signal as well as obtaining the response values of 4 resonating microcantilevers simultaneously has been used in this work. This portable electronic interface, also capable to regenerate the nanoporous coatings by thermal induced desorption, is solely fed by the 5V line from a USB connection to a host computer. The excitation Resonance frequency sweeps and dynamic tracking of the mechanical response with the 4 microcantilevers oscillating at its natural frequency are performed by means of specific

TABLE I. SURFACE FUNCTIONALIZATION CONDITIONS FOR THE AS SYNTHESIZED ETS-10 TYPE TITANOSILICATES

| Organosilane | Solvent | Reflux Temperature (K) | Zeolite (g) /organosilane (cm^3) /solvent (cm^3) | Reaction Time (h) | Extraction Solvent |
|---|---------|------------------------|--|-------------------|---|
|  Imidazolin-1-glycidyl propyltriethoxy silane (IGPTS) | Cumene | 425 K | 1/9.5/47 | 24 | 2-Propanol (centrifugation and soxhlet) |
|  3-Aminopropyl triethoxysilane (-NH ₂) | Toluene | 383 K | 1/10/150 | 24 | Ethanol (centrifugation) |

Matlab software implementation.

B. Titanosilicate type nanoporous coating preparation

ETS-10 material (Si/Ti=5.5) submicrometric in size is hydrothermally synthesized at 503 K during 24 h following our previous work [10]. The Ti enrichment of ETS-10 herein developed is based on zeolite protocols for Al enrichment materials [11]. Firstly a 0.05 M solution of sodium metatitanate (99.9% Aldrich, 200 mesh) was prepared. ETS-10 powder was added to the prepared solution 1:20 wt ratio, and kept under stirring during 10 min. Then, sodium hydroxide pellets (Aldrich) was carefully added to the solution until pH=13, and kept under mechanical stirring for 2 h at room temperature. Afterwards, the resulting solution was put in a Teflon autoclave for recrystallization at 170 °C during 12 hours.

The surface functionalization process is carried out over as synthesized ETS-10 crystals by covalent linkage using organosilane as coupling agents. In particular, amine (3-aminopropyltriethoxysilane) and imidazol (3-glycidopropyl triethoxysilane) groups are grafted on the external microporous surface. For such purposes, ETS-10 (Si/Ti=5.5) powder, previously dried under vacuum, is introduced in an inertized three-neck round bottom flask with argon to avoid the reversible hydration. Then, anhydrous solvent is injected and the resulting dispersion is sonicated for 15 minutes under Ar atmosphere. Once the reaction temperature reaches the solvent reflux temperature, the organosilane is added under mechanical stirring and kept overnight. The specific conditions for each functionalization process are presented in Table I. The main features of the so obtained powders for coating of the cantilevers are included in Table II.

TABLE II. PREPARED MICROPOROUS TITANOSILICATES FOR NITROAROMATICS SENSING

| <i>Nomenclature</i> | <i>Si/Ti At. ratio</i> * | <i>H₂O uptake wt. %</i> ** | <i>mmol organosilane g ETS-10</i> | <i>Decomposition (K)</i> ** |
|---------------------------|--------------------------|---------------------------------------|-----------------------------------|-----------------------------|
| ETS-10_1 | 5.4 | 7.9 | 0 | n.a. |
| ETS-10_2 | 4.2 | n.a. | 0 | n.a. |
| IGPTS/ETS-10_1 | 5.4 | 56.9 | 8.4 | 307 |
| NH ₂ /ETS-10_1 | 5.4 | 8.2 | 0.2 | 355 |

*estimated by SEM-EDX; **estimated by TGA

A 4% wt. ethanolic dispersion of each material is prepared for microcantilever coating by evaporative microdropping technique [4,5,8,9]. In order to control the location of the ETS-10 crystals on the Si transducer, a rapid solvent evaporation is induced during the deposition procedure thanks to the meander type resistors printed on the cantilever tip. This integrated heater is frequently used during sensing experiments for a proper degass of the microporous solids in order to ensure their sorption capabilities. Thus, regeneration cycles of 300 mW, rendering in average temperature values circa 435 K, and 10 min in duration have been systematically applied for a reliable and reproducible operation.

Table III shows the main characteristics of the four Si-microcantilevers used in this work.

TABLE III. MAIN CHARACTERISTICS OF THE TITANOSILICATES COATED MICROCANTILEVERS

| <i>Cantilever</i> | <i>Coating</i> | <i>f₀ (Hz)</i> | <i>S (Hz/ng)*</i> | <i>Coating loading (ng)</i> |
|-------------------|---------------------------|---------------------------|-------------------|-----------------------------|
| 0 | None | 75570 | 18.2 | - |
| 1 | ETS-10_1 | 76290 | 18.2 | 363 |
| 2 | ETS-10_2 | 70870 | 17.2 | 116 |
| 3 | IGPTS/ETS-10_1 | 77660 | 18.9 | 84 |
| 4 | NH ₂ /ETS-10_1 | 80520 | 20 | 152 |

*Theoretical mass sensitivity (equation 1)

C. Gas sensing measurements

The cantilevers were placed in a custom gas chamber of circa 1 cm³ with four individual micro-inlets focused onto each cantilever. Gas streams containing mixtures of the desired species and nitrogen (purity 99.999%) were fed to the chamber at set flowrates by means of mass-flow controllers through saturator trains at controlled temperature. A further dilution with mass-flow controlled stream of nitrogen allowed reaching the desired concentration levels: 10000 ppmV for H₂O and 25 ppmV for 2-nitrotoluene (o-MNT).

By using (1), the measurement of the new gas frequency following exposure to different gas atmospheres allows the estimation of the new cantilever equivalent mass therefore it is also common to relate directly the gas phase concentration of the analyte to the frequency changes of the cantilever, as will be done in this work.

III. RESULTS AND DISCUSSION

Fig. 3 shows the frequency shift variation of the ETS-10 coated microcantilevers upon the introduction of 2-nitrotoluene vapor (o-MNT, 25 ppmV) steps 10 minutes in duration followed by dry N₂ sweep; bare Si microcantilever is also included as reference. As it was expected, the response of bare Si microcantilever is unaffected by the variations in the gas phase composition. Among the tested, the most outstanding performance for o-MNT detection is shown by NH₂/ETS-10_1 coating, i.e. amine groups grafted on the surface.

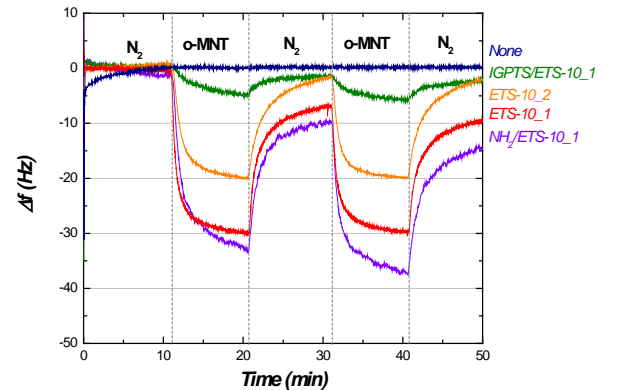


Fig. 3. Evolution of the resonance frequency shift of the ETS-10 modified microcantilevers in presence of 2-nitrotoluene vapor (o-MNT) 25 ppmV.

In fact, the adsorption capability of NH₂/ETS-10_1 titanosilicate is 2.6 folds the exhibited by the pristine ETS-10_1 titanosilicate (see Table IV). This behavior is explained on the basis of the electron deficient character of the nitroaromatic explosive, and the electron donor properties of grafted amine groups [12]; also promoted by the base character of the titanosilicates. The Ti enrichment post-treatment also enhances the o-MNT sorption compared to the as synthesized powder (0.9% wt versus 0.5%wt respectively). As it was expected, the recovery response for the cantilevers with higher affinity towards the target analyte after N₂ flushing is less pronounced. This observation agrees with the thermodynamic sorption heat involved [8] and underlines the degassing requirements for a reusable, reliable explosive detector sensor.

The o-MNT experimental results have been fitted to the following equation to characterize the kinetics of the molecular recognition event as a valuable finger print:

$$Y = Y_{eq} \left(1 - e^{-\frac{t}{t_1}} \right) \quad (2)$$

where Y_{eq} (ng_{ads}/ng_{coating}) represents the analyte absorbed per ng of ETS-10 in pseudo equilibrium conditions for a given analyte concentration in the gas phase, and t_1 is time required to attain $0.63 \cdot Y_{eq}$. As it was expected, ETS-10_1 coating provides with the faster response due to the exposed microporous surface area on unmodified crystals is higher. It is worthwhile to remark that the sensing performance of the prepared titanosilicates is comparable to the already reported for Co exchanged BEA zeolites [8,9] under similar conditions.

The hydrophilic properties of the as prepared coatings have also been analyzed due to the unavoidable presence of humidity as interference in real operation. The post-synthesis treatments increase the water uptake. Especially noticeable is the behavior of IGPTS/ETS-10_1 sample with imidazole groups grafted on the surface. Such hydrophilicity, 10 folds higher than pristine ETS-10_1 is explained on the hydrogen bonding network provided by the organosilane anchored on the surface. On the contrary, IGPTS/ETS-10_1 exhibits the lower affinity towards o-MNT. Thus, cantilever 4, i.e. with IGPTS/ETS-10_1 coating, could be postulated as the most efficient receptor within the multisensing platform for water interference evaluation.

IV. CONCLUSIONS

Microporous ETS-10 type titanosilicates with promoted sorption properties towards nitroaromatic explosives have been prepared. The detection of o-MNT by means of ETS-10 coated Si microcantilevers (loadings clearly below 400 ng) provided with embedded heaters has been successfully accomplished in this work. Particularly remarkable is the o-MNT detection performance exhibited by amino grafted and Ti enriched titanosilicates. The experimental adsorption-desorption frequency shift ratio (thermodynamics) and response time defined for the 63% of the signal (kinetics) have been identified as key parameters to improve explosives identification in complex environment. The presence of the highly hydrophilic imidazole grafted titanosilicate coating in the multisensing platform is clearly beneficial for water interference evaluation.

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TABLE IV. MICROCANTILEVER CHARACTERIZATION AFTER SENSITIVE MATERIAL DEPOSITION

| Cantilever | Coating | o-MNT Detection* | | | H ₂ O as interference |
|------------|---------------------------|------------------|---------------------------------|----------------------------------|----------------------------------|
| | | t_1 (s) | $\Delta f_{ads}/\Delta f_{des}$ | $\frac{ng_{o-MNT}}{ng_{ETS-10}}$ | $\frac{ng_{H_2O}}{ng_{ETS-10}}$ |
| 0 | None | - | - | - | - |
| 1 | ETS-10_1 | 46 | 1.25 | 0.5 % | 1.8 % |
| 2 | ETS-10_2 | 69 | 1.08 | 0.9 % | 3.5 % |
| 3 | IGPTS/ETS-10_1 | 184 | 1.35 | 0.3 % | 17.3 % |
| 4 | NH ₂ /ETS-10_1 | 78 | 1.45 | 1.3 % | 5.6 % |

*calculated from the first o-MNT step.