Chemical Sensing Properties of BaF_2-Modified *h*BN Flakes towards Detection of Volatile Organic Compounds

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1. Material Synthesis and Sensor Preparation

The hexagonal boron nitride (*h*BN) nanosheets were synthesized based on the reported procedure, whereby borazine was used a source for boron and nitrogen atoms, lithium nitride (Li_3N, 99.4 %, Alfa Aesar) as a crystallization agent and barium fluoride (BaF_2, 99%, Alfa Aesar), as a melting-point reduction agent. Typically, 5wt. % Li_3N and 0 – 10 wt.% BaF_2 [1] were added a colourless liquid polyborazylene (PBN) [2], followed by homogenization of the suspension via stirring for 10 min. The suspension was subjected to heat treatment at 200 °C in an alumina crucible for 1h, and the solid-state polymer was the annealed for 1h at 1200 °C (1 °C/min) under inert nitrogen (N_2, 98%, Air Liquide, France) atmosphere [3]. Finally, the chemical vapour sensing properties of the *h*BN samples were evaluated by screening their as-fabricated devices against the polar aprotic (acetone) and polar protic (ethanol) analytes. For device fabrication, dispersions of 2 mg/mL of the *h*BN samples with 4 mg/mL of CTAB were sonicated for 30 min at 60 °C, and then stored at 0 °C to facilitate precipitation of hydrated crystals from the excess surfactant [4]. Thereafter, ~100 µL of the *h*BN dispersions were drop casted onto an FR4 substrate containing interdigitated electrodes (ENIG-Electroless Nickel Immersion Gold, Micropress S.A.; active area ~ 64 mm^2) and dried in an oven at 100 °C for 30 min [5].

2. Results and Discussion

Concentrations of acetone and ethanol vapours (C) were determined from the amount of acetone and ethanol, added to the analysis chamber through the equation:

$$C_{ppm} = \frac{2.46vd}{VsMw} 10^7 \quad \text{……..(S1)}$$

where v represents the volume (in µL) added to the chamber (in our case 1µL, 2 µL, 3 µL, 4 µL and 5 µL, which correspond to the vapor concentrations). Vs is the volume (in mL) of the analysis chamber (here: 2400 mL), d is the density of analyte (in gmL-1) and Mw is the molecular weight of analyte in gM-1. Measurements were taken after 10 min, allowing that the analysis chamber reach steady-state conditions. Sensor response was obtained by resistance measurements, which were carried out using an Agilent 4284A LCR, with an AC signal amplitude of 1 V under dry nitrogen atmosphere.

The sensing performance of the *h*BN-based devices was determined based on the limit of detection (*LoD*) and the sensitivity (*S*), given by

$$LoD = Rb + 3db \quad \text{…….. (S2)}$$

$S = dResp/dC$…….. (S3)

where, Rb is the average resistance, db is the standard deviation of the device resistance without analyte, and C is an analyte concentration. Furthermore, the relative variation of the resistance (R) was used, based on equation S3, was used to determine the response ($Resp$) of the sensing devices;

$\Delta R/R_0 = (R_f - R_0)/R_0$ …….. (S4)

where R_f is the resistance of the sensor when exposed to analyte and R_0 the resistance of the sensor under an inert atmosphere of dry N_2.

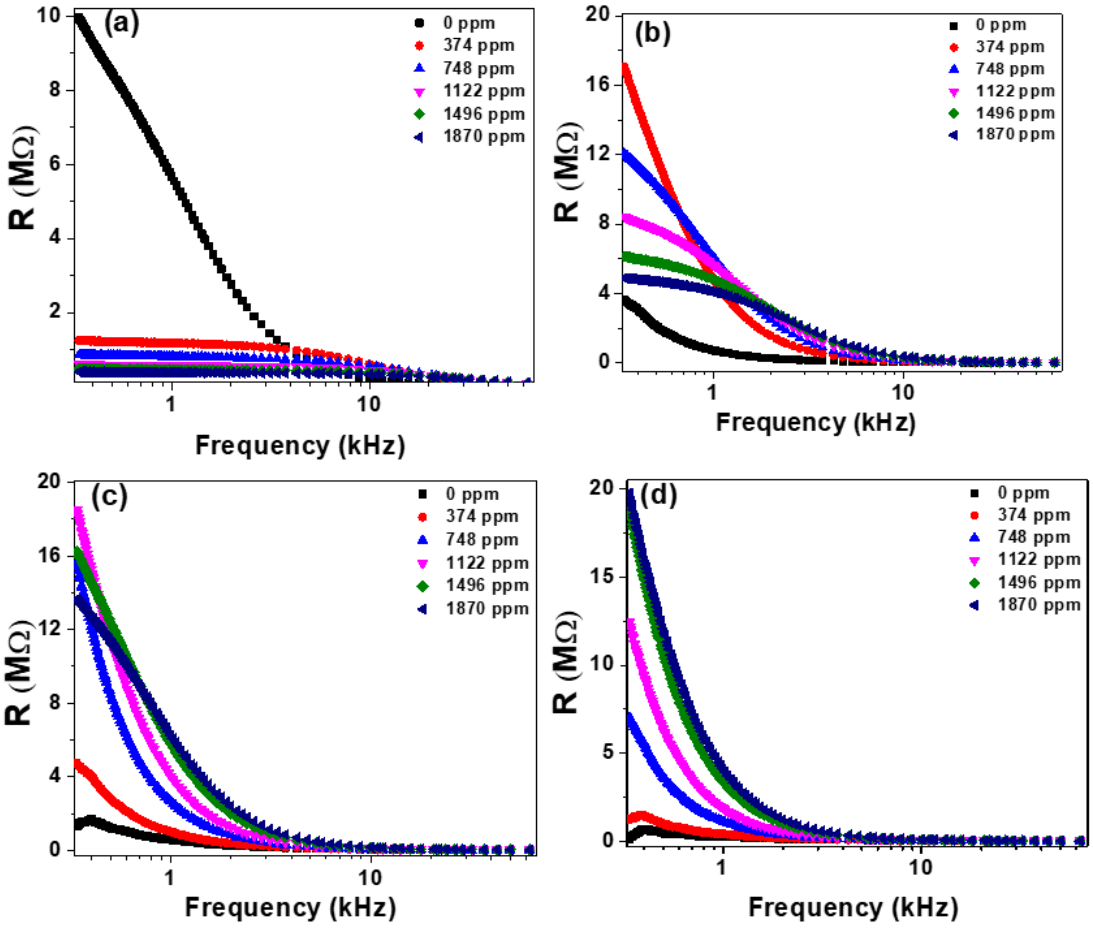

Figure S1. Dependence of sensor resistance on frequency with increasing EtOH: Acetone concentrations for (a) 0, (b) 2.5, (c) 5, and (d) 10 wt% BaF_2- modified *h*BN based sensors.

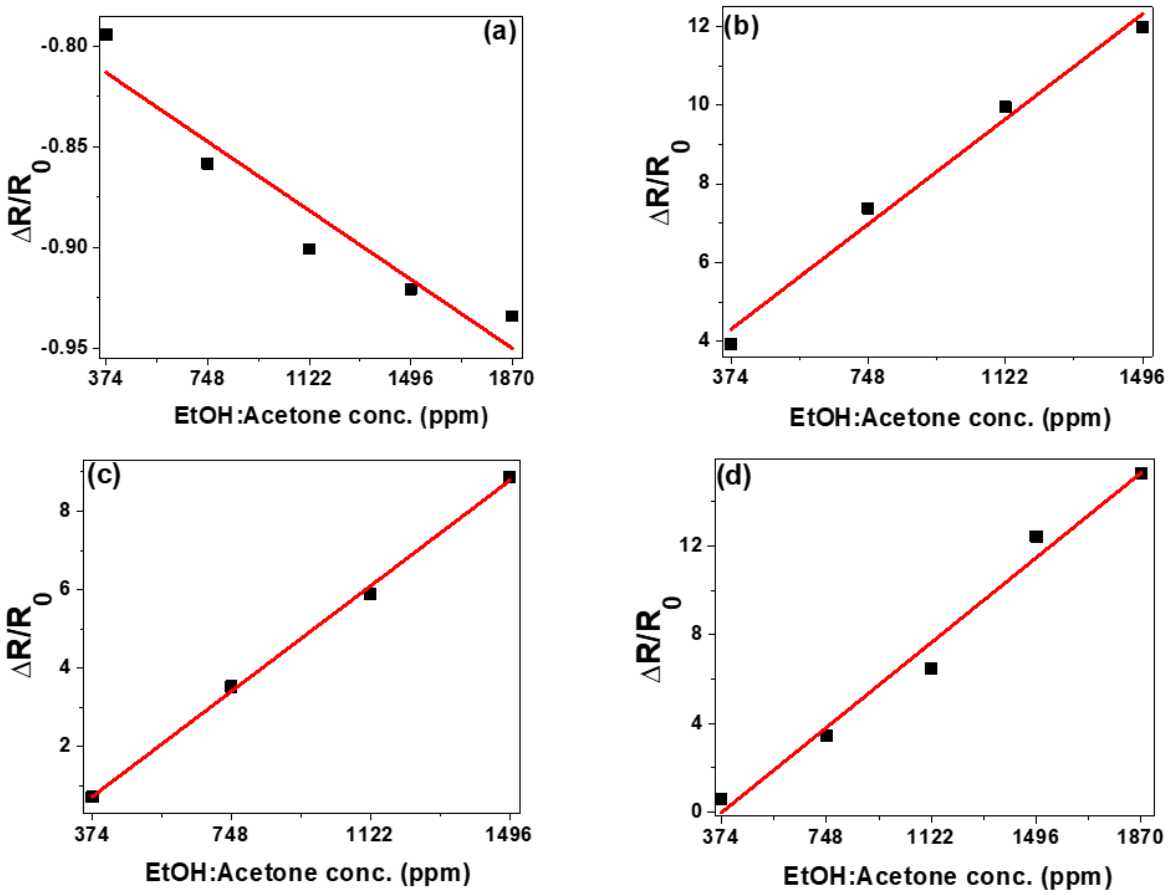

Figure S2. Sensor response versus EtOH: acetone concentrations (a) 0, (b) 2.5, (c) 5, and (d) 10 wt% BaF_2- modified *h*BN based sensors at optimum operating frequencies.

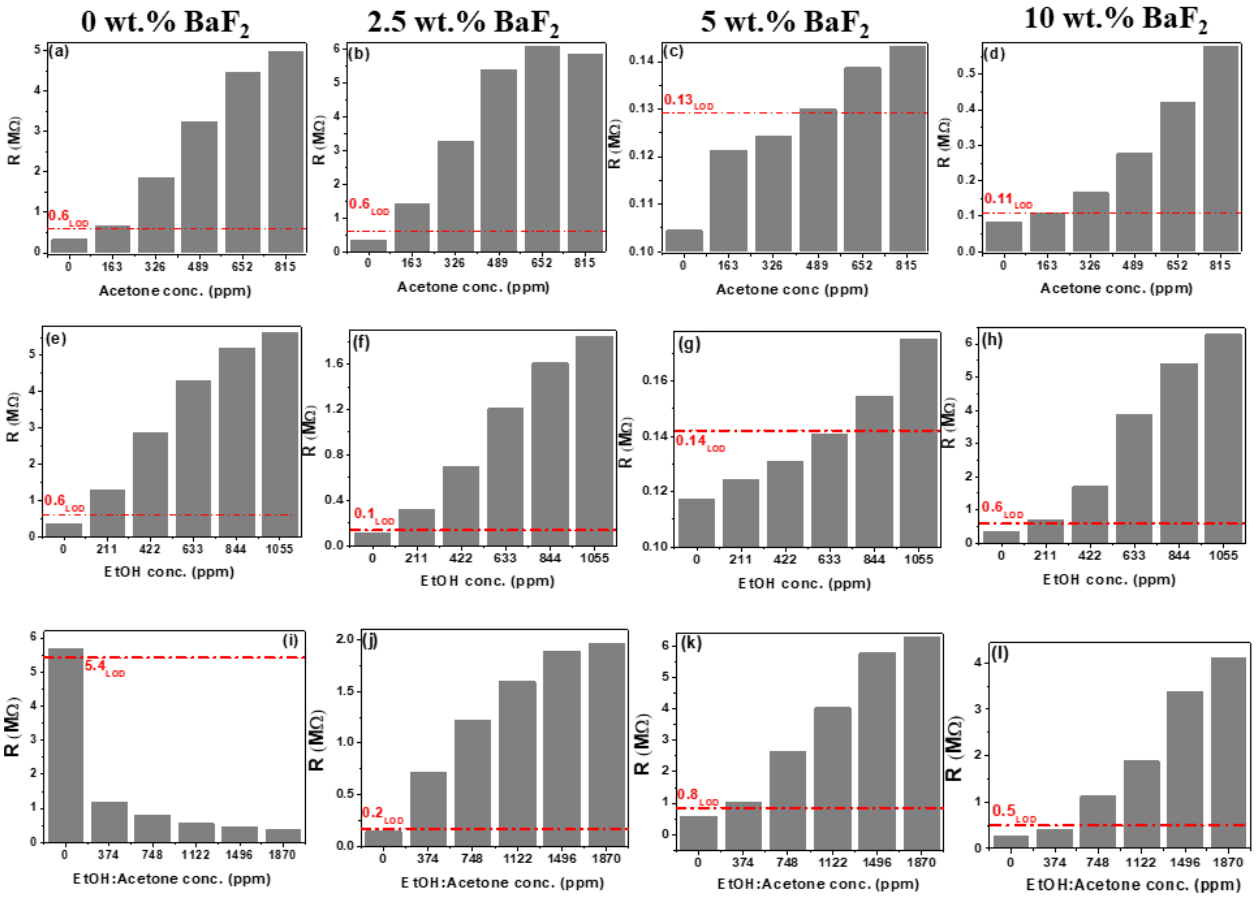

Figure S3. Sensor resistance as a function of analyte concentration for (a-d) acetone, (e-h) ethanol, and (i-l) ethanol: acetone; red line indicates the estimated LoD resistance of the corresponding sensor at the optimum frequency.

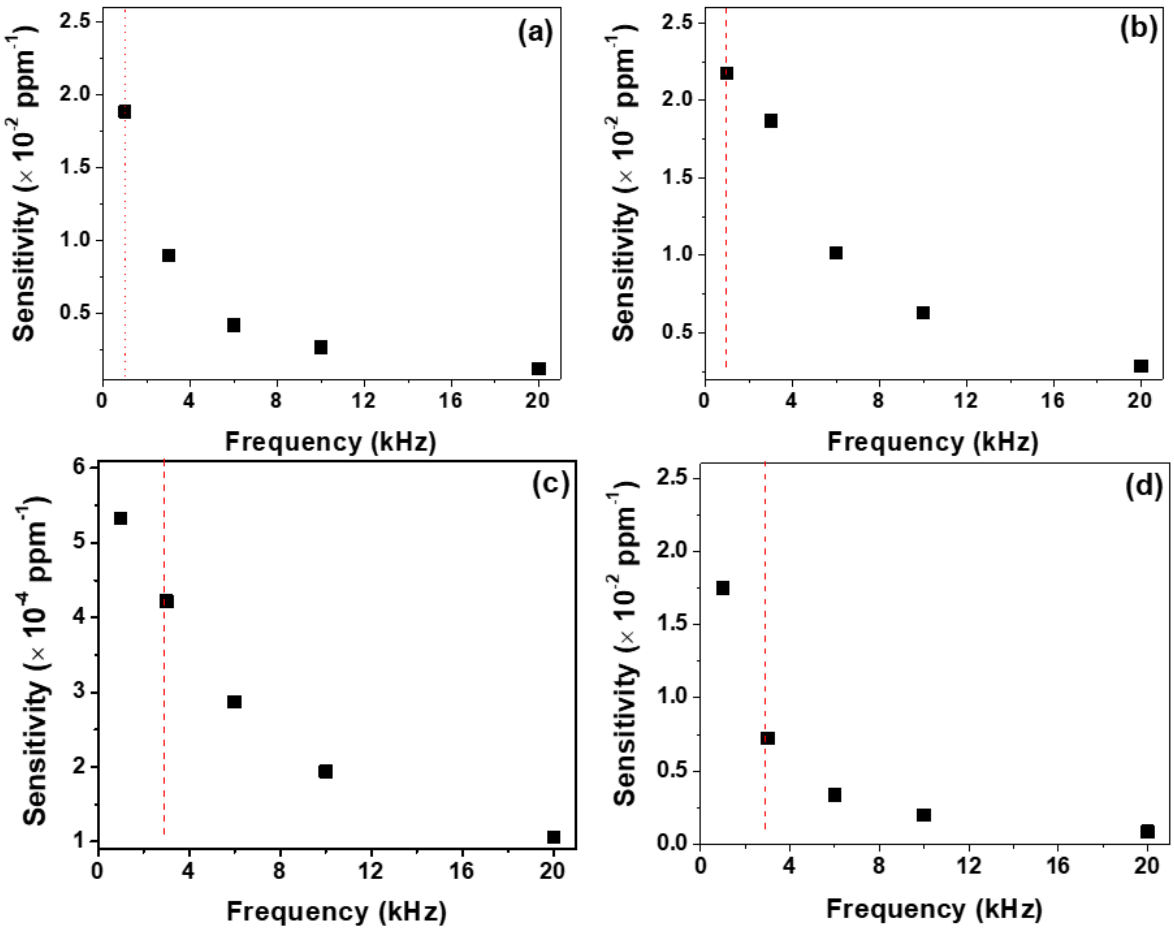

Figure S4. The sensitivities of sensors data based on hBN-BaF2 (a) 0 wt%, (b) 2.5 wt%, (c) 5 wt% and (d) 10 wt% for acetone as a function of frequency; dashed line indicates the optimum operating frequency.

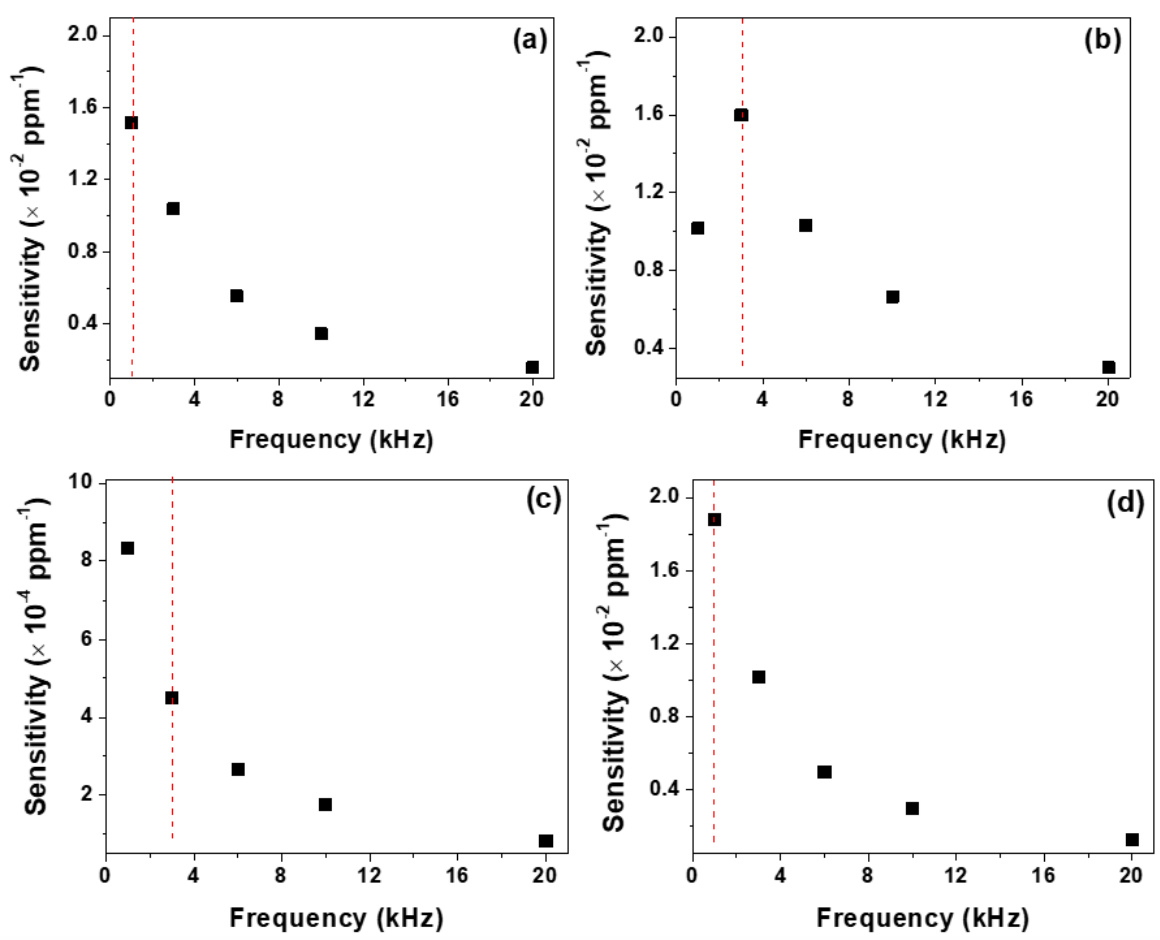

Figure S5. The sensitivities of sensors data based on hBN-BaF2 (a) 0 wt%, (b) 2.5 wt%, (c) 5 wt% and (d) 10 wt% for ethanol as a function of frequency; dashed line indicates the optimum operating frequency.

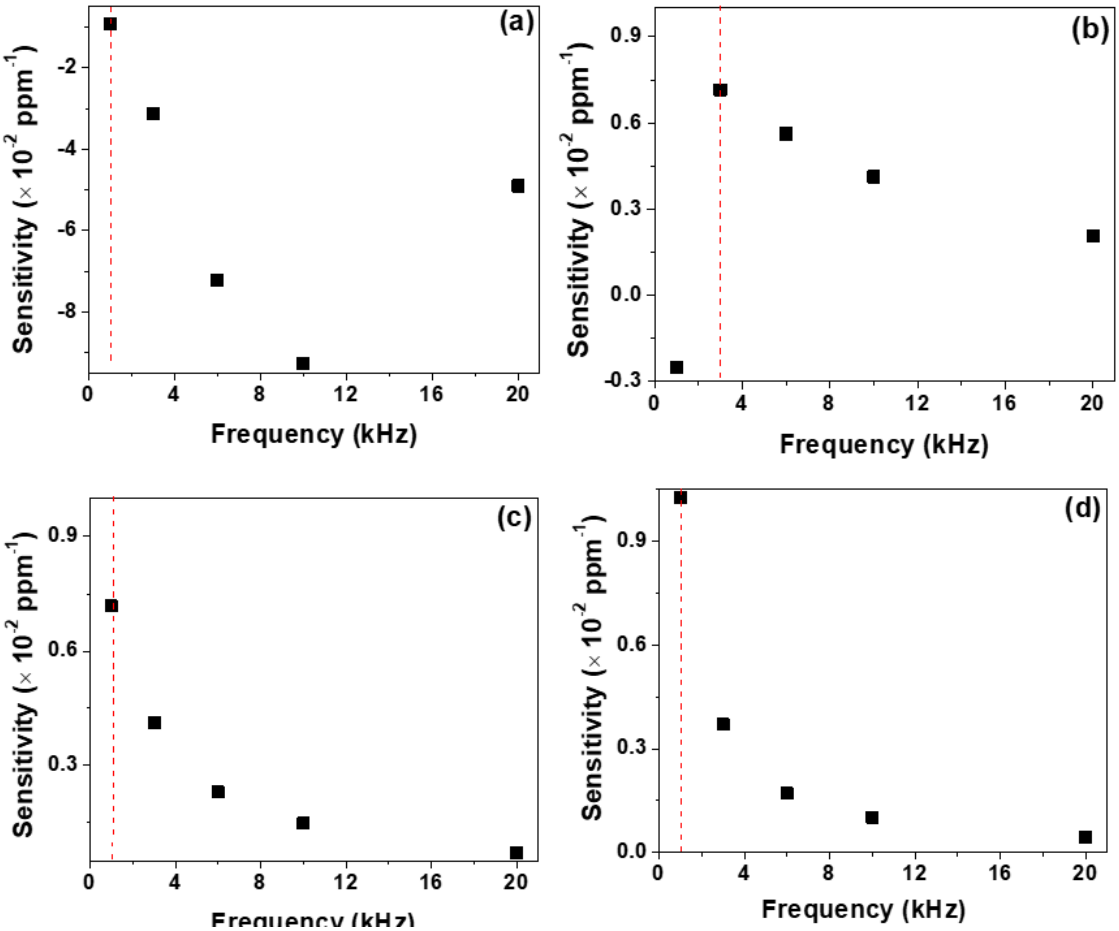

Figure S6. The sensitivities of sensors data based on hBN-BaF2 (a) 0 wt%, (b) 2.5 wt%, (c) 5 wt% and (d) 10 wt% for ethanol:acetone as a function of frequency; dashed line indicates the optimum operating frequency.

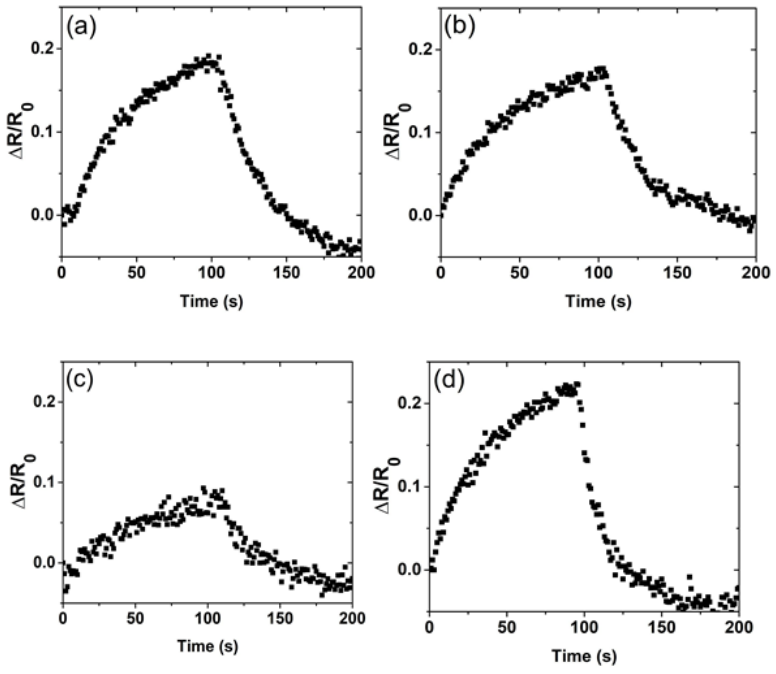

Figure S7. Responses and recovery times for (a) 0 wt%, (b) 2.5 wt%, (c) 5 wt% and (d) 10 wt% BaF_2-modified *h*BN devices fabricated 18 months ago and after exposure and removal of 160 ppm of acetone at optimum operating frequencies.

Table S1. Properties of the studied analytes [6].

Analyte	Nature of Solvent	Dielectric Constants (Ɛ)	Dipole Moment (D)
Acetone	Polar aprotic	20.7	2.88
Ethanol	Polar protic	24.3	1.69

Table S2. Optimization parameters for the *h*BN sensors.

Analyte	Parameter	0 wt%	2.5 wt%	5 wt%	10 wt%
Acetone	*f* (kHz)	1	1	3	3
	LoQ (ppm)	184	132	-	239
Ethanol	*f* (kHz)	1	3	3	1
	LoQ (ppm)	135	92	-	230

Table S3. Response and recovery times at 2 $mg.mL^{-1}$ concentration of the *h*BN dispersion.

Analyte	Samples	t_{resp} (s)	t_{recov} (s)
Acetone	0 wt%	74	95
	2.5 wt%	61	71
	5 wt%	36	44
	10 wt%	54	50
Ethanol	0 wt%	79	34
	2.5 wt%	77	40
	5 wt%	69	34
	10 wt%	71	56
Acetone: Ethanol (1:1)	0 wt%	78	15
	2.5 wt%	113	75
	5 wt%	56	15
	10 wt%	102	20

Table S4. Reproducibility of the *h*BN sensors.

Analyte	Parameter	0 wt%	2.5 wt%	5 wt%	10 wt%
Acetone	*f* (kHz)	1	1	3	1
	S ($\times 10^{-2}$ ppm^{-1})	0.04	0.1	0.04	0.12
	f (kHz)	1	1	10	1

Ethanol	S ($\times 10^{-2}$ ppm^{-1})	0.4	2.3	0.06	0.2

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