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The Effects Of Secondary Doping On Ink-Jet Printed PEDOT:PSS Gas Sensors For VOCs and NO<sub>2</sub> Detection / Vigna, L.; Verna, A.; Marasso, S. L.; Sangermano, M.; D'Angelo, P.; Pirri, F. C.; Cocuzza, M.. - In: SENSORS AND ACTUATORS. B, CHEMICAL. - ISSN 0925-4005. - ELETTRONICO. - 345:(2021), p. 130381.  
[10.1016/j.snb.2021.130381]

*Availability:*

This version is available at: 11583/2910876 since: 2021-07-05T15:32:45Z

*Publisher:*

Elsevier

*Published*

DOI:10.1016/j.snb.2021.130381

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<http://dx.doi.org/10.1016/j.snb.2021.130381>

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# The Effects Of Secondary Doping On Ink-Jet Printed PEDOT:PSS Gas Sensors For VOCs and NO<sub>2</sub> Detection

L. Vigna<sup>1</sup>, A. Verna<sup>1</sup>, S.L. Marasso<sup>1,2</sup>, M. Sangermano<sup>1</sup>, P. D'Angelo<sup>2</sup>, F.C. Pirri<sup>1,3</sup>, M. Cocuzza<sup>1,2</sup>

<sup>1</sup>Dipartimento di Scienza Applicata e Tecnologia (DISAT), Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino, Italy.

<sup>2</sup>CNR-IMEM, Parco Area delle Scienze, 37a, 43124 Parma, Italy.

<sup>3</sup>Istituto Italiano di Tecnologia, Center for Sustainable Future Technologies, Via Livorno 60, Torino, 10144, Italy.

**ABSTRACT:** In the study of conductive conjugated polymers, electrical doping has long played an important role. A new polymeric gas sensor has been successfully fabricated by means of an ink-jet printer using a conductive aqueous formulation of poly(3,4-ethylenedioxythiophene) poly(styrene-sulfonate) (PEDOT:PSS). A simple yet robust treatment method for the irreversible secondary doping was performed (by H<sub>2</sub>SO<sub>4</sub> and MeOH post-treatments) to enhance conductivity and improve gas sensing performance. The results of FTIR spectroscopy, contact angle and thickness demonstrated the removal of insulating hydrophilic PSS chains and a morphological change leading to a better connection of the hydrophobic conductive PEDOT domains. Real time gas sensing measurements were carried out by exposing the devices with **eight** different analytes in a low concentrations range of VOCs vapors up to 5% of the saturated vapor pressure, **10 ppm of NO<sub>2</sub>** and up to 10% of relative humidity (RH) at 21°C, exploiting dry air as carrier and diluting gas. The gas response, obtained as the ratio between the steady-state resistance variation and the baseline resistance of the device, was evaluated for different PEDOT:PSS post-treated sensors. An unexpected behavior of PEDOT:PSS post-treated with concentrated H<sub>2</sub>SO<sub>4</sub> was observed, while MeOH and diluted H<sub>2</sub>SO<sub>4</sub> post-treated sensors exhibited improved response towards all **investigated analytes**. The best performances were obtained towards 5% of ammonia **and NO<sub>2</sub>** with a gas response of 6% **and 28% respectively** with the device post-treated with pure methanol and 16% with the sensor post-treated with diluted sulfuric acid. **Furthermore, long-term stability and the influence of temperature were evaluated on the fabricated sensors.** Altogether, these promising results allow a better understanding of the secondary doping effects on the electrical and sensing properties, paving the way for electronic nose development.

**Keywords:** PEDOT:PSS, gas sensor, conductive polymer, ink-jet printing, secondary doping, electronic nose

## 1. INTRODUCTION

Among all intrinsically conductive conjugated polymers, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is a frontrunner material emerging on the scientific scene in the late 1980s and positioning itself as a great candidate for printed electronics [1,2]. It is becoming to organic electronics what silicon is for inorganic electronics [3]. This conjugated polymer appears as

39 an excellent material due to its peculiar properties like remarkable high electrical conductivity,  
40 stability and transparency in the visible range in its doped state associated with a low band gap, easy  
41 processability, good mechanical flexibility, low cost and excellent thermal stability [4]. We address  
42 the reader to the review article by Groenendaal *et al.* for additional detailed information about the  
43 synthesis process, all the properties and characterizations of PEDOT:PSS [5]. The aforementioned  
44 properties of PEDOT:PSS has risen its popularity in many research fields and applications that range  
45 from: electronics for transparent electrodes capacitors, photodiodes [6,7] and as a hole transport layer  
46 of organic LED to antistatic coatings [8]; in sensing and biosensing for the development of Organic  
47 Electro Chemical Transistor (OECT) devices [9–14] and the realization of stretchable and 3D printed  
48 electronics [15–18]; in neuromorphic systems for the implementation of memristive devices [19]; in  
49 additive manufacturing for the exploitation of new conductive composites and 3D printed electronics  
50 [20–23]. In this context, thanks to the high potentials of molecular modifications and tunable  
51 properties, PEDOT:PSS has been successfully used as chemiresistive gas sensor [16,24–36]  
52 especially for Volatile Organic Compounds (VOCs) detection [12,17,37–42] due to the well-known  
53 ever growing need to monitor the environmental pollution. Among all the contaminants in air, VOCs  
54 such as acetone, ethanol and 2-propanol are the most common and hazardous. Even at very low  
55 concentrations these molecules not only contaminate the environment, but also directly affect  
56 human's health and climate change [43]. Moreover, nitrogen oxides family ( $\text{NO}_x$  including NO and  
57  $\text{NO}_2$ ), are notorious pungent toxic oxidizing gases which enter the atmosphere from either natural  
58 sources or due to anthropogenic activities [44].  $\text{NO}_2$  emissions are mainly due to fossil fuel  
59 combustion, diesel automobile exhaust and biomass burning [45]. Furthermore, they play a central  
60 role in the formation of acid rains, photochemical smog and PM 2.5 as well as contributing to the  
61 potential greenhouse effect and ozone generation in the atmosphere, but also endanger people's health  
62 [46]. Traces of  $\text{NO}_2$  can damage the respiratory system and increase the risk of pneumonia and  
63 asthma. According to the National Institute for Occupational Safety and Health, when concentration  
64 is above 10 ppm, people will start feeling uncomfortable and cause harm to life at concentrations  
65 above 20 ppm [47]. Therefore, for all the above reasons, it is urgent to develop high-efficiency gas  
66 sensors that can easily detect VOCs and  $\text{NO}_2$  at room temperature with high sensitivity, fast response,  
67 low detection limit and power consumption.

68 Organic conductive polymers including polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh)  
69 and PEDOT are by far the most studied as gas sensing materials, exploiting their high sensitivity and  
70 electrical conductivity, inexpensive synthesis and wide detection range of volatiles [48–50]. PEDOT  
71 is itself intrinsically insoluble in all common solvents and very unstable in its neutral state. In order  
72 to overcome this problem and facilitate the patterning through printing technologies, PSS was added

73 to PEDOT in an eco-friendly solvent, i.e. water, making a green sustainable aqueous dispersion in  
74 comparison with other toxic organic compounds used for PANI and PPy [33]. For this reason, it was  
75 the selected as candidate for this study. In this way, the polyelectrolyte complex formed by colloidal  
76 particles made of a conductive insoluble core surrounded by PSS polyanion and generating a  
77 hydrophilic shell made possible to obtain a printable ink formulation soluble in water [42]. In  
78 addition, the tunability of secondary doping has long played a role in studies of conjugated polymers  
79 because it can increase the conductivity and improve carrier injection at electrodes enhancing sensors  
80 performance. Unlike the reversal change in conductivity by primary doping/de-doping, this process  
81 promotes an irreversible modification of the electrical conductivity even upon removal of the  
82 secondary dopant. High values of electrical conductivity can be achieved by the so-called secondary  
83 doping. During the treatment with different solvents [51–55], the band structure of PEDOT:PSS  
84 drastically changes because there are electrons that have been removed. As a consequence, polarons  
85 and spinless bipolarons, which are oxidized states of the PEDOT unit responsible of the charge carrier  
86 concentration and thus of the electrical conductivity, will form introducing energy states between the  
87 lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO)  
88 [50,56]. MacDiarmid and Epstein [57] noticed that a post treatment of primary doped PANI samples  
89 led to a change in the molecular conformation from “compact coil” to “expanded coil”, enhancing  
90 the conductivity. Similarly, Kim et al. [58] reported in 2002 a comparable improvement in  
91 conductivity in PEDOT:PSS films by a change of solvents of dimethyl sulfoxide (DMSO), N,N-  
92 dimethyl formamide (DMF), and tetrahydrofuran (THF) [59]. Nevertheless, the literature misses to  
93 describe the effects of post-treatments on PEDOT:PSS that can be easily correlated to gas sensing  
94 performance or selectivity tunability. For this reason, this study aims at gaining a better understanding  
95 of these effects on PEDOT:PSS, establishing relationships amid different post-treatments compared  
96 to the chemical and physical properties of the material and the sensing response of the ink-jet printed  
97 devices. For this purpose, ink-jet printed sensors with pristine PEDOT:PSS were obtained and the  
98 effect of different secondary doping post fabrication treatments on the devices were studied. MeOH  
99 and H<sub>2</sub>SO<sub>4</sub> were used as one-electron oxidants sufficiently strong to transfer holes to the transport  
100 levels of the PEDOT:PSS, altering the band structure by introducing polaronic states in between the  
101 band gap. Finally, the evaluation of sensing response at different temperature towards a low  
102 concentrations range of VOCs vapors up to 5% of the saturated vapor pressure, 10 ppm of NO<sub>2</sub> and  
103 up to 10% of relative humidity (RH) by means of a proper characterization system were studied on  
104 the fabricated devices along with their initial long-term stability and repeatability. The obtained  
105 results provide encouraging knowledge to develop electronic nose systems with a potential wide  
106 range of analytes detection.

## 107 2. EXPERIMENTAL

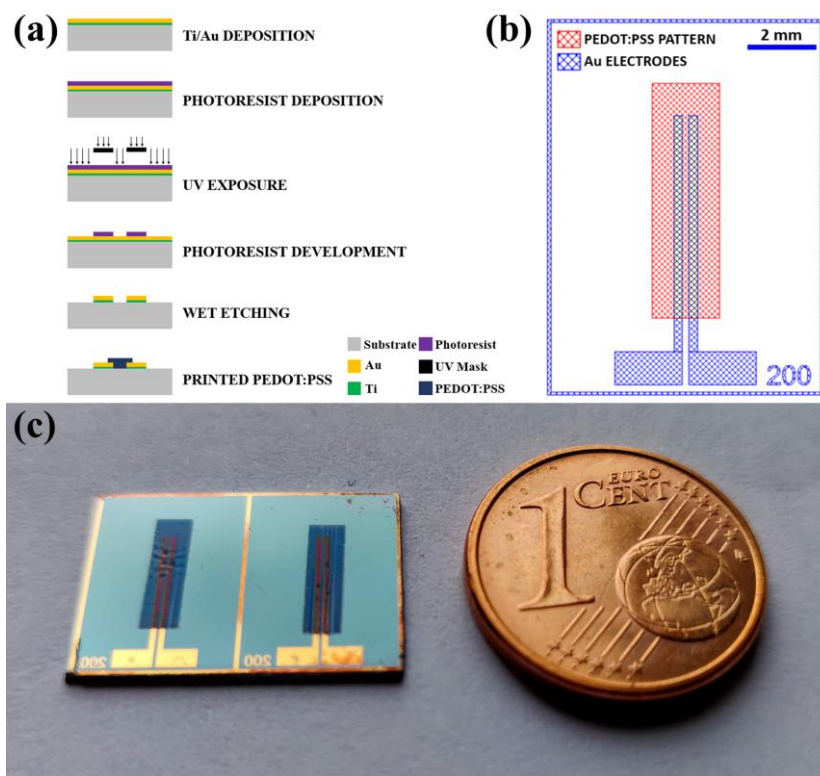
### 108 2.1 Materials

109 The poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) aqueous solution  
110 (Clevios™ PH1000) was purchased from Heraeus (Leverkusen, Germany) with a solid concentration  
111 of 1.0–1.3 wt% and a ratio of 1:2.5. Acetone (ACS reagent grade,  $\geq 99.5\%$ ), ethanol (EtOH)  
112 (Analytical standard for GC,  $\geq 99.9\%$ ), 2-propanol (IPA) (ACS reagent grade,  $\geq 99.8\%$ ), ammonium  
113 hydroxide solution ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ) (ACS reagent grade, 28.0-30.0 wt%  $\text{NH}_3$  basis), methanol (MeOH)  
114 (Anhydrous, 99.8%) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) (ACS reagent grade, 95.0-98.0%) were purchased  
115 from Sigma-Aldrich (Milano, Italy). Common household bleach based on sodium hypochlorite  
116 ( $\text{NaClO}$ ) (Solution with 2.2 wt%) was employed. Two tanks of  $\text{O}_2$  and a mixture of nitrogen and  $\text{NO}_2$   
117 in the concentration of 25 ppm were supplied by Linde Gas. All the chemicals were used as received  
118 without further purification. Deionized water (DI water) was obtained from a reverse osmosis (RO)  
119 purification system. Si 4'' wafers finished with a 1  $\mu\text{m}$  thick thermally grown  $\text{SiO}_2$  layer were  
120 purchased from Si-Mat (Kaufering, Germany) and used as a substrate for the chips fabrication.

121

### 122 2.2 Substrate preparation

123 The substrate was developed by using standard clean room processes (Figure 1a) starting from 4'',  
124 single side polished, P type, (100) Si wafers (resistivity 1–10  $\Omega \cdot \text{cm}$ ) finished with 1  $\mu\text{m}$  thermal  $\text{SiO}_2$ .  
125 A 10 nm thin layer of Ti was evaporated in order to promote the adhesion of the following 100 nm  
126 of Au that ensures the contact. Contact pads and electrodes (Figure 1b) were patterned by UV  
127 photolithography through a photomask and then wet-etched. The two fingers are 7 mm long and 250  
128  $\mu\text{m}$  wide with a gap of 200  $\mu\text{m}$ . The length and width of a single contact pad are 1 mm and 2 mm  
129 respectively.



130

131 **Figure 1:** (a) Sketch of the fabrication steps used to produce the gas sensor (b) Layout of the device: red layer is the  
 132 pattern of the ink-jet printed PEDOT:PSS film, while blue layer corresponds to the contact pads and electrodes (c) Picture  
 133 of the fabricated PEDOT:PSS gas sensors.

134

### 135 2.3 Conductive ink preparation

136 The typical ink formulation was prepared following a two steps process using pristine Clevios™  
 137 PH1000. In the former, the PEDOT:PSS aqueous dispersion underwent a sonication treatment by  
 138 means of a digital sonifier Branson SFX 250 (Danbury, U.S.A.), operating in pulse mode for 20  
 139 minutes at the 50% of the maximum power and cooled down in an ice water jacket. The latter is a  
 140 filtering step. The sonicated solution was double filtered by means of a syringe connected to a  
 141 disposable filter with a pore size of 0.45 μm. Such two steps preparation is necessary because it  
 142 ensures a better dispersion, the right viscosity range (0.5 – 40 mPa·s) for the printing process and it  
 143 ensures that the residual particulate in the conductive ink is smaller than 1% of the diameter of the  
 144 printer's nozzle, avoiding the occlusion/clogging of the nozzle and providing good repeatability and  
 145 printing performance.

146

### 147 2.4 Device fabrication by Ink-Jet printing

148 After an O<sub>2</sub> plasma activation of the substrate's surface for 15 minutes with a Diener Atto Plasma  
 149 System (Ebhausen, Germany), the PEDOT:PSS formulation was ink-jet printed onto the electrodes  
 150 to obtain a 2x7 mm<sup>2</sup> film from a digital model. The employed jet printer is a piezoelectric drop-on-  
 151 demand (DOD) Jetlab 4 supplied by MicroFab (Texas, U.S.A.). The conductive ink was loaded in the

152 reservoir, the jetting was regulated and observed from the lateral camera and then the printing was  
153 started. All the parameters were set as well described in details in the optimization printing process  
154 reported in [60]. The flow velocity was fixed at 4 mm/s, the back pressure set at -8 psi, the frequency  
155 selected at 550 Hz; a W-shaped wave was exploited with a dwell time of 3  $\mu$ s and a maximum positive  
156 voltage of 65 V. The PEDOT:PSS was then annealed on a hotplate at 120 °C for 10 minutes. The  
157 sensors, used as prepared, were compared with the treated ones in a MeOH bath or in a H<sub>2</sub>SO<sub>4</sub> one at  
158 different concentrations. After the post-treatment, the devices were rinsed in DI water and dried on a  
159 hotplate for 3 minutes at 120 °C.

160

## 161 **2.5 Characterization**

### 162 **2.5.1 FTIR**

163 FTIR analyses were performed in transmission mode in order to evaluate the chemical composition.  
164 The experiments were conducted on dried samples by means of a Thermo Scientific Nicolet iS50  
165 FTIR Spectrometer (Milano, Italy). The solutions were analyzed after being applied onto a silicon  
166 wafer before and after the MeOH and H<sub>2</sub>SO<sub>4</sub> treatments. The analysis was carried out with a  
167 resolution of 4 cm<sup>-1</sup> and samples were scanned 32 times in the wavenumber range between 650 and  
168 4000 cm<sup>-1</sup>. A background measurement was performed on all samples prior to FT-IR analysis. The  
169 results were acquired and evaluated using the Omnic software.

170

### 171 **2.5.2 Contact Angle**

172 Contact angle measurements were performed on a Kruss DSA10 instrument (Hamburg, Germany),  
173 equipped with a digital camera and an image analyzer. Analyses were performed at room temperature  
174 by means of the sessile drop technique. Five to eight measurements were acquired on each sample  
175 and the mean values estimated. The measuring liquid was distilled water ( $\gamma=72.1$  mNm<sup>-1</sup>).

176

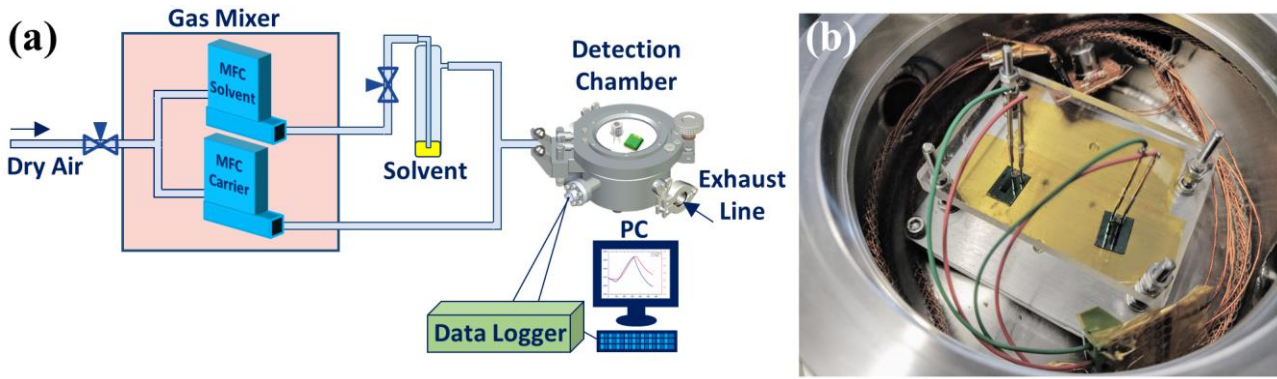
### 177 **2.5.3 Profilometer**

178 The polymer films thickness and roughness were measured with a KLA Tencor P10 surface stylus  
179 profiler (California, U.S.A.). Multiple measurements were performed on each sample before and after  
180 the post-treatments and the mean values were estimated.

181

### 182 **2.5.4 Sensing Setup**

183 Figure 2 shows the custom-made experimental setup used to retrieve the PEDOT:PSS sensing  
184 responses [61].



185

186 **Figure 2:** (a) Scheme of the experimental sensing setup used to perform gas sensing measurements (b) Interior of the gas  
 187 detection chamber.

188 More in detail, in order to produce and deliver selected concentrations of solvent vapors to the  
 189 samples, a custom-built sensing setup was exploited for the real-time characterizations. In the system,  
 190 a stream of oil-free dry air (DA) is exploited as carrier and diluting gas. The main stream is divided  
 191 and regulated into two fluxes inside an Environics Gas Mixing System (series 4000) equipped with  
 192 two mass flow controllers (MFC) and controlled by a dedicated software for the mass flow regulation.  
 193 The DA flows through a bubbler properly filled with the volatile organic compound (VOC) to be  
 194 tested, producing its saturated vapor. Then, the two flows are recombined, mixed, and directed to a  
 195 detection chamber made of a stainless-steel assembly with a 100 mm inner diameter. **There exists a**  
 196 **latency period from the opening time of the valve and moment in which the vapor fills the chamber**  
 197 **and can be detected. This delay affects the response and recovery time.** The operational temperature  
 198 for the sensing measurements herein reported is 21 °C and it was measured with a **PT1000** sensor. **In**  
 199 **order to evaluate the effect of the temperature on the gas sensor, a Supercool Peltier thermoelectric**  
 200 **module is installed beneath the sample holder platform inside the sensing chamber and bonded to a**  
 201 **machined aluminium heat sink for heat transfer. In this way, it is possible to modulate the operational**  
 202 **temperature, cooling down to 10 °C and heating up to 60 °C by applying different current values. In**  
 203 **addition, a Figaro TGS2600 sensor is placed inside the sensing chamber and it is used as a reference**  
 204 **in order to validate the whole sensing setup.** 200 sccm of DA were set to flow on the samples. **All the**  
 205 **experiments carried out in this work exploited six different liquid analytes, namely acetone, EtOH,**  
 206 **IPA, NaClO solution (testing chlorine-based vapor), NH<sub>4</sub>OH solution (testing NH<sub>3</sub> vapor), H<sub>2</sub>O and**  
 207 **two gases, O<sub>2</sub> and NO<sub>2</sub>.**

208

### 209 2.5.5 Sensing Analyses

210 The electrical resistance was investigated by using two-probes measurements, exploiting a data  
 211 acquisition unit 34970A supplied by Keysight (Milano, Italy). In the DC analysis, a voltage was  
 212 applied between the electrodes and the current was measured, acquiring directly the resistance as a



213 function of the time. For each test, dry air was introduced for 120 s in order to get the baseline.  
214 Successively, the sensor was exposed to the analyte at the desired concentration for 300 s, followed  
215 by further 300 s that was set as recovery time. Initial long-term stability measurements were carried  
216 out over a period of almost 2 hours, repeating 12 times the gas sensing cycle.

217 The typical response of the sensor to a particular gas (S) is calculated as the ratio between the steady-  
218 state resistance variation  $\Delta R$  and the baseline resistance of the device (Eq. 1):

$$219 \quad S = \frac{\Delta R}{R_{Baseline}} \quad (\text{Equation 1})$$

220 In this work, the formula used is reported below (Eq. 2):

$$221 \quad S\% = 1 - \frac{R_{Gas}}{R_{Baseline}} \times 100 \quad (\text{Equation 2})$$

222  $O_2$  and  $NO_2$  fluxes were regulated using dry air as diluting gas in order to obtain the requested  
223 concentrations; while saturated vapors of the VOCs were extracted by bubbling dry air through the  
224 bubbler. The concentration of the volatile vapor is expressed as a percentage obtained from the ratio  
225 between the saturated vapor flow coming out of the bubbler and divided by the total flow reaching  
226 the detection chamber, using the following equation (Eq. 3):

$$227 \quad C(\text{Saturated vapor \%}) = \left( \frac{P^*}{P} \times \frac{f}{f+F} \right) \times 100 \quad (\text{Equation 3})$$

228 where P is the input air pressure (atmospheric pressure in this case),  $P^*$  is the saturated partial pressure  
229 of the analyte, f and F are the mass flow rate of MFC of the pure dry air and MFC of the carrier  
230 respectively.  $P^*$  is calculated by Antoine's equation (Eq. 4) as a function of the temperature and  
231 Antoine's component-specific constants A, B and C [39,62–64]:

$$232 \quad P^* = 10^{\left( A - \frac{B}{C+T} \right)} \quad (\text{Equation 4})$$

233 At room temperature the saturated vapor pressures of acetone, ethanol, IPA, NaClO,  $NH_3$  and  $H_2O$   
234 are 0.254 atm, 0.061 atm, 0.045 atm, 0.020 atm, 0.732 atm and 0.0245 atm respectively. More in  
235 detail, in order to evaluate the contribution of  $NH_3$  vapor from  $NH_4OH$  liquid solution, it was assumed  
236 negligible the humidity due to the presence of water molecules. In fact, at 21 °C the partial vapor  
237 pressures of  $NH_3$  and  $H_2O$  of a 30%  $NH_3$  aqueous solution are 0.732 atm and 0.017 atm respectively  
238 [62,65]. Hence, the molar fraction of  $NH_3$  is 97.7%.

239 Sensing measurements at 10 °C, 20 °C, 30 °C, 40 °C, 50 °C and 60 °C were carried out by exploiting  
240 a Peltier module and changing the current between 0.2 A and 2 A through a power supply, using a  
241 PT1000 sensor as a temperature reference.

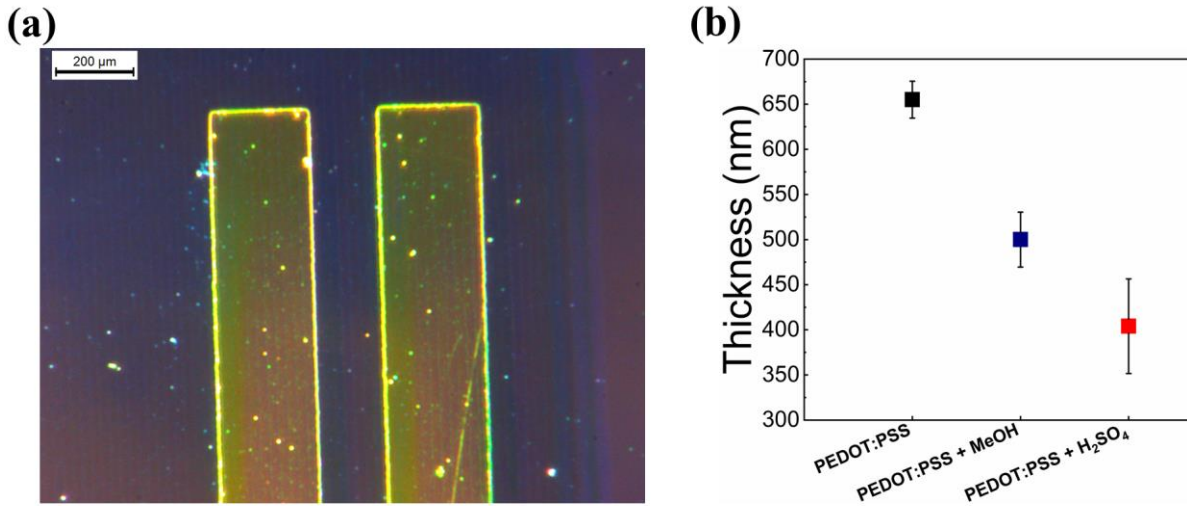
### 242 3. RESULTS AND DISCUSSION

243 As a first step, in order to evaluate the effects of doping, ink-jet printed sensors with pristine  
 244 PEDOT:PSS were prepared and, for some of them, the already coated film was immersed in  
 245 secondary doping solutions and then dried. MeOH and H<sub>2</sub>SO<sub>4</sub> were used as one-electron oxidants  
 246 sufficiently strong to transfer holes to the transport levels of the PEDOT:PSS structure and alter its  
 247 band gap. This process led to an enhancement in conductivity from 0.5 S/cm of the untreated sample  
 248 to 1021 S/cm for the treated ones, reducing significantly the energy barrier for the intra-grain and  
 249 inter-domain charge hopping. The resistances of the PEDOT:PSS films were evaluated and are  
 250 summarized in Table 1. Both charge-carriers mobility and carrier density were affected by doping  
 251 [3]. We observed a significant drop in resistance of three orders of magnitude for the films treated  
 252 with H<sub>2</sub>SO<sub>4</sub> and two for the ones doped with MeOH. By diluting the H<sub>2</sub>SO<sub>4</sub> with different ratios and  
 253 controlling the dipping time, the change in resistance is less pronounced because the doping level is  
 254 lower. In this way, it is possible to modulate the oxidation level. All the films showed a good stability  
 255 concerning the conductivity. Indeed, no appreciable variations were observed after 10 months.

256 **Table 1:** Resistance values for the PEDOT:PSS films before and after the post-treatment with MeOH and several  
 257 concentrations of H<sub>2</sub>SO<sub>4</sub>.

Post-Treatment	Resistance	
	Untreated Film	Treated Film
PEDOT:PSS + MeOH	22.52 kΩ	1221 Ω
PEDOT:PSS + H <sub>2</sub> SO <sub>4</sub>	9.75 kΩ	10 Ω
PEDOT:PSS + H <sub>2</sub> SO <sub>4</sub> :H <sub>2</sub> O 2:1	9.42 kΩ	20 Ω
PEDOT:PSS + H <sub>2</sub> SO <sub>4</sub> :H <sub>2</sub> O 1:1	9.75 kΩ	85 Ω
PEDOT:PSS + H <sub>2</sub> SO <sub>4</sub> :H <sub>2</sub> O 1:2	13.67 kΩ	200 Ω
PEDOT:PSS + H <sub>2</sub> SO <sub>4</sub> :H <sub>2</sub> O 1:4	14.18 kΩ	900 Ω

258  
 259 Figure 3(a) shows the PEDOT:PSS film printed on top of the electrodes. The thin film appears  
 260 homogeneous and it is possible to notice the regular stripes of the ink-jet printer. There are no  
 261 satellites during the printing process and, after an O<sub>2</sub> plasma treatment, the wettability is enhanced  
 262 both on the gold and on the silicon. As a consequence of the dipping treatment, the thickness of  
 263 PEDOT:PSS films changed as illustrated in Figure 3(b). The pristine PEDOT:PSS thin film has a  
 264 thickness of 655 nm, while it is significantly reduced to 500 nm after the post-treatment with MeOH  
 265 and 403 nm after H<sub>2</sub>SO<sub>4</sub> doping. For the MeOH treatment, the reduction is less pronounced.

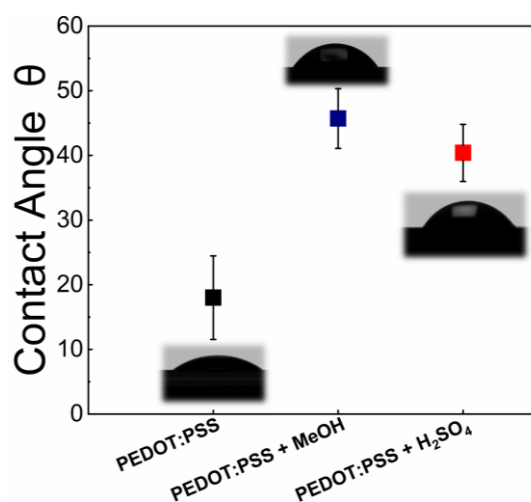


266

267 **Figure 3:** (a) Optical image of PEDOT:PSS thin film ink-jet printed on top of gold electrodes (b) Comparison of the  
 268 thickness of pristine, H<sub>2</sub>SO<sub>4</sub>-doped and MeOH-treated PEDOT:PSS films.

269 In order to explain the experimental evidence, it is worth analyzing the PEDOT:PSS structure and its  
 270 functionality, from the atomistic point of view all the way to its macroscopic dimensions. In fact,  
 271 pristine PEDOT is typically insoluble, the chains are in a natural disorder in the so-called random coil  
 272 configuration and, in its neutral state, appears unstable with a peculiar pale bluish color [5]. However,  
 273 when dispersion polymerized with the polyanion poly(4-styrenesulfonate) (PSS), a colloidal water-  
 274 soluble solution is achieved. The polyelectrolyte complex is formed by nanoparticles where the  
 275 PEDOT inner core is hydrophobic and conductive, while the outer shell is formed by PSS chains that  
 276 are hydrophilic and insulating. Those nanoparticles are dispersed in an amorphous region formed by  
 277 non-stoichiometric excess of PSS. This polymer blend has proven to be a stable formulation for the  
 278 printing process also due to its viscosity in the range of 0.5 – 40 mPa·s [42]. In this system, PEDOT  
 279 is already primary doped and in its oxidized state. In fact, about one third of the monomers on the  
 280 chain has been oxidized [66]. The effect of secondary doping through the post-treatment can be  
 281 explained by a change in morphology [67–69] and to a small extent by a modification of the oxidation  
 282 level of the conducting polymer. The reduction in thickness is related to a screening effect by the  
 283 dopant that facilitates a phase separation of PEDOT and PSS, leading to a better interconnection  
 284 between the conducting PEDOT domains through the film [66]. **Furthermore, it implies an**  
 285 **enhancement of volumetric capacitance and, consequently, its attitude at implementing an efficient**  
 286 **electrochemical activity in presence of oxidizing/reducing agents.** During the secondary doping there  
 287 is a removal of the PSS that is likely washed away from the surface during the process. In fact, in  
 288 water H<sub>2</sub>SO<sub>4</sub> dissociates into H<sup>+</sup> and HSO<sub>4</sub><sup>-</sup>. During the post-treatment, the proton released by the  
 289 acid will interact with the PSS<sup>-</sup> counter anion. The reaction can be summarized as H<sub>2</sub>SO<sub>4</sub> + PSS<sup>-</sup> →  
 290 HSO<sub>4</sub><sup>-</sup> + PSSH [70–72]. In this way, the enhancement in conductivity after the H<sub>2</sub>SO<sub>4</sub> treatment is  
 291 attributed to the fact that the non-conductive anions of some PSS<sup>-</sup> were substituted by the conductive

292 anions of  $\text{HSO}_4^-$ . While for the other doping with MeOH, even though there isn't an ionic substitution,  
293 the polar hydrophilic alcohol with a high dielectric constant still induces the screening effect and the  
294 solvation process of the PSS between counter ions and charge carriers, which reduces the Coulomb  
295 interaction between positively charged PEDOT and negatively charged PSS [51,73]. For this reason,  
296 the segregated hydrophilic PSS can be easily removed from the surface of the film after the treatment  
297 with MeOH. In both secondary doping post-treatments, from the morphological point of view, the  
298 configuration changes from random coil to a more linear structure, presumably due to the employment  
299 of small-sized, less steric counter-ions (Figure 5b) [51,66,67,74]. Hence, it promotes a better  
300 interaction between different polymer chains, allowing an easier hopping charge transfer and further  
301 delocalizing the positive charges. The doped films present a more oriented system where the  
302 linearization of the chains allows the generation of crystallites of  $\pi$ - $\pi$  stacked chains embedded into  
303 amorphous regions of less ordered chains. During the linearization of the chains, PEDOT backbones  
304 undergo a transition from the aromatic to quinoid state in the region where the polarons are localized  
305 due to a change in the bond length [3]. In this way, carrier transport involves hopping of the charge  
306 carriers from one site to another within a manifold of transport levels that are relatively close to one  
307 another both energetically and spatially. Therefore, the combined effects of chain linearization,  
308 increased doping level through further oxidation, removal of insulating polymers, and resulting  
309 morphological change are considered to give rise to the enhanced conductivity of PEDOT:PSS system  
310 by secondary doping post-treatments. It has to be underlined that the doping process is very quick  
311 and the change in conductivity happens with a short treatment time for both solutions.  
312 As a support for this evaluation, water contact angle measurements were performed, and the results  
313 are summarized in Figure 4.

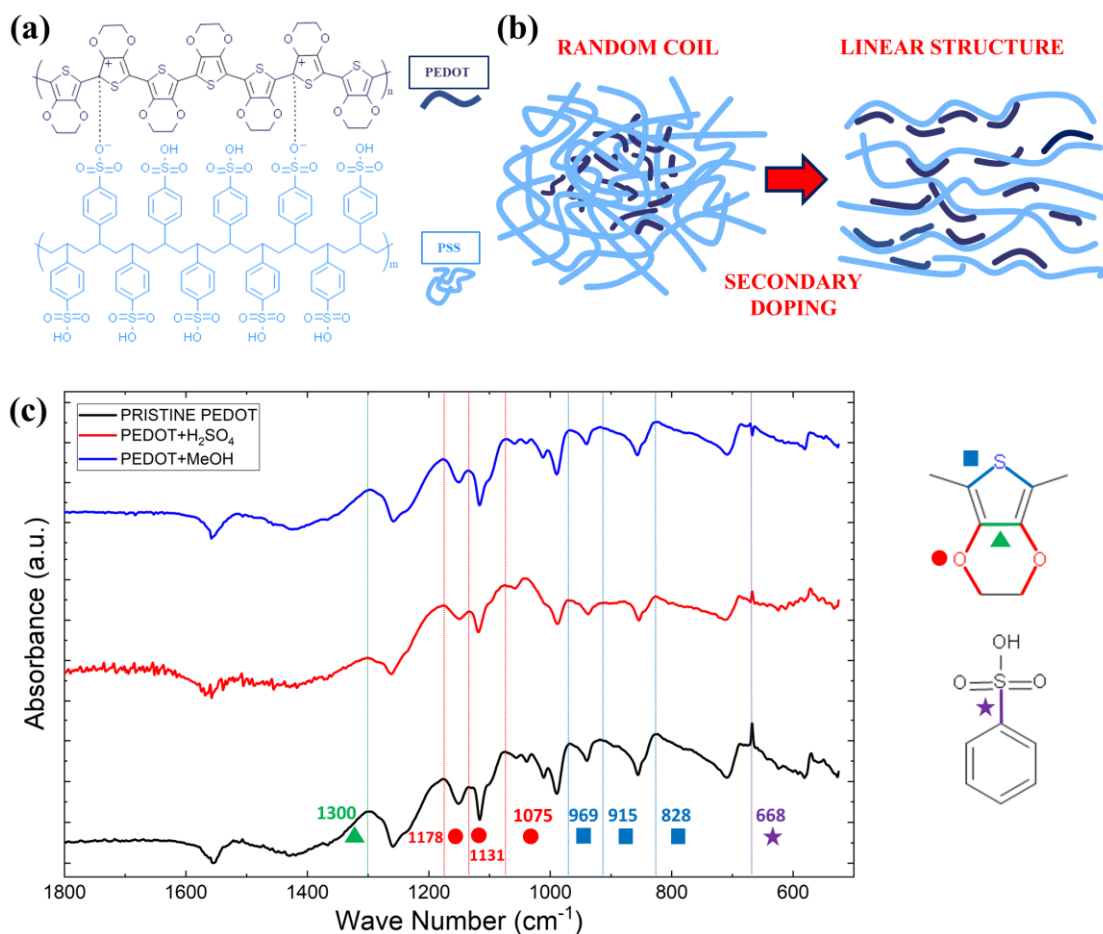


314

315

**Figure 4:** Comparison of the contact angles of pristine,  $\text{H}_2\text{SO}_4$ -doped and MeOH-treated PEDOT:PSS films.

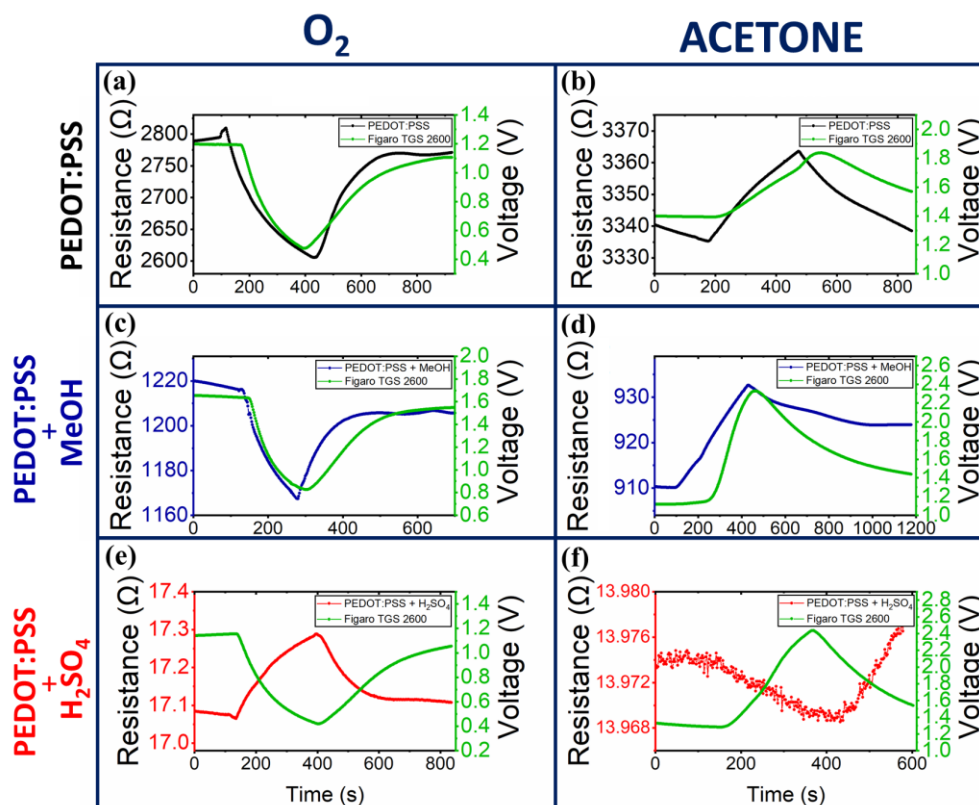
316 A significant difference in surface properties is appreciable before and after the secondary doping.  
 317 The contact angle of pristine PEDOT:PSS is around 18 degrees. This is coherent with the core-shell  
 318 structure where the highly hydrophilic PSS rich region is in the external part exposed to the film  
 319 surface, while the hydrophobic PEDOT chains are in the core. The PSS presence allows a good water  
 320 dispersion and the wettability results to be very good with a low contact angle. On the contrary, after  
 321 the treatment in H<sub>2</sub>SO<sub>4</sub> and MeOH, the wettability was reduced. Contact angles were 40 and 46  
 322 degrees respectively. This is due to the intrinsic property of PEDOT that is hardly soluble in water.  
 323 After the secondary doping, part of the PSS was washed away and a separation process happened,  
 324 letting part of the PEDOT molecules to be exposed on the surface.  
 325 Figure 5(a) shows the chemical structure of PEDOT:PSS with their interactions. FTIR spectroscopy  
 326 was undertaken to explore the chemical environment of PEDOT:PSS thin films before and after  
 327 secondary doping, trying to explain the de-sulfonation of PSS (Figure 5c).



328  
 329 **Figure 5:** (a) PEDOT:PSS polyelectrolyte complex structure (b) Sketch of the structural rearrangement of PEDOT:PSS  
 330 from random coil to a linear structure (c) Transmission FTIR spectra of pristine, H<sub>2</sub>SO<sub>4</sub> post treated and MeOH doped  
 331 PEDOT:PSS thin films.  
 332 The main characteristic PEDOT:PSS IR peaks were identified. The vibrations at 828, 915 and 969  
 333 cm<sup>-1</sup> are assigned to the PEDOT C-S bonds in thiophene rings [75,76]. The stretching mode of the C-  
 334 O-C bonds can be seen at 1075, 1131 and 1178 cm<sup>-1</sup>. The vibration at 1300 cm<sup>-1</sup> can be attributed to

335 the C-C asymmetric stretching mode of the quinoid structure in thiophene rings. The peaks near 600  
336  $\text{cm}^{-1}$  are assigned to the sulfate ions with the S-O stretching [70]. This band is absent in the pristine  
337 PEDOT:PSS film, while it appears on the  $\text{H}_2\text{SO}_4$  treated spectrum. This indicates that some sulfate  
338 ions  $\text{SO}_4^{2-}$  remain in the PEDOT:PSS film after the secondary doping, even after a precise rinse in  
339 deionized water. It is very likely that some PSS undergoes de-sulfonation process and ion substitution.  
340 The impact of acid post-treatment also affects the band at  $668 \text{ cm}^{-1}$ . This peak has been debatably  
341 attributed to the PSS C-S bond [77]. It can be seen that its intensity is reduced after the  $\text{H}_2\text{SO}_4$  post-  
342 treatment. This may be explained with the removal of some PSS, leaving PEDOT stacks free of it.  
343 This is in agreement with the results observed by Kim *et al* during their spectroscopy analysis [78].  
344 Three different types of devices described in the aforementioned section were selected to be tested in  
345 their sensing behavior as chemiresistors towards **eight** different analytes at room temperature,  
346 following the protocol reported in the experimental part. **Various vapors and gases were investigated**  
347 **starting either from the liquid, including one ketone (acetone), two alcohols (EtOH and IPA), common**  
348 **bleach based on NaClO,  $\text{NH}_3$  molecules from  $\text{NH}_4\text{OH}$  solution,  $\text{H}_2\text{O}$  vapor (RH from 0% to 10% at**  
349  **$21 \text{ }^\circ\text{C}$ ) or fluxing directly two oxidizing gases:  $\text{O}_2$  and  $\text{NO}_2$ .** These VOCs were selected because of  
350 their different chemical and physical properties like chain length and functional groups. The gas  
351 concentrations for real time exposure are reported in percentage respect to the saturation vapor  
352 pressures. Figure 6 displays the dynamic sensing curves of the three different PEDOT:PSS systems  
353 exposed to an oxidizing gas (top) and towards a reducing vapor like acetone (bottom). The resistance  
354 is expressed as a function of time and the **green** curves are related to a commercial MOS sensor  
355 (Figaro TGS 2600) that has been used as a reference. **Differently from the MOS sensors, they manage**  
356 **to properly operate at room temperature, without the need of a heating element, which represents a**  
357 **clear advantage from the point of view of power consumption, making them suitable for flammable**  
358 **or explosive environments or portable detection systems.** By observing the reported curves, it is  
359 possible to state that the drift of the resistance is almost negligible and all the times the sensor  
360 recovered to the original value of the steady state baseline. Only in the case of ammonia vapor the  
361 recovery was incomplete within the time scale of the experiment. An encouraging result is the  
362 response time. In all the carried out experiments, the sensors made with PEDOT:PSS always had a  
363 faster response compared to the commercial Figaro TGS 2600, sensing the different gases earlier.  
364 The faster response and recovery may be due to high diffusion and deep penetration of the gas  
365 molecules on the very smooth surface of the sensing film. The response time was estimated to be in  
366 the range of few hundreds seconds that is a good achievement with respect to the time found **in other**  
367 **manuscripts.** In good agreement with the literature, the electrical resistance of our sensors made with

368 pristine PEDOT:PSS and the one doped with MeOH significantly increased when exposed to all the  
 369 VOCs, while it sharply decreased when in contact with oxygen.



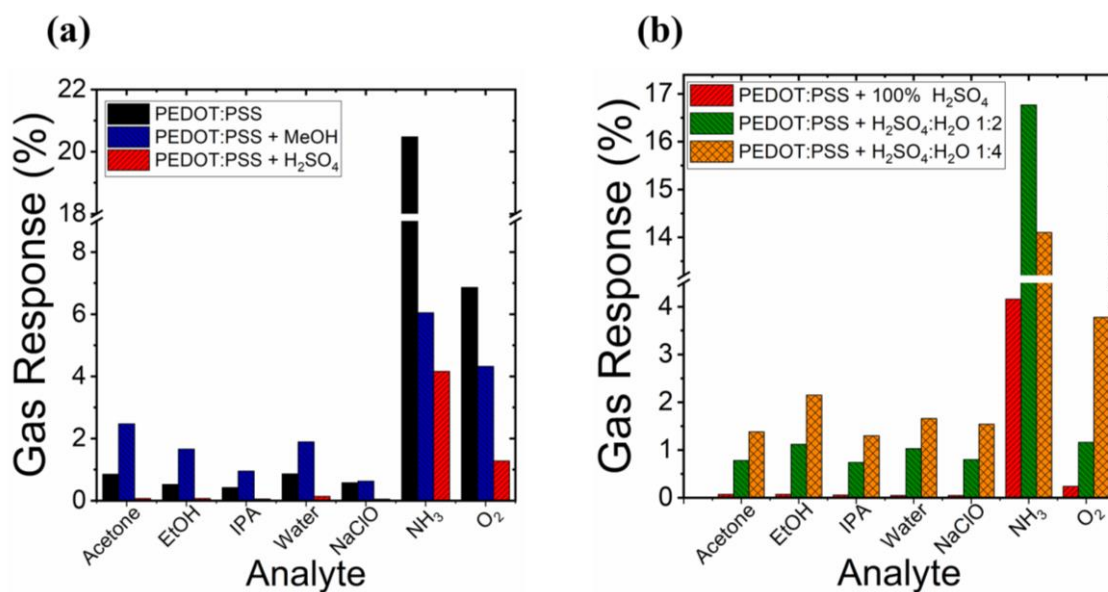
370  
 371 **Figure 6:** (a) Dynamic sensing response of pristine PEDOT:PSS sensor towards oxygen; (b) Sensing response of pristine  
 372 PEDOT:PSS sensor towards acetone; (c) Sensing response of PEDOT:PSS MeOH doped sensor towards oxygen; (d)  
 373 Sensing response of PEDOT:PSS MeOH doped sensor towards acetone; (e) Sensing response of PEDOT:PSS  $H_2SO_4$   
 374 doped sensor towards oxygen; (f) Sensing response of PEDOT:PSS  $H_2SO_4$  doped sensor towards acetone.

375 This behavior is correct because PEDOT:PSS is a p-type material where the main charge carriers are  
 376 holes. Different changes in resistances are related to the nature of the gas/vapor. When the sensor is  
 377 exposed to a reducing gas, the polymer loses some electrons. Therefore, the resistance will drop  
 378 because more holes are able to contribute to the conductivity. Instead, an oxidizing gas, reducing  
 379 itself, oxides the material that gains some electrons. In this case, the resistance will increase. The  
 380 doping of the material by the analyte is a reversible process, while the secondary doping is  
 381 irreversible. When the gas is gone, the polymeric film will de-dope and the resistance returns to the  
 382 initial value. In contrast, the sensor doped with concentrated  $H_2SO_4$  (third row) shows an atypical  
 383 behavior for a p-type sensor: the resistance increased after the oxygen exposure and decreased when  
 384 acetone vapor was flowed.

385 The sensing results (Figure 7) demonstrate the effect of doping on gas response with respect to the  
 386 different VOCs analytes at a fixed concentration of 5% of saturated vapor. It appears that the post-  
 387 treatment with MeOH increased the sensing response by a factor 2 or more with respect to the pristine  
 388 PEDOT:PSS towards all gases except ammonia and oxygen. While the treatment with concentrated  
 389  $H_2SO_4$  was always detrimental. With this post-treatment the conductivity had the best enhancement

390 and we observed an inversion of behavior never found in the literature before. A possible explanation  
 391 is that the concentrated  $\text{H}_2\text{SO}_4$  is too strong as a dopant and some **partial** over-doping reactions occur,  
 392 compromising the electrical response with respect to the pristine system. This over-doping effect  
 393 slightly deteriorates the electrical conductivity of the device after a critical value [79,80]. This effect,  
 394 where the curve of conductivity as a function of the doping shows a maximum, was already observed  
 395 for PEDOT:PSS [70]. **In addition, it can be seen that the pristine PEDOT:PSS shows relatively high**  
 396 **response towards  $\text{NH}_3$  compared with the other VOCs and the secondary doping seems not to improve**  
 397 **the gas sensing response towards this gas.**

398 The next step was a study on the dilution of  $\text{H}_2\text{SO}_4$  as doping bath. Figure 7(b) shows that the gas  
 399 response increased as the concentration of  $\text{H}_2\text{SO}_4$  used for the post-treatment decreased. The doping  
 400 with 1:4  $\text{H}_2\text{SO}_4$  dilution displayed the best performance towards all gases except  $\text{NH}_3$ . In fact, the  
 401 sensing response was higher than the pristine PEDOT:PSS sensor and, in some cases, even higher  
 402 than the sensor doped with MeOH. It was possible to notice that up to 2:1  $\text{H}_2\text{SO}_4$  dilution the sensor  
 403 showed the atypical behavior, while starting from 1:1 dilution the curves were coherent with the  
 404 pristine and MeOH doped sensors with a higher response as the dilution increased.

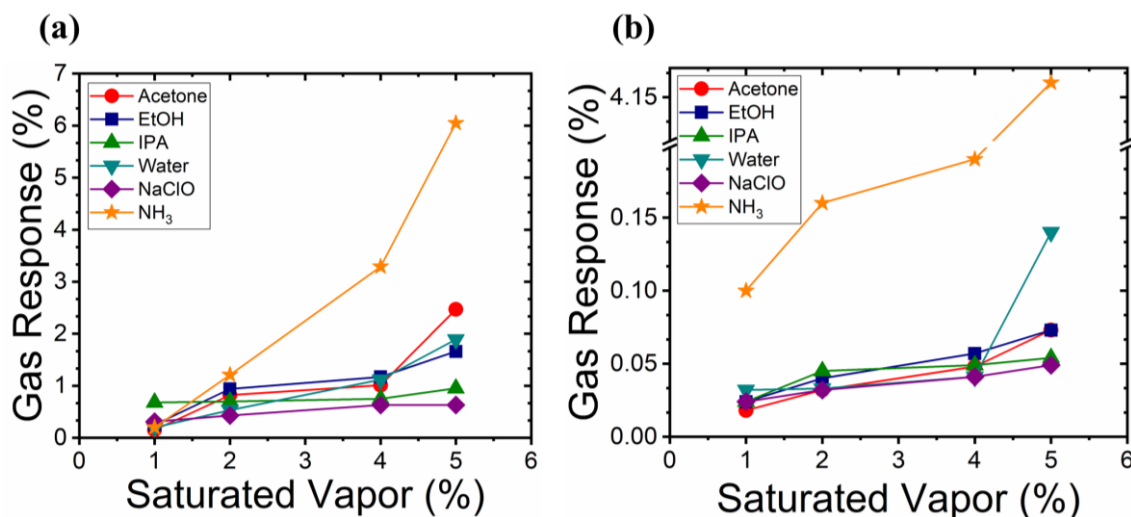


405  
 406 **Figure 7: (a) Sensing response of pristine PEDOT:PSS, PEDOT:PSS  $\text{H}_2\text{SO}_4$  doped and PEDOT:PSS MeOH doped sensor**  
 407 **towards different analytes at a fixed concentration of 5% of saturated vapor (100% for oxygen due to setup limitations)**  
 408 **at room temperature. (b) Sensing response of PEDOT:PSS sensor doped with different  $\text{H}_2\text{SO}_4$  concentrations towards**  
 409 **various analytes at a fixed concentration of 5% of saturated vapor (100% for oxygen due to setup limitations) at room**  
 410 **temperature. The breaks were inserted to illustrate the relative sensing response of most of the vapors.**

411 Figure 8 reports the trend towards the **VOCs** analytes at different concentrations. As a general  
 412 behavior, the gas sensing response grows monotonically with the vapor concentration. In addition,  
 413 all the sensors exhibited a remarkably high affinity towards  $\text{NH}_3$  among all of the tested VOCs, while  
 414 a very tiny responsive signal was observed with NaClO and IPA. Moreover, these devices are more  
 415 sensitive towards the amines functional group that has an electron lone pair. When sensors are



416 impinged with an electron donating gas like ammonia, the depletion of holes from the valence band  
417 of PEDOT:PSS occurs resulting in a significant increase in resistance with a sensing response in the  
418 range of 14-20%. This result suggests PEDOT:PSS as a good candidate for the detection of  $\text{NH}_3$  and  
419 its derivatives.



420

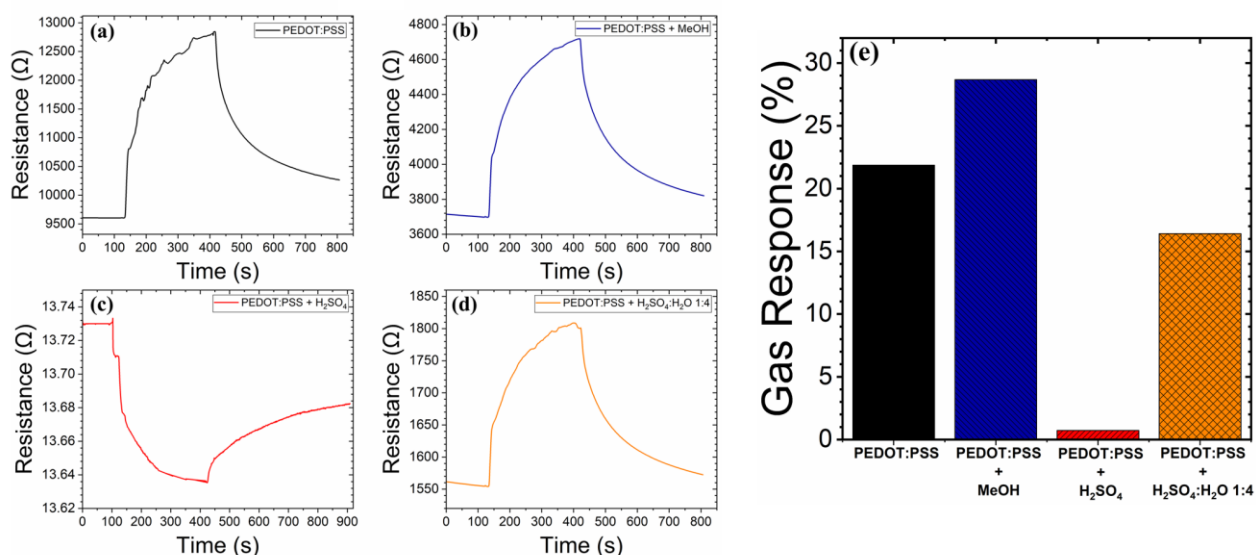
421 **Figure 8:** (a) Gas sensing response as a function of gas content for the different tested gas analytes at room temperature  
422 for PEDOT:PSS doped with MeOH; (b) Gas sensing response as a function of gas content for the different tested gas  
423 analytes at room temperature for PEDOT:PSS doped with  $\text{H}_2\text{SO}_4$ . The analytes concentration is reported in percent of  
424 their saturated partial vapor pressure.

425 The actual lower detection limit is under further investigation due to long bubbler retention times at  
426 low partial pressures. In the present work we tested **VOCs** concentrations as low as 2% of the  
427 saturated vapor pressure with a readable sensing response. Based on the current results we expect to  
428 detect even lower concentrations of the VOCs and also be able to detect other analytes of interest.

429 Another study has been carried out investigating the effects of  $\text{NO}_2$  on the fabricated chemiresistive  
430 gas sensors, revealing a strong influence on the active materials. Figure 9 shows the general response  
431 of the pristine PEDOT:PSS and their respective post-treatments thin films to 10 ppm  $\text{NO}_2$  gas at room  
432 temperature.  $\text{NO}_2$  is known to be a highly active and electron donating free radical. All sensors were  
433 highly affected by the release of the gas inside the chamber with an immediate increase until the  
434 saturation of the electrical resistance due to the electron transfer from  $\text{NO}_2$  to the partially positive  
435 charged sulfur site on the backbone of the p-type PEDOT:PSS sensors; while the device doped with  
436 pure  $\text{H}_2\text{SO}_4$  still maintained the opposite trend behavior as it was observed previously. All of them  
437 fully recovered to the original baseline except the pure  $\text{H}_2\text{SO}_4$  doped one. Evaluating the sensing  
438 responses, it is possible to notice the beneficial secondary doping of MeOH leading with a 29%  
439 response respect to the pristine one and the sensor doped with diluted  $\text{H}_2\text{SO}_4$  with 21% and 17%  
440 respectively. Much lower was the response of the pure  $\text{H}_2\text{SO}_4$  doped sensor. Compared to the other  
441 VOCs analytes, it appears that all the tested devices have better performances with the same trend in

442 the gas sensing response. This strong influence of this abundant gas in the atmosphere can potentially  
 443 introduce on the market PEDOT:PSS devices with different doping as great candidate for the NO<sub>x</sub>  
 444 detection in air quality monitoring.

## 10 ppm NO<sub>2</sub>



445  
 446 **Figure 9:** Dynamic Sensing curves of (a) PEDOT:PSS sensor, (b) PEDOT:PSS MeOH doped sensor, (c) and (d)  
 447 PEDOT:PSS doped with different concentrations of H<sub>2</sub>SO<sub>4</sub>, and (e) gas sensing response towards 10 ppm of NO<sub>2</sub>.

448 In addition, long-term stability was tested and there were some fluctuations regarding the baseline  
 449 resistance and the sensing response as shown in Table 2 and Figure 10. More precisely, the electrical  
 450 resistance generally increased in ambient air over a period of 10 months in different ways. After 6  
 451 months, films doped with H<sub>2</sub>SO<sub>4</sub> presented a variation up to 10%, while after 10 months it increased  
 452 of up to 30% and 53% for the 1:4 dilution respect to the original values. The same trend was observed  
 453 for the pristine PEDOT:PSS: 6% and 25% respectively. Sensors doped with MeOH showed a much  
 454 higher change with a variation of 43% and 178% respectively. It is worth noting that when placing  
 455 the devices in the sensing chamber and fluxing dry air, the resistance decreased, reducing the variation  
 456 and approaching to a new baseline stabilization without further abrupt fluctuations.

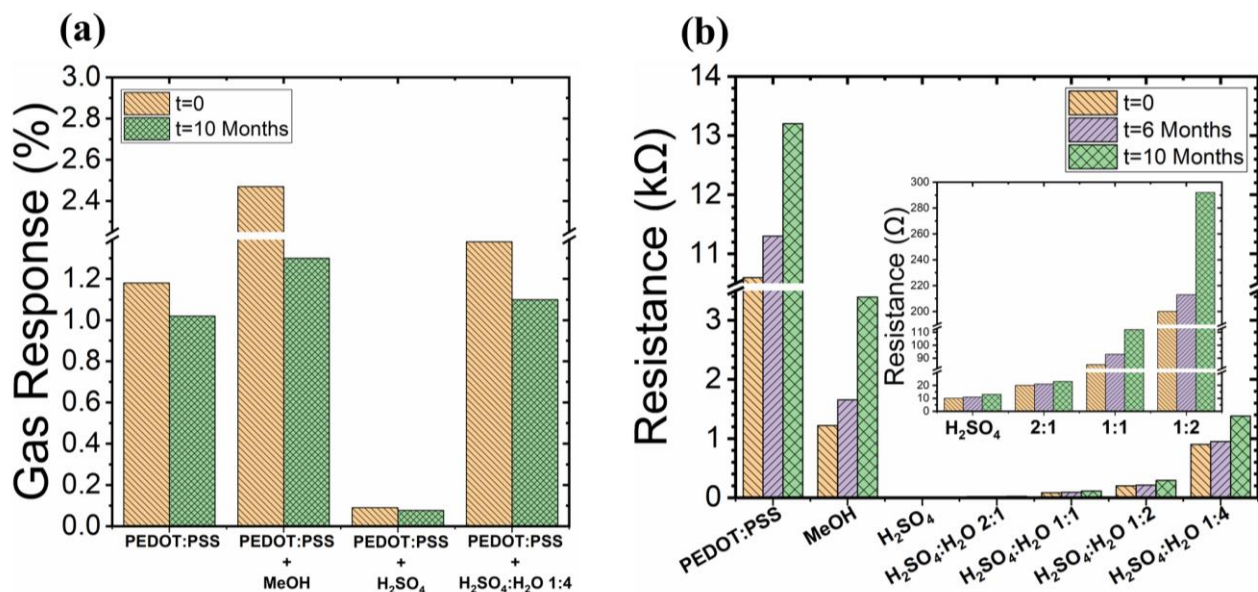
457 **Table 2:** Resistance values for PEDOT:PSS films with different post-treatments after 6 and 10 months.

Post-Treatment	Resistance		
	t=0	t=6 months	t=10 months
PRISTINE PEDOT:PSS	10.6 kΩ	11.3 kΩ	13.2 kΩ
PEDOT:PSS + MeOH	1221 Ω	1657 Ω	3390 Ω
PEDOT:PSS + H <sub>2</sub> SO <sub>4</sub>	10 Ω	11 Ω	13 Ω
PEDOT:PSS + H <sub>2</sub> SO <sub>4</sub> :H <sub>2</sub> O 2:1	20 Ω	21 Ω	23 Ω

PEDOT:PSS + H <sub>2</sub> SO <sub>4</sub> :H <sub>2</sub> O 1:1	85 Ω	93 Ω	112 Ω
PEDOT:PSS + H <sub>2</sub> SO <sub>4</sub> :H <sub>2</sub> O 1:2	200 Ω	213 Ω	292 Ω
PEDOT:PSS + H <sub>2</sub> SO <sub>4</sub> :H <sub>2</sub> O 1:4	900 Ω	949 Ω	1380 Ω

458

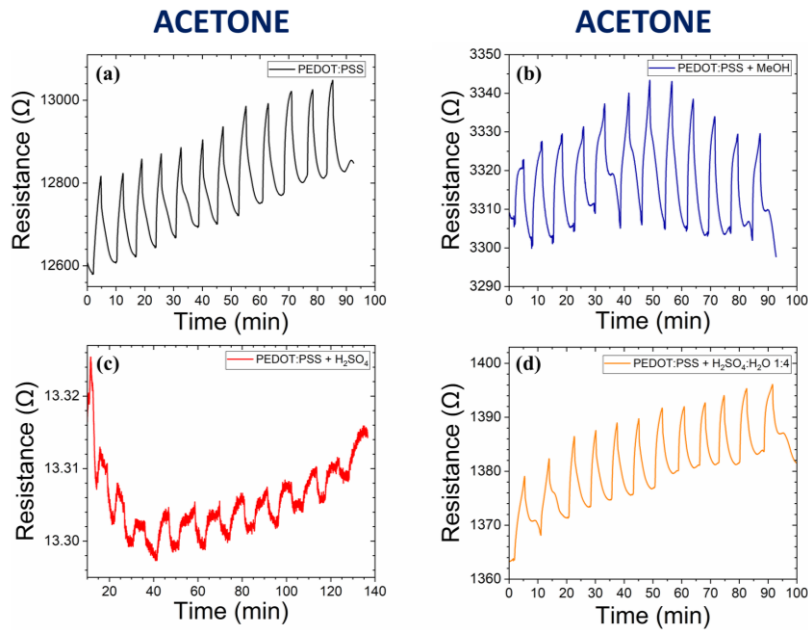
459 Moreover, Figure 10(a) compares the sensing response after 10 months. The very same devices were  
 460 able to detect the analytes and recover, maintaining their performance with a slight reduction of gas  
 461 response that could be due to environmental effects. This result allows utilizing these sensors multiple  
 462 times over a long period of time.



463

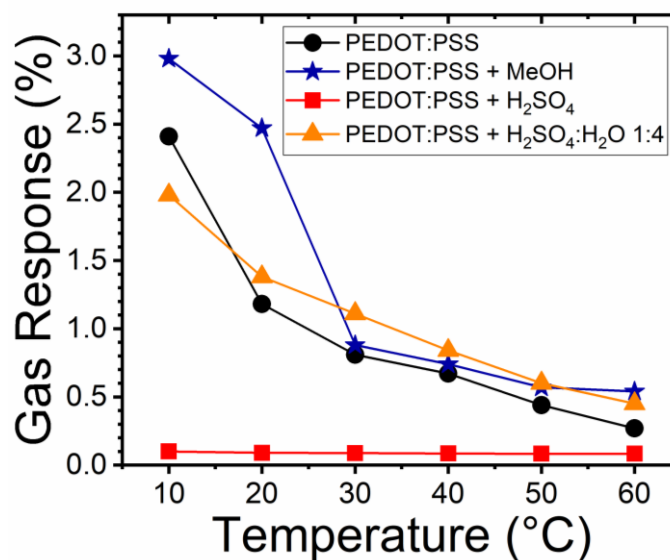
464 **Figure 10:** (a) Gas sensing response towards acetone at a fixed concentration of 5% of saturated vapor at room  
 465 temperature before and after 10 months, (b) behavior of the baseline resistance of PEDOT:PSS with different secondary  
 466 doping in ambient air as a function of time. The inset magnifies low resistance values in the range of 0-300 Ω.

467 Furthermore, 12 consecutive cycles were performed over a period of almost 2 hours in order to  
 468 evaluate the initial long-term stability of the different electronic devices and the repeatability of the  
 469 measurements. Figure 11 shows an example of the responses towards acetone at 5% of the saturated  
 470 vapor. As expected, all the films behave with an increase of the electrical resistance, while the one  
 471 post treated with concentrated H<sub>2</sub>SO<sub>4</sub> showed the inverted behavior. All the cycles presented almost  
 472 the same sensitivity, always fully recovering from the previous step, with a small constant drift  
 473 towards higher resistances. In conclusion, it can be said that the repeatability and stability were  
 474 verified, enabling these polymeric gas sensors for different practical applications.



475  
476 **Figure 11:** 12 cycles real-time measurements towards acetone at a fixed concentration of 5% of saturated vapor at room  
477 temperature for (a) pristine PEDOT:PSS, (b) PEDOT:PSS doped with MeOH, (c) PEDOT:PSS doped with concentrated  
478  $H_2SO_4$  and (d) PEDOT:PSS doped with 1:4 dilution of  $H_2SO_4$ .

479 As a final step, the effect of temperature was studied over a range from 10 °C up to 60 °C. From  
480 Figure 12, it is interesting to observe that increasing the temperature, the sensors performance  
481 decreased, except for the films doped with  $H_2SO_4$  that also presented the lowest response. The best  
482 performances were obtained at 10 °C. After a sharp reduction, raising the temperature from 30 °C to  
483 60°C, the gas response was almost unaltered.



484  
485 **Figure 12:** Gas sensing response of pristine PEDOT:PSS, PEDOT:PSS MeOH doped and PEDOT:PSS  $H_2SO_4$  doped  
486 sensors as a function of the temperature towards 5% of saturated vapor of acetone.

487 Concerning the sensing mechanism, different theories have been proposed for the conducting polymer  
488 systems including redox reactions between the polymer chains and the analytes, charge transfer and  
489 polymer swelling [3,50,56,68]. It's difficult to have a clear understanding of the mechanism

490 governing the interaction of PEDOT:PSS with the analyte because, most of the time, it's a  
491 combination of all of them where one is slightly predominant with respect to the others. The sensing  
492 response is affected by the polymer oxidation level which is influenced by primary and secondary  
493 doping. In PEDOT:PSS electrons in  $\pi$ -bonds are delocalized along the polymer chain due to the  $\pi$ -  
494 orbital overlapping and they are responsible for the carrier's transportation. The effects of doping  
495 undertake changes that contribute to make PEDOT:PSS encompassing near metallic to  
496 semiconductor or insulating behavior. More in detail, the sensing mechanism taking place through  
497 conduction occurs by intra- and inter-chain transport that can be affected by multiple factors. Through  
498 secondary doping post treatments, defect density, chain orientation and crystallinity can be tuned.  
499 Hence, PEDOT:PSS assumes an extended conjugation favoring a more regioregularity of the polymer  
500 tertiary structure. In this way, there are more active sites for the interaction between gas molecules  
501 and the conductive polymer. Furthermore, the reduction of PEDOT:PSS thickness upon secondary  
502 doping implies an enhancement of volumetric capacitance and, consequently, its attitude at  
503 implementing an efficient electrochemical activity in presence of oxidizing/reducing agents. By  
504 immersing the electronic devices in the dopant baths, the further oxidation introduces polarons and  
505 bipolarons as energy states between the LUMO and the HOMO [3,81]. Thus, it is important noting  
506 that the removing of electrons leads not only to the appearance of oxidizing states but to a change of  
507 the electronic structure, drastically reducing the 5.33 eV band gap in the neutral state [81]. It is also  
508 noteworthy that the spatial extent of polaron and bipolaron states is smaller but still comparable to  
509 the length of PEDOT polymer chains. For this reason, the overlap between polaron/bipolaron  
510 wavefunctions belonging to the same chain is strong in comparison to those belonging to the  
511 neighboring ones. Hence, the intra-chain hopping rate is estimated to greatly exceed the inter-chain  
512 one due to the alignment of the crystallite, and therefore for the PEDOT:PSS, the inter-chain motion  
513 represents the bottleneck determining the electron mobility and it is dictated by the tertiary structure  
514 influenced by the packing arrangement. This kind of conduction is of essential importance because  
515 most polymer chains do not extend between the gap across electrodes.

516 When the gas molecules interact with the surface of the sensing film, the hydrophilic PSS matrix,  
517 upon which smaller PEDOT chains are bound, present a swelling process where adsorbates increase  
518 the carriers hopping distance for charge transport creating an increase in electrical resistance for all  
519 analytes. At the same time, interaction between the PEDOT chains and the vapors, due to redox  
520 reactions, reversibly alter the conductivity and thus the presence of polarons and bipolarons on the  
521 backbone of the polymer by transferring electrons/holes and delocalizing the conjugated  $\pi$ -electrons  
522 of the sensing film. In fact, gas molecules behave as electrons donors/acceptors contributing a charge  
523 carrier to the polymer and consequently participating as dopants that reversibly increase or decrease

524 the carrier concentration, respectively and the measured signal variation. In summary, the doping  
525 process is crucial in enhancing electrical conductivity that is strictly related to the sensing mechanism  
526 and thus the sensing performance.

527

#### 528 **4. CONCLUSIONS**

529 This work illustrates a simple yet robust treatment method for the irreversible secondary doping of  
530 PEDOT:PSS in order to significantly enhance conductivity and improve gas sensing performance.  
531 For this reason, PEDOT:PSS gas sensors have been successfully fabricated by ink-jet printing  
532 technique and post-treated by immersing thin films in H<sub>2</sub>SO<sub>4</sub> with different concentrations and pure  
533 MeOH. In both cases, the conductivity was enhanced due to the combined effects of chain  
534 linearization from a random coil structure, increased doping level through further oxidation and  
535 removal of insulating PSS chains leading to a better connection of the PEDOT domain. Contact angle  
536 measurements, thickness evaluation, FTIR spectroscopy and real time gas sensing tests were  
537 performed by exposing the devices with **eight** analytes with different chemical and physical  
538 properties. Furthermore, the MeOH-doped sensor displayed the best sensing response towards all  
539 VOCs investigated, except O<sub>2</sub> and NH<sub>3</sub>. It was noticed that pure H<sub>2</sub>SO<sub>4</sub> affects the gas response,  
540 decreasing the sensitivity due to a possible PEDOT:PSS over-doping and, surprisingly, inverting the  
541 behavior of a p-type semiconductor. The H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O 2:1 solution still showed the same trend with  
542 an increased gas response, while further dilution caused a change in behavior in accordance with  
543 pristine PEDOT:PSS. The H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O 1:4 solution exhibited the best responses, improving pristine  
544 PEDOT:PSS performance. As the dilution concentration increased, the sensing response improved  
545 with values comparable with the MeOH doped sensor. **All of the thin films exhibited a higher**  
546 **response towards NO<sub>2</sub> with respect to VOCs vapors, allowing them to be utilized for a wide range of**  
547 **different applications.** Further investigation could be performed in order to exploit the same material  
548 with a dual nature and improved selectivity by different secondary doping for the implementation of  
549 a simple and selective electronic nose prototype.

550

#### 551 **ACKNOWLEDGMENT**

552 **The Authors want to acknowledge for their help with the NO<sub>x</sub> sensing measurements and set-up**  
553 **Andrea Marchisio and Jean Marc Tulliani.**

554

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