

# Diamondoid Nanostructures as $sp^3$ -Carbon-Based Gas Sensors

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**Abstract:** *Diamondoids,  $sp^3$ -hybridized nanometer-sized diamond-like hydrocarbons (nanodiamonds), difunctionalized with hydroxyl and primary phosphine oxide groups enable the assembly of the first  $sp^3$ -C-based chemical sensors by vapor deposition. Both pristine nanodiamonds and palladium nanolayered composites can be used to detect toxic  $NO_2$  and  $NH_3$  gases. This carbon-based gas sensor technology allows reversible  $NO_2$  detection down to 50 ppb and  $NH_3$  detection at 25–100 ppm concentration with fast response and recovery processes at 100 °C. Reversible gas adsorption and detection is compatible with 50% humidity conditions. Semiconducting p-type sensing properties are achieved from devices based on primary phosphine-diamantanol, in which high specific area (ca. 140 m<sup>2</sup> g<sup>-1</sup>) and channel nanoporosity derive from H-bonding.*

Outdoor air pollution, associated with global climate change, causes several million deaths per year.<sup>[1]</sup> Many toxic gases are produced through combustion processes from vehicles as well as industrial plants. Nitrogen dioxide ( $NO_2$ ) is the most hazardous gas with a 3 ppm threshold limit value (TLV, human level of exposure to be strictly controlled).<sup>[2]</sup>  $NO_2$  plays a role in atmospheric reactions causing acid rain, and contributing to ozone formation, which is the major cause of photochemically produced smog.<sup>[1,2]</sup> Detection and emission control of nitrogen oxides are thus essential objectives to reduce their hazardous effects on environment and mankind.<sup>[1-3]</sup>

Metal oxide semiconductors are low-cost, robust sensors most frequently used for the  $NO_2$  detection.<sup>[4,5]</sup> These usually operate at temperatures of a few hundred degrees Celsius, which is costly and reduces sensor lifetime. Other significant limitations are cross-sensitivities with other gases, and detrimental interference from relative humidity. Because of the emergence of nanotechnology a shift in sensor materials occurred toward more sensitive recognition layers,<sup>[6]</sup> increasingly elaborate architectures,<sup>[7,8]</sup> and reduced dimensionality.<sup>[2,9]</sup> Research

addresses low-power devices from sensitive and stable sensors usable at moderate temperatures, and thus suited for trace detection for a wide spectrum of applications ranging from lab-on-a-chip and *in vivo* biosensors to environmental monitoring and warfare agent detection.<sup>[10]</sup> In 2000, the Dai group demonstrated the potential of carbon nanotube (CNT)-based gas sensors.<sup>[3]</sup> The role of graphene in fabricating gas sensors for the detection of various hazardous gases, including  $NO_2$  rapidly emerged.<sup>[11,12]</sup> Thus, sensor development experienced a remarkable rise in attention focusing on  $sp^2$ -hybridized carbon structures.<sup>[13]</sup> There is, however, a large group of  $sp^3$ -hybridized carbon semiconductor materials, the so-called diamondoids, which essentially are hydrogen-terminated diamond nanoparticles (i.e., pristine nanodiamonds).<sup>[14]</sup> These mechanically rigid and thermodynamically extremely stable structures<sup>[15]</sup> are available in large quantities from fossil resources and in part through chemical synthesis.<sup>[16]</sup> Diamondoids are promising for nanoelectronics,<sup>[17]</sup> since they exhibit unique effects such as quantum confinement, hence offering possibilities for band gap tuning.<sup>[18,19]</sup> Diamondoid derivatives serve as building blocks in “bottom-up” strategies to build unique  $sp^3$ -carbon-based nanocomposites.<sup>[20,21]</sup>

Surfaces of CNT-based  $NO_2$  sensor materials react with the detected gas in mechanisms involving charge-transfer or Schottky-barrier modification<sup>[2,22]</sup> which results in a measurable change in resistance. In semiconducting p-type sensors, electron-donation into the valence band results in charge-carrier recombination causing an increase in resistance. Conversely, electron-withdrawing effects increase the hole concentration in the material, leading to lower resistance.<sup>[2]</sup> Additionally,  $NO_2$  adsorption is more favorable on CNTs with high metallic character than on semiconducting nanotubes.<sup>[23]</sup> We thus envisioned that nanocomposites combining  $sp^3$ -carbon 3-D molecular-size diamondoids coated with thin metal nanolayers would yield hybrid materials with electronically modified surfaces. These materials would then be potential catalysts or sensors. This band-structure doping inspired approach would combine  $sp^3$ -C nanodiamond semiconductors with transition metals. Accordingly, we recently reported robust self-assemblies of volatile P-functionalized diamondoids into nanocrystals via mild vapor deposition,<sup>[20]</sup> followed by Pd nanolayer coating under mild CVD conditions.<sup>[21]</sup>

Here we present the first use of  $sp^3$ -C-based nanostructures as high sensitivity gas sensors for the reversible detection of  $NO_2$ ,  $NH_3$ , and  $H_2$ . These new materials were structurally characterized at different scales (single-crystal X-ray diffraction, powder X-Ray diffraction, porosity measurements, Time-of-Flight Secondary Ion Mass Spectrometry, ToF-SIMS). The materials proved gas responsive both in pristine form and used as metal composite with a thin Pd nanolayer in surface. These chemical p-type sensors promote reversible  $NO_2$  detection at 50 ppb to 100 ppm concentration with fast response and recovery processes at 100 °C;  $NO_2$  detection was even possible in 50% relative humidity.  $NH_3$  detection at 25–100 ppm was also found to be highly efficient.

The primary phosphine 9-(hydroxydiamant-4-yl)phosphine ( $H_2P$ -DiamOH, **1**) and its oxide ( $H_2(O)P$ -DiamOH, **2**) were

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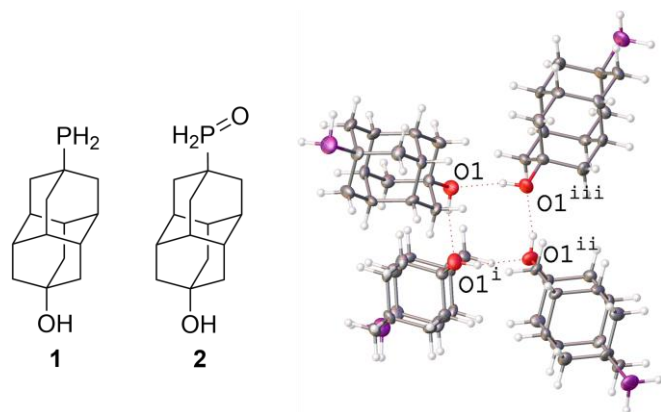
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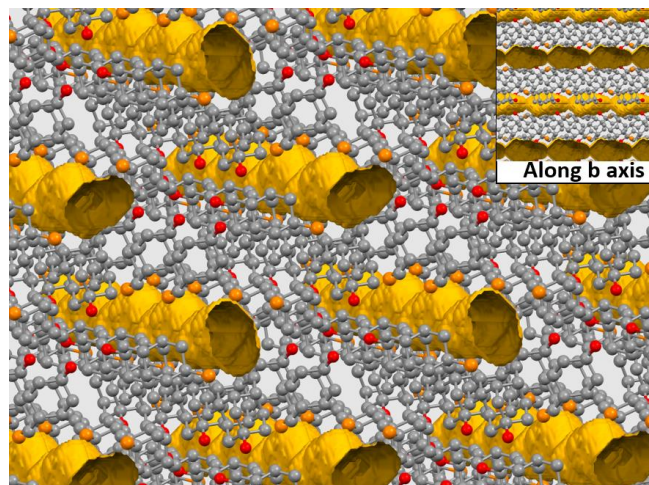
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synthesized from diamantane (Figures 1 and S1-S2). These diamondoid derivatives were used in powder form, first for their vapor-phase self-assembly, then for generating the metal composites Pd@PH<sub>2</sub>-DiamOH (**3**) and Pd@P(O)H<sub>2</sub>-DiamOH (**4**), respectively.<sup>[21]</sup> This was achieved by low-temperature chemical vapor deposition of a Pd nanolayer over the crystal self-assembly.<sup>[24]</sup> We elucidated the structure of **1** by growing single crystals in the vapor phase since all our attempts in solution failed. We found for **1** tetragonal symmetry (space group I-4, with  $a = b = 17.8965(4)$  Å,  $c = 8.1224(2)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 2601.48(13)$  Å<sup>3</sup>, Tables S1-S4). There is a single molecule in the asymmetric unit with strong H-bonding that leads to tetrameric arrangement (Fig.1).<sup>[25]</sup> We observed a large-scale arrangement of the crystalline structure in which a significant nanoporosity appears. Channel voids with a total volume of 168 Å<sup>3</sup> (~ 6.4% of unit cell, Figure 2) is accessible to small molecules or solvent. We examined voids within related diamondoid structures to establish that cavities in **1** are larger (or exist) than observed for related crystalline diamantane derivatives (see details in Figures S3).

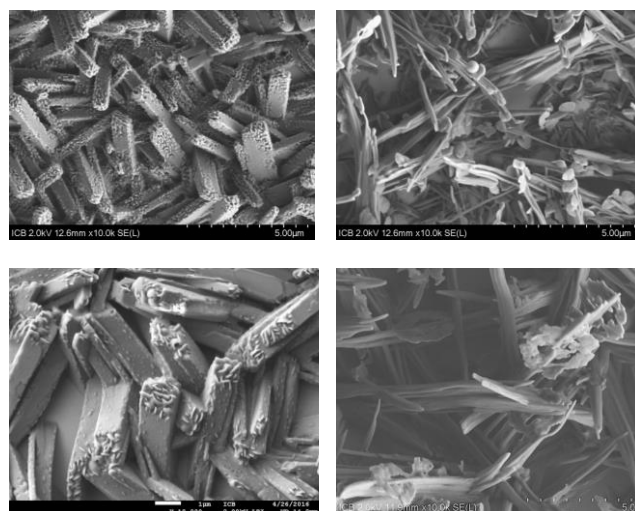


**Figure 1.** 9-(Hydroxydiamant-4-yl)phosphine **1** and its oxide **2** (left). Tetramer arrangement for **1** with  $O1-H1 \cdots O1' = 2.737(4)$  Å and  $O1-H-O1' = 164.8^\circ$  (right). Ortep thermal ellipsoids are drawn at 50% probability level.

The powder X-ray diffraction (PXRD) confirmed that this crystalline arrangement is conserved in the granular materials arising from diamantane functionalization, which was used for vapor phase self-assembly of **1** and **2**. We found excellent agreement between the experimental (Figures S4) and simulated PXRD patterns that were obtained from the single crystal unit cell by Le Bail refinement. Two major peaks at  $2\theta$  15.2° and 15.8°, completed with smaller peaks at 6.9, 9.8, 13.9, and 18.2 ° were observed and calculated. In relation with the XRD channel voids and the highly textured surface observed from SEM (Figure 3, top left), we measured from the crystalline powder the surface area of **1** following the Langmuir method using CO<sub>2</sub> absorption at 198 K (Figures S5a-c). We surprisingly found for this purely organic phosphine a  $S_{BET} = 138$  m<sup>2</sup> g<sup>-1</sup>, which is significantly higher than several reported porous composite materials.<sup>[26]</sup> Accordingly, we measured the surface area of the parent diamantyl phosphine (9-hydroxydiamant-4-yl)phosphonic dichloride<sup>[15a]</sup> (**5**, named Cl<sub>2</sub>(O)P-DiamOH) and its chlorinated analogue (9-chlorodiamant-4-yl)phosphonic dichloride (**6**, Cl<sub>2</sub>(O)P-Diam-Cl) to found much lower values  $S_{BET} = 40$  and 25 m<sup>2</sup> g<sup>-1</sup>, respectively (Fig. S5d). While single crystals of **5** could not be obtained, the XRD structure of Cl<sub>2</sub>(O)P-DiamCl,<sup>[15a]</sup> clearly reveals no voids. A  $S_{BET} = 54$  m<sup>2</sup> g<sup>-1</sup> was found for the oxide H<sub>2</sub>(O)P-DiamOH, **2**.



**Figure 2.** View of accessible channel voids in diamondoid **1** (Platon program crystallographic tool; probe 1.2 Å, grid 0.2 Å).

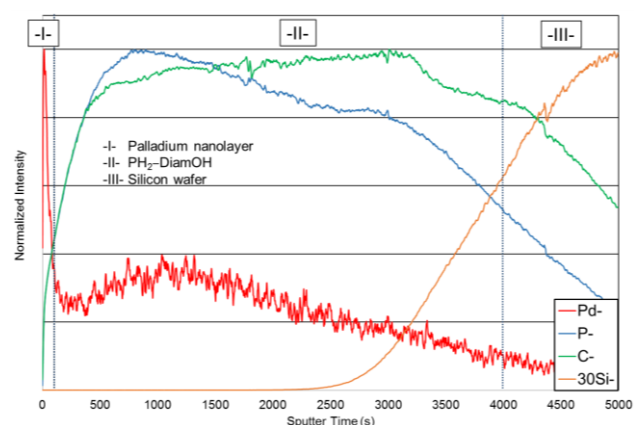


**Figure 3.** Scanning electron microscopy (SEM) of **1** (top left) and **2** (top right), and metal nanocomposites Pd@PH<sub>2</sub>-DiamOH, **3** (bottom left) and Pd@P(O)H<sub>2</sub>-DiamOH **4** (bottom right).

The nanolayering of palladium over self-assembled **1** and **2** led to nanocomposites **3** and **4**, respectively, for which scanning electron microscopy views are given in Fig. 3. The self-assemblies of **1-4** were produced with high structural uniformity and reproducibility.<sup>[21]</sup> The surfaces composition of these materials has been characterized by XPS, showing covalently built robust Pd@diamondoid hybrids that incorporate Pd-O-P(H)<sub>n</sub>-diamantane binding motifs. Our initial studies had been limited to a low surface depth below 10 nm, and we thus achieved bulk characterization of these materials in view of gas sensing.

ToF-SIMS analyses (Table S5, Figures S6-S9) from self-assembly of **1** indicated that the surface of primary diamantane phosphines is mostly in the oxidized form. Additionally, in composite **3** the palladium interactions with oxygen are prevalent, with the palladium isotopic distribution visible in many mass fragments attributable to palladium phosphorus oxides (Table S5, Fig. S6-S9). This is in full agreement with a Pd-O-P bonding scheme suggested by XPS. The ToF-SIMS technique also allowed monitoring and quantifying the different elements of our materials in-depth (bulk) owing to dual beam sputtering and analysis. Figure 4 represents the profile of the elements of interest (Pd, P, C, Si) as a function of sputter time for nanocomposite

Pd@PH<sub>2</sub>-DiamOH **3**. The clearly distinguishable areas correspond to the palladium layer (I), diamondoid phosphine deposit (II), and silicon support (III). The steep decrease of curve I from an initially dominant detection attested the Pd present as a thin nanolayer on the surface. The monitoring of phosphorus and carbon from the diamondoid cages (curves II) was achieved through the detection of characteristic fragments (Fig. S6-S9). P and C content detection follow first an increase, while the Pd trace diminishes (the lines cross at 70 s), then they decrease with the emergence of signals from the silicon wafer (curve III, line crossing at 4000 s). The profiles for P-containing and C-containing fragments follow a remarkable parallel evolution that attests to excellent homogeneity of the phosphine diamondoid deposit. According to Yamamura's sputter yield calculation as a function of the sputter type and energy,<sup>[27]</sup> it is possible to estimate sputter rate for Pd nanolayer ( $\leq 0.07 \text{ nm s}^{-1}$ ). ToF-SIMS depth profiling indicates thus a Pd nanolayer thinner than 5 nm. From SEM the diamondoid deposit thickness was estimated above 175 nm.

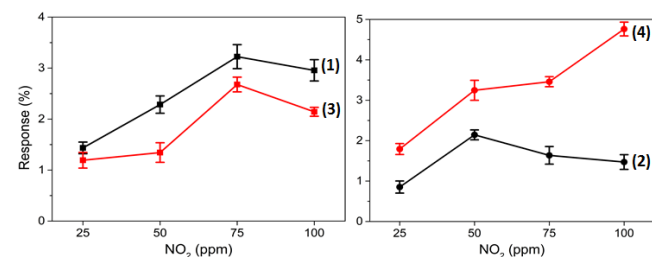


**Figure 4.** ToF-SIMS depth profile of nanocomposite Pd@PH<sub>2</sub>-DiamOH, **3**.

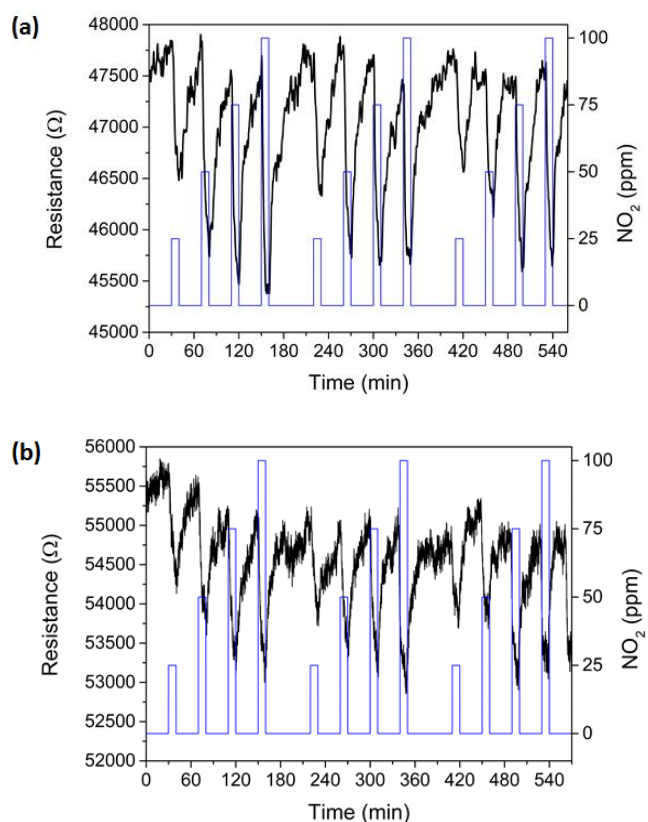
NO<sub>2</sub> gas sensing experiments were conducted with Pd nanocomposites **3** and **4**, but for comparison also with crystal self-assemblies of **1** and **2**. We conducted our experiments in a 35 cm<sup>3</sup> airtight test chamber, with the pieces of silicon wafers glued to a miniaturized ceramic hotplate and connected to a printed circuit board (Figures S10-S11). The exposure to NO<sub>2</sub> was 10 min with a recovery process of 30 min at 100 mL min<sup>-1</sup> flow of dry air. Nanocomposites operated at 100 °C and their electrical resistance was monitored within repeated response-recovery cycles. The materials were all found responsive (Figure 5). The self-assembly of diamondoid phosphine H<sub>2</sub>P-DiamOH **1** showed a NO<sub>2</sub> response (3.0% at 100 ppm, cycling time-resolved detection in Figure 6a) slightly superior to its oxide H<sub>2</sub>(O)P-DiamOH **2** (1.5% at 100 ppm) and its Pd nanocomposite Pd@PH<sub>2</sub>-DiamOH **3** (2.1% at 100 ppm). A significant NO<sub>2</sub> response was achieved with metal nanocomposite Pd@P(O)H<sub>2</sub>-DiamOH **4** with fast response and recovery processes (4.8% at 100 ppm, cycling detection in Fig. 6b).

The same samples were used for NH<sub>3</sub> detection in the 25–100 ppm concentration range under the same conditions (air flow 100 mL min<sup>-1</sup>, 100 °C, 35 cm<sup>3</sup> chamber) showing an even higher sensitivity for the NH<sub>3</sub> response (>10.0% for H<sub>2</sub>P-DiamOH **1** and >7.0% for Pd@PH<sub>2</sub>-DiamOH **3** at 100 ppm NH<sub>3</sub>, see cycling time-resolved detection in Fig. 6c and 6d, respectively, and Figure 7a). Exposure to NH<sub>3</sub> (as an electron-donating species) resulted in a resistance increase while the presence of NO<sub>2</sub> (electron-

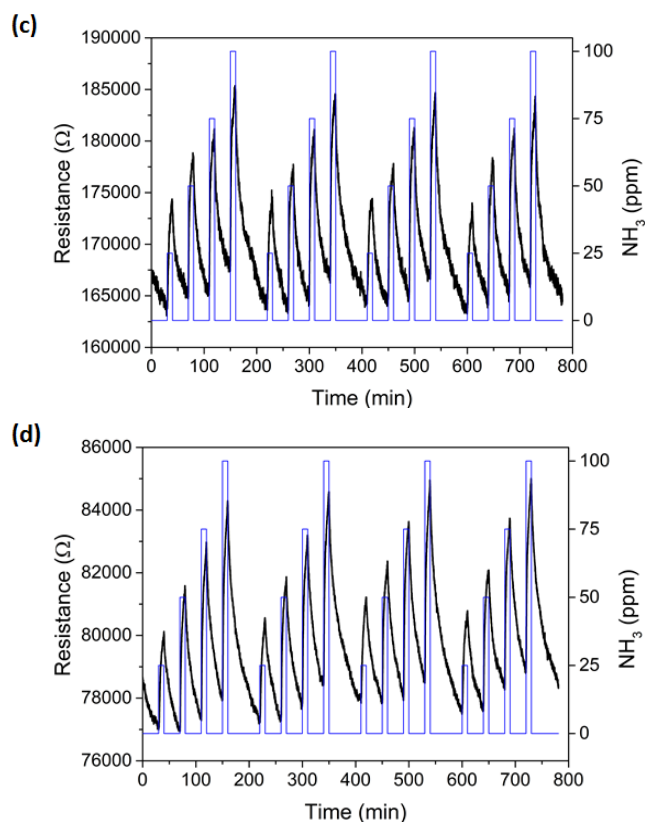
withdrawing) resulted in resistance decrease, which correspond to a typical semiconducting p-type behavior for all samples. Consistently, we found that uptake of H<sub>2</sub> was also possible with nanomaterials **1–4**, inducing resistance increase (Figures S12) that confirms the p-type character of these gas sensors. Using the diamondoid phosphine **5** Cl<sub>2</sub>(O)P-DiamOH,<sup>[21]</sup> we checked that efficient gas sensing properties were related to the primary phosphine-based diamantanol compounds. We observed for Cl<sub>2</sub>(O)P-DiamOH-based materials much lower H<sub>2</sub> uptake (if any) compared to **1** (Fig. S12a). This is visibly consistent with the high surface area for gas adsorption in **1** which is found 3.5 time higher than in **5** (138 vs 40 m<sup>2</sup> g<sup>-1</sup>).



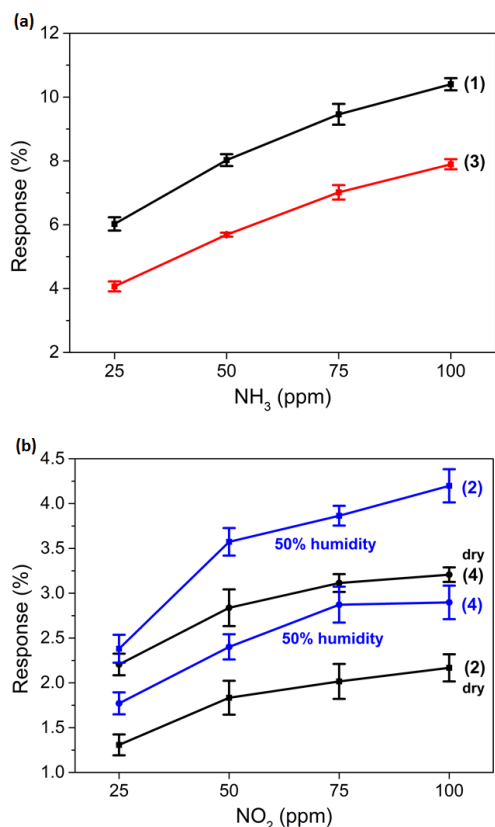
**Figure 5.** NO<sub>2</sub> response with chemical sensors **1–4** at increasing 25 to 100 ppm concentration: ■ = H<sub>2</sub>P-DiamOH (**1**), ● = H<sub>2</sub>(O)P-DiamOH (**2**), ■ = Pd@PH<sub>2</sub>-DiamOH (**3**), ● = Pd@P(O)H<sub>2</sub>-DiamOH (**4**). Response is defined as the relative  $(R_{\text{air}} - R_{\text{gas}})/R_{\text{air}}$  after 10 min exposure to NO<sub>2</sub>. See also in supporting information (Figures S11).



**Figure 6a,b.** Reversible NO<sub>2</sub> detection for sensors of higher sensitivity at 25, 50, 75, and 100 ppm: H<sub>2</sub>P-DiamOH **1** (chart a), Pd@P(O)H<sub>2</sub>-DiamOH **4** (chart b). Signals smoothed using the Savitzky-Golay method.



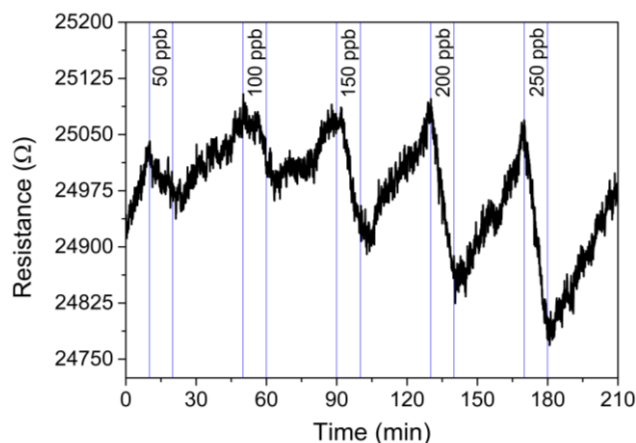
**Figure 6c,d.** Reversible  $\text{NH}_3$  detection for sensors of higher sensitivity at 25, 50, 75, and 100 ppm:  $\text{H}_2\text{P}$ -DiamOH 1 (chart c) and  $\text{Pd@PH}_2$ -DiamOH 3 (chart d). Signals smoothed using the Savitzky-Golay method.



**Figure 7.** (a)  $\text{NH}_3$  response of 1 and 3 at increasing 25–100 ppm concentrations (after 10 months storing); (b)  $\text{NO}_2$  response with sensors 2 and 4 in dry or humid conditions (after six months storing): ■ =  $\text{H}_2\text{P(O)}$ -DiamOH (2), ● =  $\text{Pd@P(O)H}_2$ -DiamOH (4) in dry conditions; ■ =  $\text{H}_2\text{P(O)}$ -DiamOH (2), ● =  $\text{Pd@P(O)H}_2$ -DiamOH (4) in humid conditions (50% relative humidity).

An issue of low-temperature sensing is the potential interference of relative humidity and the sensitivity to water is a factor to consider for practical devices.<sup>[2,10]</sup> For  $\text{NO}_2$  detection we compared the performances of nanomaterials 1–4 under dry and humid atmospheres (50% relative humidity) as illustrated in Figure 7b with 4 and 2 (1 and 3 in Fig. S11.5). The detection of  $\text{NO}_2$  was effective under either set of conditions, with different behavior still to rationalize, since 2 (and 3) increases the sensitivity in humid atmosphere compared to dry conditions, while 4 (and 1) performed better under dry conditions. In any case the responses were kept detectable in the same range (1–4%). Remarkably, uptake experiments reported in Fig. 7 were achieved six months ( $\text{NO}_2$  sensing) to ten months ( $\text{NH}_3$  sensing) after device preparation, attesting their robustness upon storing.

Operational devices for toxic gas request a TLV at low level of 25 ppm for  $\text{NH}_3$  and 3 ppm for  $\text{NO}_2$ .<sup>[2]</sup> While our  $\text{sp}^3\text{-C}$ -based diamondoid sensors efficiently detected  $\text{NH}_3$  at this environmental level requirement (Figs. 6 and 7b), we further explored the detection limit of our systems for  $\text{NO}_2$  in a 13  $\text{cm}^3$  airtight test chamber, reducing the dead volume with unchanged operating temperature (100 °C) and exposure/recovery times. Under these conditions, the detection of  $\text{NO}_2$  concentrations from 50 to 1000 ppb was successfully achieved, and confirmed the suitability of  $\text{sp}^3\text{-carbon}$ -based sensors for detecting few ten ppb of nitrogen dioxide.



**Figure 8.** Reversible  $\text{NO}_2$  detection at 50–250 ppb level for high sensitivity hybrid nanostructure sensor  $\text{Pd@PH}_2$ -DiamOH 3.

In summary, we report the first application of  $\text{sp}^3\text{-C}$ -based gas sensors ( $\text{NO}_2$ ,  $\text{NH}_3$ , and  $\text{H}_2$ ). Remarkably, they tolerate humid conditions and achieve sensing of  $\text{NO}_2$  at ppb levels at 100 °C. Pristine and metal-nanolayered diamondoids can both be gas responsive. Such gas sensing properties are related to primary phosphine-diamantanol based compounds for which channel nanoporosity (and  $S_{\text{Bet}}$  ca. 140  $\text{m}^2 \text{g}^{-1}$ ) derives from H-bonding in the solid state. We aim at extending our new approach to other metals and nanoobjects built on suitably functionalized diamondoid  $\text{sp}^3\text{-carbon}$ -based nanostructures.

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