Diamondoids Hot Paper

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Diamondoid Nanostructures as sp³-Carbon-Based Gas Sensors

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Abstract: Diamondoids, sp³-hybridized nanometer-sized diamond-like hydrocarbons (nanodiamonds), difunctionalized with hydroxy and primary phosphine oxide groups, enable the assembly of the first sp³-C-based chemical sensors by vapor deposition. Both pristine nanodiamonds and palladium nanolayered composites can be used to detect toxic NO₂ and NH₃ gases. This carbon-based gas sensor technology allows reversible NO₂ detection down to 50 ppb and NH₃ 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 m²g⁻¹) and channel nanoporosity derive from Hbonding.

Outdoor air pollution, associated with global climate change, causes several million deaths per year.^[1] Many toxic gases are produced through combustion processes from vehicles as well as industrial plants. Nitrogen dioxide (NO₂) is the most hazardous gas with a 3 ppm threshold limit value (TLV, human level of exposure to be strictly controlled).^[2] NO₂ plays a role in atmospheric reactions causing acid rain, and contributes to ozone formation, which is the major cause of photochemically produced smog.^[1,2] Detection and emission control of nitrogen oxides are thus essential objectives to reduce their hazardous effects on environment and man-kind.^[1–3]

Metal oxide semiconductors are low-cost, robust sensors most frequently used for the NO_2 detection.^[4,5] 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,^[6] increasingly elaborate architectures,^[7,8] and reduced dimensionality.^[2,9] 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.^[10] In 2000, the Dai group demonstrated the potential of carbon nanotube (CNT)-based gas sensors.^[3] The role of graphene in fabricating gas sensors for the detection of various hazardous gases, including NO₂, rapidly emerged.^[11,12] Thus, sensor development experienced a remarkable rise in attention focusing on sp²-hybridized carbon structures.^[13] There is, however, a large group of sp³-hydridized carbon semiconductor materials, the so-called diamondoids, which essentially are hydrogen-terminated diamond nanoparticles (that is, pristine nanodiamonds).^[14] These mechanically rigid and thermodynamically extremely stable structures^[15] are available in large quantities from fossil resources and in part through chemical synthesis.^[16] Diamondoids are promising for nanoelectronics,^[17] since they exhibit unique effects such as quantum confinement, hence offering possibilities for band gap tuning.^[18,19] Diamondoid derivatives serve as building blocks in "bottomup" strategies to build unique sp³-carbon-based nanocomposites.[20,21]

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Surfaces of CNT-based NO2 sensor materials react with the detected gas in mechanisms involving charge-transfer or Schottky-barrier modification,^[2,22] which results in a measurable change in resistance. In semiconducting p-type sensors, electron donation into the valence band results in chargecarrier recombination causing an increase in resistance. Conversely, electron-withdrawing effects increase the hole concentration in the material, leading to lower resistance.^[2] Additionally, NO2 adsorption is more favorable on CNTs with high metallic character than on semiconducting nanotubes.^[23] We thus envisioned that nanocomposites combining sp³carbon 3D 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 sp³-C nanodiamond semiconductors with transition metals. Accordingly, we recently reported robust self-assemblies of volatile P-functionalized diamondoids into nanocrystals by mild vapor deposition,^[20] followed by Pd nanolayer coating under mild CVD conditions.^[21]

Herein we present the first use of sp³-C-based nanostructures as high sensitivity gas sensors for the reversible detection of NO₂, NH₃, and H₂. These new materials were structurally characterized at different scales (single-crystal Xray 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 on the surface. These chemical p-type sensors promote reversible NO₂ detection at 50 ppb to 100 ppm concentration with fast response and recovery processes at 100 °C; NO₂ detection was even possible in 50 % relative humidity. NH₃ detection at 25– 100 ppm was also found to be highly efficient.

The primary phosphine 9-(hydroxydiamant-4-yl)phosphine (H₂P-DiamOH, **1**) and its oxide (H₂(O)P-DiamOH, **2**) were synthesized from diamantane (Figure 1; Supporting Information, Figure S1,S2). These diamondoid derivatives were used in powder form, first for their vapor-phase self-assembly, then for generating the metal composites Pd@PH₂-DiamOH (**3**) and Pd@P(O)H₂-DiamOH (**4**), respectively.^[21] This was achieved by low-temperature chemical vapor deposition of a Pd nanolayer over the crystal self-assembly.^[24] We elucidated the structure of **1** by growing single crystals in the vapor phase since all our attempts in solution failed. We



Figure 1. 9-(Hydroxydiamant-4-yl)phosphine 1 and its oxide 2 (left). Tetramer arrangement for 1 with $O1-H1\cdotsO1^{i} = 2.737(4)$ Å and $O1-H-O1^{i} = 164.8^{\circ}$ (right). ORTEP ellipsoids are set at 50% probability.

found for **1** tetragonal symmetry (space group $I\overline{4}$, with a = b = 17.8965(4) Å, c = 8.1224(2) Å, V = 2601.48(13) Å³, Supporting Information, Tables S1–S4). There is a single molecule in the asymmetric unit with strong H-bonding that leads to tetrameric arrangement (Figure 1).^[25] We observed a large-scale arrangement of the crystalline structure in which significant nanoporosity appears. Channel voids with a total volume of 168 Å³ (ca. 6.4% of the 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 the Supporting Information, Figure S3).



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

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 (Supporting Information, Figure S4) and simulated PXRD patterns that were obtained from the single-crystal unit cell by Le Bail refinement. Two major peaks at 2θ 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 the surface area of 1 from the crystalline powder following the Langmuir method using CO₂ absorption at 198 K (Supporting Information, Figure S5a-c). We surprisingly found for this purely organic phosphine a S_{BET}= 138 m²g⁻¹, which is significantly higher than several reported porous composite materials.^[26] Accordingly, we measured the surface area of (9-hydroxydiamant-4-yl)phosphonic dichlor $ide^{[15a]}$ (5, named $\mathrm{Cl}_2(\mathrm{O})\text{P-DiamOH})$ and its chlorinated analogue (9-chlorodiamant-4-yl)phosphonic dichloride (6, $Cl_2(O)P$ -Diam-Cl) to found much lower values $S_{BET} = 40$ and 25 m²g⁻¹, respectively (Supporting Information, Figure S5d). While single crystals of 5 could not be obtained, the XRD structure of Cl₂(O)P-DiamCl,^[15a] clearly reveals no

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Figure 3. Scanning electron microscopy (SEM) of 1 (top left) and 2 (top right), and metal nanocomposites $Pd@PH_2$ -DiamOH, 3 (bottom left) and $Pd@P(O)H_2$ -DiamOH 4 (bottom right).

voids. A $S_{BET} = 54 \text{ m}^2 \text{g}^{-1}$ was found for the oxide $H_2(O)P$ -DiamOH, **2**.

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 Figure 3. The self-assemblies of **1–4** were produced with high structural uniformity and reproducibility.^[21] The surfaces composition of these materials has been characterized by XPS, showing covalently built robust Pd@diamondoid hybrids that incorporate Pd–O–P(H)_n–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 (Supporting Information, Table S5, Figures S6-S9) from self-assembly of 1 indicated that the surface of primary diamantanol 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 (Supporting Information, Table S5, Figures S6–S9). This is in full agreement with a Pd-O-P bonding 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@PH₂-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 (Supporting Information, Figures 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



Figure 4. ToF-SIMS depth profile of nanocomposite Pd@PH₂-DiamOH, **3**.

for P- and C-containing fragments follow a remarkable parallel evolution that attests to excellent homogeneity of the diamondoid phosphine deposit. According to Yamamura's sputter yield calculation as a function of the sputter type and energy,^[27] 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.

NO₂ 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 cm³ airtight test chamber, with pieces of silicon wafers glued to a miniaturized ceramic hotplate and connected to a printed circuit board (Supporting Information, Figures S10 and S11). The exposure to NO_2 was 10 min with a recovery process of 30 min at 100 mLmin⁻¹ 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 selfassembly of diamondoid phosphine H₂P-DiamOH 1 showed an NO₂ response (3.0% at 100 ppm, cycling time-resolved detection in Figure 6 a) slightly superior to its oxide $H_2(O)P$ -DiamOH 2 (1.5% at 100 ppm) and its Pd nanocomposite Pd@PH₂-DiamOH 3 (2.1% at 100 ppm). A significant NO₂ response was achieved with metal nanocomposite Pd@P-



Figure 5. NO₂ response with chemical sensors 1–4 at increasing 25 to 100 ppm concentration: black $\nu = H_2P$ –DiamOH (1), black $\lambda = H_2$ -(O)P–DiamOH (2), red $\nu = Pd@PH_2$ –DiamOH (3), red $\lambda = Pd@P$ -(O)H₂-DiamOH (4). Response is defined as the relative $(R_{air}-R_{gas})/R_{air}$ after 10 min exposure to NO₂. See also the Supporting Information, Figure S11.







Figure 6. a),b) Reversible NO₂ detection for sensors of higher sensitivity at 25, 50, 75, and 100 ppm: H_2P –DiamOH 1 (a), Pd@P(O) H_2 -DiamOH 4 (b). Signals are smoothed using the Savitzky–Golay method. c),d) Reversible NH₃ detection for sensors of higher sensitivity at 25, 50, 75, and 100 ppm: H_2P –DiamOH 1 (c) and Pd@PH₂-DiamOH 3 (d). Signals smoothed using the Savitzky–Golay method.

(O)H₂-DiamOH 4 with fast response and recovery processes (4.8 % at 100 ppm, cycling detection in Figure 6b).

The same samples were used for NH₃ detection in the 25-100 ppm concentration range under the same conditions (air flow 100 mLmin⁻¹, 100 °C, 35 cm³ chamber) showing an even higher sensitivity for the NH₃ response (>10.0 % for H_2P -DiamOH 1 and >7.0% for Pd@PH₂-DiamOH 3 at 100 ppm NH₃, see cycling time-resolved detection in Figure 6c and d, respectively, and Figure 7a). Exposure to NH₃ (as an electron-donating species) resulted in a resistance increase while the presence of NO₂ (electron-withdrawing) resulted in resistance decrease, which corresponds to typical semiconducting p-type behavior for all samples. Consistently, we found that uptake of H₂ was also possible with nanomaterials 1-4, inducing resistance increase (Supporting Information, Figure S12) that confirms the p-type character of these gas sensors. Using the diamondoid phosphine 5 Cl₂(O)P-DiamOH,^[21] we checked that efficient gas sensing properties were related to the primary phosphine-based diamantanol compounds. We observed for Cl₂(O)P-DiamOH-based materials much lower H₂ uptake (if any) compared to 1 (Supporting Information, Figure 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 $m^2 g^{-1}$).



Figure 7. a) NH₃ response of **1** and **3** at increasing 25–100 ppm concentrations (after 10 months storing); b) NO₂ response with sensors **2** and **4** in dry or humid conditions (after six months storing): black $\nu = H_2P(O)$ -DiamOH (**2**), black $\lambda = Pd@P(O)H_2$ -DiamOH (**4**) in dry conditions; blue $\nu = H_2P(O)$ -DiamOH (**2**), blue $\lambda = Pd@P(O)H_2$ -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.^[2,10] For NO₂ 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 the Supporting Information, Figure S11.5). The detection of NO₂ 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 Figure 7 were achieved six months (NO₂ sensing) to ten months (NH₃ sensing) after device preparation, attesting their robustness upon storing.

Operational devices for toxic gas request a TLV at low levels of 25 ppm for NH_3 and 3 ppm for NO_2 .^[2] While our sp³-C-based diamondoid sensors efficiently detected NH_3 at this environmental level requirement (Figure 6 and Figure 7b), we further explored the detection limit of our systems for NO_2 in a 13 cm³ airtight test chamber, reducing the dead volume with unchanged operating temperature (100 °C) and exposure/recovery times. Under these conditions, the detection of NO_2 concentrations from 50 to 1000 ppb was successfully achieved, and confirmed the suitability of sp³-carbon-based sensors for detecting few ten ppb of nitrogen dioxide (Figure 8).



Figure 8. Reversible NO₂ detection at 50–250 ppb level for highsensitivity hybrid nanostructure sensor Pd@PH2–DiamOH 3.

In summary, we report the first application of sp³-C-based gas sensors (NO₂, NH₃, and H₂). Remarkably, they tolerate humid conditions and achieve sensing of NO₂ 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_{Bet} ca. 140 m²g⁻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 sp³-carbon-based nanostructures.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: gas sensing \cdot hybrid materials \cdot nanodiamonds \cdot palladium \cdot phosphine

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