Room temperature ammonia vapour detection on hBN flakes

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Abstract

The chemical vapour sensing behaviour of pristine and variously modified hexagonal boron nitride (hBN) nanostructures was investigated towards the polar protic analyte in the form of ammonia. Morphological characterization with TEM revealed formation of well-define shaped and crystal sized hBN flakes (2.9 ± 0.7 µm to 3.3 ± 0.3 µm) by using a low temperature and atmospheric pressure modified polymer derived ceramics (PDCs) route. Room temperature chemical sensing studies showed that the hBN-based devices were sensitive to ammonia, at sensitivity values of 2.8 × 10⁻² ppm⁻¹ for the pristine hBN flakes, and 2.0 × 10⁻² ppm⁻¹, 2.4 × 10⁻² ppm⁻¹, 2.1 × 10⁻² ppm⁻¹ for the 2.5, 5 and 10 wt.% BaF₂ modified hBN flakes, respectively. On the contrary, improvement in structure for the 5 wt.% BaF₂ modified hBN flakes had detrimental influence on the detection performance of ammonia, as evidenced by the poor LoD value of 49.7 ppm, in comparison to 1.1, 2.4 and 1.7 ppm for the pristine, 2.5, and 10 wt.% BaF₂ modified hBN flakes, respectively. The improved sensing performance was attributed to the presence of nitrogen vacancies generated during the modification process, as well as the presence of impurities. Indeed, the values measured were higher than those reported for other 2D nanomaterial based sensors. This study demonstrates the critical role played by structural properties on the surface chemistry in the ammonia sensing properties of hBN flakes. Generally, the study highlighted the potential application of hBN nanostructured materials for detection of ammonia vapours at room temperature.

1. Introduction

The development of portable and low cost gas sensor devices, exhibiting fast response and high sensitivity for humidity, volatile organic compounds or hazardous gases, has recently gained prominence in material technology for easy environmental monitoring and emission control; production control in agriculture, chemical, automotive and food industry; as well as in clinical diagnostics [1–3]. Among the various gaseous chemicals of interest, the control and monitoring of the toxic and odorous ammonia (NH₃) remains one of the extensively studied fields [1, 3]. Despite being a naturally occurring chemical, ammonia is also considered to be the most abundant man-made global inorganic pollutant. Moreover, high concentrations of ammonia in the environment have been found to be extremely hazardous to human health, aquatic life as well as vegetation [4–6]. Thus, detection of ammonia is vital for comprehension of its deleterious impacts on ecosystems and animal and/or human health, so as to attain sustainable environmental pollution monitoring and affordable healthcare for today’s global community.
For decades, the reliable detection of gaseous NH\textsubscript{3} has been achieved through the use of conventional methods like colorimetry, chromatography, and spectroscopy [7–9]. However, these techniques are prone to drawbacks such as requirements for complex and expensive instrumentation, large operating costs, need for high expertise, and time-consuming sample pretreatment and/or preparation. As a result, recent nanotechnological advancements have led to the development of novel nanomaterials for fabrication of advanced sensors exhibiting outstanding ammonia sensing capabilities. Such nanomaterials include metal oxides [10], composites [11], conducting polymers [12], and structured carbon-based materials [13, 14]. However, most of these materials suffer from numerous disadvantages that greatly hinder their practical application [15, 16].

To circumvent the challenges met by most commonly used nanomaterials, focus has shifted to two-dimensional materials (2DMs). Much interest in 2DMs have been driven largely by the ground-breaking isolation of graphene [17]. Since then, 2DMs have emerged as novel and promising materials for gas sensing by virtue of their fascinating and unique physicochemical, mechanical, and opto-electrical properties [18–21]. Amongst the various 2DMs that have been extensively studied for gas-sensing technology, hexagonal boron nitride (hBN) has also been employed for gas sensing [22, 23]. The sensing capability of hBN is made possible by the chemical alteration of boron and nitrogen atoms within the layers of hBN as well as the change in the electrical properties upon adsorption of the gas molecules. Furthermore, its 2D morphology allows for a complete exposure of all its atoms to the gas molecule, thereby increasing the sensitivity of hBN-based sensors. Additionally, the good thermal conductivity and stability, as well as chemical inertness [21, 24] enable hBN to be exploited as a promising material for use in harsh environmental conditions where other materials cannot be used. However, the defacto insulating behaviour of hBN have rendered this 2D material an unfavoured or barely studied material for application in resistive chemical sensors. Therefore, this work aims to provide a new platform for utilising hBN flakes as cost-effective chemoresistive ammonia sensors at room temperature.

2. Experimental

2.1. hBN nanosheet synthesis

The flakes of hBN were synthesized based on a procedure described elsewhere [25]. Typically, a pure monomer of borazine was prepared from a reaction between ammonium sulphate ((NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, ≳99%, Aldrich) and sodium borohydride (NaBH\textsubscript{4}, 98% purity, Aldrich) in tetraethylene glycol dimethyl ether or tetruglyme (C\textsubscript{10}H\textsubscript{22}O\textsubscript{8}, ≳99%, Alfa Aesar) solvent [26]. Thereafter, purification was achieved via distillation and then poly-condensation of borazine at 55 °C inside a pressure-sealed system under argon for 5 d was performed in order to generate a liquid and colourless polyborazylene (PBN) [27]. Finally, inside the glove-box and under inert gas atmosphere, lithium nitride (Li\textsubscript{3}N, 99.4%, Alfa Aesar) at a 5 wt.% ratio, and varying amounts (0–10 wt.%) of barium fluoride (BaF\textsubscript{2}, 99%, Alfa Aesar), were added to PBN, after which the mixture was homogenized through magnetic stirring for 10 min. The suspension was heated to 200 °C in an alumina crucible and after 1 h of solid-state polymer formation [28], the mixture was annealed for 1 h at 1200 °C (1 °C min\textsuperscript{-1}) under inert nitrogen (N\textsubscript{2}, 98%, Air Liquide, France) atmosphere.

2.2. Sensor preparation

In order to evaluate the sensing properties of the variously modified hBN samples, their fabricated devices were screened with the polar aprotic analyte in the form of ammonia. In a typical device fabrication procedure, dispersion solutions were prepared by separately dissolving 2 mg ml\textsuperscript{-1} of the hBN samples in water using 4 mg ml\textsuperscript{-1} of hexadecyltrimethylammonium bromide (CTAB) as a surfactant, then sonicate at 60 °C for 30 min and a further 30 min at 0 °C [14, 29]. Thereafter, the dispersions were kept for 3 d at a temperature lower than (i.e. 0 °C) the Kraft temperature of CTAB, 25 °C [30]. This was done to facilitate the precipitation of the hydrated crystals from the excess surfactant. Finally, after careful decantation of the supernatant, ∼100 μl of the hBN dispersions were drop casted onto an FR4 substrate containing the interdigitated electrodes (ENIG-Electroless Nickel Immersion Gold, supplied by Micropress S.A.) with an active area of ∼64 mm\textsuperscript{2} and a separation of 0.1 mm between the electrodes strip [31] and then dried in an oven at 100 °C for 30 min. For measurements of the resistances of the samples upon exposure to ammonia, an ICR meter (Agilent 4284A) was used. These measurements were carried out under steady inert nitrogen atmosphere (N\textsubscript{2}, 99.999%) state chamber conditions containing the vapour of ammonia, which was dropped at varying volumes into a sealed 2.4 l glass chamber using a micropipette (scheme S1 (available online at stacks.iop.org/JPMATER/4/044007/mmedia)), then the measurements were recorded after 10 min saturation time [14]. The concentration (C\textsubscript{ppm}) of ammonia in the gas phase was determined from the added volume using equation (1) [32];
Raman vibrating mode of consequently leading to better crystallization of without incorporation of BaF annealed after addition of 0, 2.5, 5, and 10 wt.% of BaF analysis (figure S1) showed better crystallization and purity of the addition of BaF the B atoms to N atoms, as indicated by the pronounced peaks corresponding to B–N and N–B bonds. Additionally, determination of bonding states of the constituent elements by XPS showed the high affinity of the bigger quality of the formation of the crystals with a more defined shape and exhibited an average crystal size of 2.74–8.41 irregular shaped and jagged-edged plate-like crystals. On the other hand, introduction of BaF nanostructures, with average crystal sizes of 0.89 µm, TEM micrographs revealed that the samples are mainly composed of overlapping, well-defined and plate-like electron microscopy (SEM) and transmission electron microscopy (TEM). From figure 3.1.Morphological and structural analysis The morphological properties of the as-synthesized hBN flakes were investigated using both scanning electron microscopy (SEM) and transmission electron microscopy (TEM). From figure 1, low magnification TEM micrographs revealed that the samples are mainly composed of overlapping, well-defined and plate-like nanostructures, with average crystal sizes of 0.89 ± 0.01, 2.9 ± 0.7, 3.3 ± 0.3, and 3.2 ± 0.7 µm, for samples annealed after addition of 0, 2.5, 5, and 10 wt.% of BaF2, respectively. Additionally, the SEM images (figure 1, inset) showed an improvement in the morphology of the samples upon addition of BaF2. In particular, without incorporation of BaF2 (i.e. 0 wt.% BaF2 hBN, figure 1(a)), the sample was an agglomerated mass of irregular shaped and jagged-edged plate-like crystals. On the other hand, introduction of BaF2 led to formation of the crystals with a more defined shape and exhibited an average crystal size of 2.74–8.41 µm [25]. The improvement in the morphology was attributed to the faster melting of Li3N, facilitated by BaF2, consequently leading to better crystallization of hBN from PBN [25]. Furthermore, Raman spectra (figure 2(a)) confirmed the phenomenon of improved crystallinity upon addition of BaF2 by showing a single peak, at ~1365 ± 2 cm−1, corresponding to the first-order active Raman vibrating mode of hBN (E2g) [33]. Additionally, the narrowing of the bandwidth values (figure 2, inset) was indicative of the formation of larger crystallites and subsequently improved crystallinity and quality of the hBN flakes [34] on addition of BaF2 to the pre-ceramic mixture. Likewise, powder XRD analysis (figure S1) showed better crystallization and purity of the hBN samples as evidenced by the characteristic fingerprint diffraction patterns for highly crystalline hBN, highlighted by the pronounced (002) diffraction peak at 2θ≈26.5°–26.8°, as well as the less intense (004), (110) and (112) peaks centred at 2θ≈55.4°, 2θ≈76.2°, 2θ≈81.7°, respectively. Similarly, integration of the area under the peaks of the survey XPS spectra of the samples showed an increased content of both boron and nitrogen atoms, thereby leading to B/N ratios of 1.62, 1.64, 1.57, and 1.50 for the hBN flakes grown after addition of 0, 2.5, 5, and 10 wt. % BaF2, respectively (table S1). Although the B/N ratios are found to be >1, this can be ascribed to the excess B atoms which are bonded to O, thus leading to the formation of the B2O2 domains [35]. Most importantly, the decreasing B/N ratio corroborated XRD results by suggesting increased coalescence into bigger hBN domains, as a result of better crystallization of hBN from PBN due to the presence of BaF2. Additionally, determination of bonding states of the constituent elements by XPS showed the high affinity of the B atoms to N atoms, as indicated by the pronounced peaks corresponding to B–N and N–B bonds.
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Figure 1. Low magnification TEM images of hBN samples annealed at 1200 °C, after addition of 5 wt% Li$_3$N and (a) 0, (b) 2.5, (c) 5, and (d) 10 wt% BaF$_2$. Inset: SEM micrographs of the as-synthesized samples (1 µm scale bar) [25]. Reproduced from [25]. CC BY 4.0.

Figure 2. (a) Raman plots and (b) textual analysis of hBN samples annealed at 1200 °C; after addition of 5 wt% Li$_3$N and 0–10 wt.% BaF$_2$. Inset: Bandwidth of the Raman spectra as a function of BaF$_2$ wt% [25]. Reproduced from [25]. CC BY 4.0.

(figure S2). However, the specific surface area of the hBN samples was, expectedly, greatly compromised with improved purity and crystallinity (figure 2(b)), as shown by the surface area values of 8.7, 3.5, 3.6 and 2.9 m$^2$ g$^{-1}$ for samples prepared after addition of 0, 2.5, 5 and 10 wt.% of BaF$_2$, respectively. This suggested that adsorption and desorption of nitrogen gas on the improved samples is only via the hBN flakes' external rough surface of the basal planes, due to lack of porosity.

3.2. Sensing properties of the hBN flakes

3.2.1. Determination of operating frequency

Following the determination of the chemical sensing capabilities of the variously modified hBN-based ammonia sensors, the optimum working frequency for future experiments was investigated as shown in figure 3, whereby the sensors’ resistance as a function of frequency upon exposure to increasing ammonia concentrations was measured. For all samples, the resistance was observed to drop with increasing frequency due to the high dependence of resistance to the sensor response as based on equations (2) and (4). Remarkably, varying effects of the frequency on the sensor response were observed for the different hBN-based devices and this can be ascribed to the contribution from the morphology of the individual sensor materials. For instance, in case of the 5 wt.% modified hBN-based device, the observed rapid drop in the resistivity at low frequencies, regardless of the increasing concentration, can be attributed to the applied alternating electric field and to the possible existence of defects on the well-defined layered 2D structure of the hBN flakes [36]. As a result, the charge carriers tend to travel relatively long distances in order to overcome potential barriers with several height of the layered 2D nanostructure. Similar phenomena were observed for the pristine, 2.5 wt.% and 10 wt.% BaF$_2$ modified hBN-based devices at low ammonia concentrations. However, at high ammonia concentrations a gradual decrease in the resistance was evident at low frequencies with increasing ammonia concentration. This could signify that the charge carriers are unable to follow the oscillating signal, thus their movement becomes restricted to medium to short distances within the structure of the sensor material. Similar restriction of the charge carrier mobility is observed at
high frequencies for all samples, thus indicating conversion to high conductivity state for all samples at high frequencies [36]. In light of the observations, the optimum operating working frequencies, at room temperature, were determined to be 20 kHz for the pristine, 2.5 wt.% and 10 wt.% BaF$_2$ modified hBN-based devices, whilst the 5 wt.% BaF$_2$ modified hBN-based device exhibited the optimum working frequency of 3 kHz. The results showed that the morphology of the sensor material has a great influence on the sensing capability of the hBN flakes towards ammonia, thus showing potential for the as-synthesized materials for room temperature ammonia-based sensors. In particular, the low operating frequency for the well-defined large area hBN flakes samples was better than and/or comparable to that of the reported large area hBN nanosheets, other 2D nanomaterials, as well as the commonly used sensor materials for ammonia (table 2). For instance, Lu et.al reported an operating frequency of 6 kHz for the 6 µm hBN nanosheets for ammonia detection at 300 °C [37], whilst 3 kHz optimum frequency for ammonia sensing devices were reported for TMDs, graphene nanoflakes, N-doped graphene nanosheets, and metal oxides [38–42].

3.2.2. Response and recovery time
The sensing properties of the pristine and modified hBN flakes towards ammonia were then evaluated. The chemical sensing capabilities of the as-fabricated sensing devices towards ammonium gas were investigated via the determination of the response time upon exposure to ammonia and recovery time on removal of ammonia gas from the chamber. Figure 4 shows the response and recovery time profiles of the pristine and the modified hBN flakes after exposure of 160 ppm of ammonia at room temperature and optimum operating frequencies. All samples showed relatively excellent gas sensing performance towards ammonia, evident by fast response and recovery times (table S2) at the operating frequency of 3 kHz. Despite hBN being an electric insulator, the recorded response and recovery times were comparable and/or better than most of those recorded in literature for ammonia sensors [38, 41, 42]. From the results, it is interesting to observe that the atomic-layered h-BN flakes can function as good resistance-based gas sensors, similar to their graphene counter-parts and conductive transitional metal dichalcogenides (TMDs) [41, 42]. Moreover, varying sensing performance mechanisms were observed for the adsorption of ammonia up to a saturation time of 100s, thus suggesting varying adsorption/desorption behaviours of the sensing materials to ammonia.

Generally, the sensing performance of a material is influenced by the interaction between the different adsorbed oxygen species (i.e. O$_2^-$, O$^-$, or O$^{2-}$) and the gas molecule. This is because the gas detection mechanism for a sensor is governed by the variation in conductance caused by the chemical adsorption-desorption of the oxygen molecules on the sensor material's surface [43]. For instance, in this study, upon exposure of the active hBN materials to the inert N$_2$ atmosphere, the oxygen impurities in the inert gas become adsorbed on the planar surface and/or gain boundaries of h-BN and become ionized by withdrawing electrons from the conduction band and vacancies [44, 45], as according to step (a) of scheme 1. However, depletion of the generated holes by the residual Li and Ba nanoparticles led to an increased conductivity for both pristine and 2.5 wt.% BaF$_2$ modified hBN-based devices, as a result of an injection of electrons from the electron-donating NH$_3$ back to the h-BN conduction band occurs (step (c),
Figure 4. Responses and recovery times for devices fabricated from (a) pristine hBN, and hBN prepared after addition of (b) 2.5 wt% BaF$_2$, (c) 5 wt% BaF$_2$ and (d) 10 wt% BaF$_2$ at optimum operating frequencies.

scheme 1), thus leading to the abrupt decrease in resistance, as seen in figures 3(a) and (b). Moreover, the defective morphology of both pristine and 2.5 wt.% BaF$_2$ modified hBN samples (figures 1(a) and (b)) facilitates its surface interaction with ammonia molecules, allowing more available hopping sites and increasing charge carrier mobility, thus leading to an increased conductivity state within the nanostructures and the observed response times. On the contrary, the long recovery times are an indication of the strong interaction of the NH$_3$ with the defective surface of both pristine and 2.5 wt.% BaF$_2$ modified hBN sample, hence compromising the quality of both pristine and 2.5 wt.% BaF$_2$ modified hBN-based sensors. However, the lack residual hole depletion nanostructures in the 5 wt.% BaF$_2$ and 10 wt.% BaF$_2$ modified hBN samples meant that these devices functioned as p-type semiconductors through the generation of more ionized oxygen moieties on the surface of the highly ordered morphology of the 5 wt.% BaF$_2$ and 10 wt.% BaF$_2$ modified hBN samples, hence the observed increased resistance. The observed longer response times and increased resistance for these samples could be attributed to the retention of charge carriers due to the longer barriers and the electron hoping effect within the hBN planar structure. Furthermore, weak interaction of the NH$_3$ molecule with the less defective planar hBN surface lead to shorter recovery times of 35 and 38 s for the 5 wt.% BaF$_2$ and 10 wt.% BaF$_2$ modified hBN-based devices, respectively.

3.2.3. Ammonia sensitivity

At chosen operating frequency, that equilibrates to high magnitude of the response (figure 3) and high signal to noise ratio (SNR) value, the resistance as a function of ammonia concentration for the modified materials of interest are presented in figure 5, from which the limit of detection (LoD) and sensitivities (S, figures S3 and S4) were estimated. Based on the sensor responses ($\Delta R/R_0$) presented in figure 3, the sensitivities were calculated by assuming a linear dependence, and the attained data is listed in table 1. Generally, the sensor responses (figures 5 and S3) are observed to increase with ammonia concentration, an indication that these hBN-based sensors exhibited a p-type semiconducting behaviour. In particular, lower concentration limit of detection (LoD, 1.1 ppm) and high sensitivity value ($2.8 \times 10^{-2}$ ppm$^{-1}$) was recorded for the sensing devices based on the pristine hBN flakes, despite the high operating frequency of 20 kHz. This could be ascribed to the presence of the abundant nitrogen vacancies ($V_N$) in the defective structure of hBN. The nitrogen vacancies then act as electron capture sites during exposure of the active material to ammonia, thereby resulting in improved sensitivity. Furthermore, the stronger surface interaction to ammonia molecule due to the increase in the surface area and presence of the impurity nanoparticle contaminates likely contributed to the higher ammonia sensitivity [14]. Similar argument could also be used for the recorded LoD of 2.4 ppm and 1.7 ppm as well as sensitivities of $2.8 \times 10^{-2}$ ppm$^{-1}$ and $2.1 \times 10^{-2}$ ppm$^{-1}$ for the 2.5 wt.% BaF$_2$ modified hBN- and 10 wt.% BaF$_2$ modified hBN- based devices, respectively. On the other hand, limited amount of nitrogen vacancies and the low surface area of the well-ordered 5 wt.% BaF$_2$ modified hBN samples resulted in slightly higher sensitivity ($2.4 \times 10^{-2}$ ppm$^{-1}$) towards ammonia and a relatively poor LoD (49.7 ppm), irrespective of the interestingly low optimum working frequency of 1 kHz. In summary, the
Scheme 1. Adsorption and reaction mechanism of NH$_3$ on the hBN surface.

Figure 5. Sensor resistance as a function of analyte concentration, the red line indicates the estimated LoD resistance of the corresponding sensor based on (a) pristine hBN, (b) 2.5 wt% BaF$_2$, (c) 5 wt% BaF$_2$ and (d) 10 wt% BaF$_2$ additions samples at optimum operating frequencies.

Table 1. Frequency $f$, determined limit of detection concentration (LoD) and sensitivity, $S$ for detection of ammonia at 2 mg ml$^{-1}$ concentration of the hBN dispersions.

| Parameter       | 0 wt% | 2.5 wt% | 5 wt% | 10 wt% |
|-----------------|-------|---------|-------|--------|
| $f$ (kHz)       | 20    | 20      | 1     | 20     |
| $S$ ($\times 10^{-2}$ ppm$^{-1}$) | 2.8   | 2.0     | 2.4   | 2.1    |
| LoD (ppm)       | 1.1   | 2.4     | 49.7  | 1.7    |

results indicated that wide bandgap semiconductor or defacto insulator hBN flakes can be considered to be as good chemoresistive gas sensors as their zero-bandgap graphene or conductive 2D counterparts. Moreover, presence of impurities was found to improve their functionality at room temperature; thus, addressing one of the pressing issues of the commonly developed and/or explored chemoresistive ammonia gas sensors.
Table 2. Comparative ammonia chemoresistive sensors for the hBN samples with other related 2D materials in literature.

| Sensor material | Temp. (°C) | LoD (ppm) | Reference |
|-----------------|------------|-----------|-----------|
| MoS₂            | RT         | 0.3       | [46]      |
| T₃C₅Tₓ         | RT         | 0.05      | [47]      |
| MoS₂/WO₃       | 200        | 1.0       | [48]      |
| rGO/WO₃        | RT         | 1.5       | [49]      |
| hBN—0 wt. % BaF₂ | RT        | 1.1       | This work |
| hBN—2.5 wt. % BaF₂ |         | 2.4       |           |
| hBN—5 wt. % BaF₂ |           | 49.7      |           |
| hBN—10 wt. % BaF₂ |           | 1.7       |           |
| rGO            | RT         | 0.005     | [50]      |
| F-GO           | RT         | 0.006     | [39]      |

MoS₂ → molybdenum disulphide, WO₃ → tungsten oxide, ZnO → zinc oxide, hBN → hexagonal boron nitride, BaF₂ → barium fluoride, rGO → reduced graphene oxide, F-GO → fluorinated graphene oxide, T₃C₅Tₓ → bimetallic Mxene.

The observed ammonia sensor responses for the pristine and variously BaF₂ modified hBN samples were then compared with the chemoresistive sensors in the literature (table 2) based on the 2D materials. The hBN-based sensors showed relatively comparable sensitivity, LoD and comfortable working concentration range to those of its 2D family members such as graphene oxide and transition metal dichalcogenides (TMDs). The results indicated that with further improvement in the structural properties of hBN synthesized via the PDCs technique, the sensitivity and detection of these hBN flakes towards ammonia can be achieved at very low concentration levels (ppb).

4. Conclusions

The study reports on the sensing properties of hexagonal boron nitride (hBN) flakes to ammonia vapour. Well-define shaped and crystal sized (2.9 ± 0.7 µm to 3.3 ± 0.3 µm) hBN flakes were successfully synthesized at low temperatures (1200 °C) and atmospheric pressure through the barium fluoride (BaF₂)-assisted polymer-derived ceramics (PDCs) technique. The flakes were then successfully characterized by XRD, TEM and Raman spectroscopy, followed by sensor screening in the atmosphere of ammonia vapour. The results show that the constructed sensors are active for ammonia detection. In particular, for the pristine as well as the 2.5 wt.% and 10 wt.% BaF₂ modified hBN-based sensors, interaction of ammonia and the active material was observed to be facilitated by the nitrogen vacancies at the defective sites and presence of impurities, thereby translating to high sensitivities and low concentration LoD's. On the other hand, the generation of an increased electronic cloud on the well-ordered 5 wt.% BaF₂ modified hBN-based sensors hindered good sensing of ammonia, evident by the slightly higher sensitivities and very poor concentration LoD's. Despite the relatively low surface areas of the hBN flakes (2.9–3.5 m² g⁻¹), the samples showed great potential for application in chemical vapour sensing of reduced organic molecules with high sensitivity as well as quite fast response and recovery. In general, the study provided a platform for the production of large-scale and good-quality hBN crystals at relatively low temperature and atmospheric pressure conditions, as well as the development of hBN-based sensing devices for ammonia chemical vapours.

Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: 10.3390/nano10030443.

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References

[1] Zhang J, Liu X, Neri G and Pinna N 2016 Nanostructured materials for room-temperature gas sensors Adv. Mater. 28 795–831
[2] Choi S-J, Jang B-H, Lee S-J, Min B K, Rothschild A and Kim I-D 2014 Selective detection of acetone and hydrogen sulfide for the diagnosis of diabetes and halitosis using SnO2 nanofibers functionalized with reduced graphene oxide nanosheets ACS Appl. Mater. Interfaces 6 2588–97
[3] Fine G F, Cavanagh L M, Afonja A and Binions R 2010 Metal oxide semi-conductor gas sensors in environmental monitoring Sensors 10 5469–502
[4] Fangmeier A, Hadwiger-Fangmeier A, Van Der Eerden L and Jäger H-J 1994 Effects of atmospheric ammonia on vegetation—a review Environ. Pollut. 86 43–82
[5] Shin K W, Kim S-H, Kim J-H, Hwang S D and Kang J-C 2016 Toxic effects of ammonia exposure on growth performance, hematological parameters, and plasma components in rockfish, Sebastes schlegelii, during thermal stress Fish. Aquat. Sci. 19 44
[6] Peart F B 2003 Potential effects on human health of an ammonia rich atmospheric environment in an archaeologically important cove in southeast Asia Occup. Environ. Med. 60 986–8
[7] Lewicki R, Wysoczki G, Kosterev A A and Tittel F K 2007 Carbon dioxide and ammonia detection using 2 μm diode laser based quartz-enhanced photoacoustic spectroscopy Appl. Phys. B 87 157–62
[8] Cho Y B, Jeong S H, Chun H and Kim Y S 2018 Selective colorimetric detection of dissolved ammonia in water via modified Berthelot’s reaction on porous paper Sens. Actuators B 256 167–75
[9] Amirjani A and Fatmehsari D H 2018 Colorimetric detection of ammonia using smartphones based on localized surface plasmon resonance of silver nanoparticles Talanta 176 242–6
[10] Liu D, Wang C, Yu Y, Zhao B-H, Wang W, Du Y and Zhang B 2019 Understanding the nature of ammonia treatment to synthesize oxygen vacancy-enriched transition metal oxides Chem 5 376–89
[11] Malook K, Khan H, Shah M and Haque I-U 2019 Highly selective and sensitive response of Polyppyror–MnO2 based composites towards ammonia gas Polym. Compos. 40 1676–83
[12] Sonkusare A G, Tyagi S, Mishra S, Kaur M and Kumar R 2018 Ammonia sensing using conducting polymer Polyppyror-coated silicon wafer Int. J. Appl. Environ. Sci. 13 59–69
[13] Panes-Ruiz L A, Shayyan M, Fu Y, Liu Y, Khavrus V, Oswald S, Gemming T, Baraban L, Bezugly V and Cuniberti G 2018 Toward highly sensitive and energy efficient ammonia gas detection with modified single-walled carbon nanotubes at room temperature ACS Sensors 3 79–86
[14] Mutuma B K, Rodrigues R, Ranganathan K, Matsoso B, Wamwangi D, Hummelgen I A and Coville N J 2017 Hollow carbon spheres and a hollow carbon sphere/polypyrorylidolone composite as ammonia sensors J. Mater. Chem. A 5 2367–992
[15] Zhang L, Du W, Nautiyal A, Liu Z and Zhang X 2018 Recent progress on nanostructured conducting polymers and composites: synthesis, application and future aspects Sci. China Mater. 61 303–52
[16] Dey A 2018 Semiconductor metal oxide gas sensors: a review Mater. Sci. Eng. C 82 229 206–17
[17] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric field effect in atomically thin carbon films Science 306 666 LF–669
[18] Geim A K and Novoselov K S 2007 The rise of graphene Nat. Mater. 6 183
[19] Gogotsi Y and Anasori B 2019 The rise of MXenes ACS Nano 13 18491–4
[20] Manzeli S, Ovchinnikov D, Pasquier D, Yazyev O V and Kis A 2017 2D transition metal dichalcogenides Nat. Rev. Mater. 2 17033
[21] Kubota Y, Watanabe K, Tsuda O and Taniguchi T 2007 Deep ultraviolet light-emitting hexagonal boron nitride synthesized at atmospheric pressure Science 317 932–4
[22] Peyghan A A, Noei M and Yourdkhani S 2013 Towards graphene-like BN nanosheet as a sensor for para-nitrophenol: DFT study Superlattices Microstruct. 59 35–22
[23] Zhang Y-H, Zhou K-G, Gou X-C, Xie K-F, Zhang H-L and Peng Y 2010 Effects of dopant and defect on the adsorption of carbon monoxide on graphitic boron nitride sheet: a first-principles study Chem. Phys. Lett. 484 266–70
[24] Liu L, Feng Y P and Shen Z X 2003 Structural and electronic properties of h-BN Phys. Rev. B 68 104102
[25] Matsoso B J, Vuillet-a-ciles V, Bois L, Toury B and Journet C 2020 Improving formation conditions and properties of hBN nanosheets through BaF–assisted polymer derived ceramics (PDGs) technique Nanomaterials 10 6–10
[26] Wideman T and Sneddon L G 1995 Convenient procedures for the laboratory preparation of borazine Inorg. Chem. 34 1002–3
[27] Bernard S and Miele P 2014 Polymer-derived boron nitride: a review on the chemistry, shaping and ceramic conversion of borazine derivatives Materials 7 7436–59
[28] Yuan S, Toury B, Journet C and Brioude A 2014 Synthesis of hexagonal boron nitride graphene-like few layers Nanoscale 6 14
[29] Rodrigues R, Mamo M A, Coville N J and Hummelgen I A 2014 Hydrostatic pressure sensors based on carbon spheres dispersed in polyvinyl alcohol prepared using hexadecyltrimethylammonium bromide as surfactant and water as solvent Mater. Res. Express 1 15605
[30] Dölle S, Lechner B-D, Park J H, Schymura S, Lagerwall J P F and Scalla G 2012 Utilizing the Krafft phenomenon to generate ideal Micelle-free surfactant-stabilized nanoparticle suspensions Angew. Chem., Int. Ed. 51 3254–7
[31] Cunha B B, Greenshields M W, Coyle D, Mamo M A, Coville N J and Hummelgen I A 2015 A surfactant dispersed N-doped carbon sphere-poly(vinyl alcohol) composite as relative humidity sensor J. Mater. Sci. Mater. Electron. 26 4198–201
[32] Liu L, Zhai J, Wang D, Zhang Y, Wang P, Zhao Q and Xie T 2010 Size- and photoelectric characteristics-dependent formaldehyde sensitivity of ZnO irradiated with UV light Sens. Actuators B 148 66–73
[33] Gorbachev R V et al 2011 Hunting for monolayer boron nitride: optical and Raman signatures Small 7 465–8
[34] Nemanich R J, Solin S A and Martin R M 1981 Light scattering study of borazine microcrystals Phys. Rev. B 23 6348–56
[35] Matsoso B J, Ranganathan K, Mutuma B K, Lerotholi T, Jones G and Coville N J 2017 Synthesis and characterization of boron carbon oxynitride films with tunable composition using methane, boric acid and ammonia New J. Chem. 41 9497–504
[36] Mahvash F, Paradis E, Drouin D, Szkopek T and Siaj M 2015 Space-charge limited transport in large-area monolayer hexagonal boron nitride Nano Lett. 15 2263–8
[37] Lin L, Liu T, Zhang Y, Sun R, Zeng W and Wang Z 2016 Synthesis of boron nitride nanosheets with a few atomic layers and their gas-sensing performance Ceram. Int. 42 971–5
[38] Lee E, VahidMohammadi A, Prorok B C, Yoon Y S, Beidaghi M and Kim D-J 2017 Room temperature gas sensing of two-dimensional titanium carbide (MXene) ACS Appl. Mater. Interfaces 9 37184–90
[39] Kim Y H et al 2017 Chemically fluorinated graphene oxide for room temperature ammonia detection at ppb levels J. Mater. Chem. A 5 19116–25
[40] Mortazavi Zanjani S M, Sadeghi M M, Holt M, Chowdhury S F, Tao L and Akinwande D 2016 Enhanced sensitivity of graphene ammonia gas sensors using molecular doping Appl. Phys. Lett. 108 33106
[41] Mackin C, Schroeder V, Zurutuza A, Su C, Kong J, Swager T M and Palacios T 2018 Chemiresistive graphene sensors for ammonia detection ACS Appl. Mater. Interfaces 10 16169–76
[42] Late D J et al 2013 Sensing behavior of atomically thin-layered MoS2 transistors ACS Nano 7 4879–91
[43] Zhang K, Feng Y, Wang F, Yang Z and Wang J 2017 Two dimensional hexagonal boron nitride (2D-hBN): synthesis, properties and applications J. Mater. Chem. C 5 11992–2022
[44] Huixia L, Yong L, Yanni T, Lianlan L, Qing Z, Kun L and Hanchun T 2015 Room temperature gas sensing properties of tubular hydroxyapatite New J. Chem. 39 3465–74
[45] Sharma N, Sharma N, Srinivasan P, Kumar S, Balaguru Rayappan J B and Kailasam K 2018 Heptazine based organic framework as a chemiresistive sensor for ammonia detection at room temperature J. Mater. Chem. A 6 18389–93
[46] Lee K, Gatensby R, McEvoy N, Hallam T and Duesberg G S 2013 High-performance sensors based on molybdenum disulfide thin films. Adv. Mater. 25 6699–702
[47] Kim S J et al 2018 Metallic Ti3C2T1 MXene gas sensors with ultrahigh signal-to-noise ratio ACS Nano 12 986–93
[48] Singh S, Deb J, Sarkar U and Sharma S 2021 MoS2/WO3 nanosheets for detection of ammonia ACS Appl. Nano Mater. 4 2594–605
[49] Jeevitha G, Abhinayaa R, Mangalaraj D, Ponpandian N, Meena P, Mounasamy V and Madanagurusamy S 2019 Porous reduced graphene oxide (rGO)/WO3 nanocomposites for the enhanced detection of NH3 at room temperature Nanoscale Adv. 1 1799–811
[50] Wang Y, Zhang L, Hu N, Wang Y, Zhang Y, Zhou Z, Liu Y, Shen S and Peng C 2014 Ammonia gas sensors based on chemically reduced graphene oxide sheets self-assembled on Au electrodes Nanoscale Res. Lett. 9 1–12