Enhanced Hydrolytic Stability of Porous Boron Nitride via the Control of Crystallinity, Porosity and Chemical Composition

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Abstract

Porous boron nitride is gaining significant attention for applications in molecular separations, photocatalysis, and drug delivery. All these areas call for a high degree of stability (or a controlled stability) over a range of chemical environments, and particularly under humid conditions. The hydrolytic stability of the various forms of boron nitride, including porous boron nitride, has been sparingly addressed in the literature. Here, we map the physical-chemical properties of the material to its hydrolytic stability for a range of conditions. Using analytical, imaging and spectroscopic techniques, we identify the links between the hydrolytic instability of porous boron nitride and its limited crystallinity, high porosity as well as the presence of oxygen atoms. To address this instability issue, we demonstrate that subjecting the material to a thermal treatment leads to the formation of crystalline domains of $h$-BN exhibiting a hydrophobic character. The heat-treated sample exhibits enhanced hydrolytic stability, while maintaining a high porosity. This work provides an effective and simple approach to producing stable porous boron nitride structures, and will progress the implementation of the material in applications involving interfacial phenomena.
1. Introduction

Over the past 5 years, studies reporting the use of boron nitride (BN)-based materials for molecular separation, energy storage, drug delivery and catalysis have surged, many highlighting the superior capability of the materials compared to benchmarks in the respective field.\(^1\)\textendash}\(^6\) This line of research stems in part from a demand for novel, robust nanomaterials, whose unique physical-chemical properties can be tailored towards a range of applications. Within the family of BN-based materials, we focus here on the particular case of porous BN, a disordered 3-D nanomaterial similar to some extent to activated carbon, but consisting of boron and nitrogen atoms instead of carbon atoms. Most atoms are \(\text{sp}^2\)-hybrids arranged into a hexagonal lattice in the 2-D planes (nanosheets), and the different layers are tilted among each other in random directions resulting in a lack of long-range order and large amount of defects leading to a turbostratic or completely amorphous material. Despite the structural similarity to carbonaceous materials, porous BN exhibits a range of unique physical-chemical properties, such as a bond polarity, resistance towards oxidation and mechanical stability.\(^1\)\textendash}\(^2\), \(^6\)\textendash}\(^13\) As a case is being made to use porous BN for a number of applications involving interfacial phenomena (\textit{i.e.} sorption and catalysis), we focus here on its stability in, and reactivity with, water/moisture. We note indeed that moisture/water is present in many of the applications highlighted above. Interestingly, the literature has not addressed this aspect.

There is a common belief that porous BN shares the hydrophobic property and chemical robustness of its ‘cousin’, \(h\)-BN. In fact, several authors have reported porous BN to exhibit high stability in the presence of water/moisture.\(^14\)\textendash}\(^16\) Contrastingly however, signs of hydrolysis have been reported for non-porous turbostratic BN.\(^17\)\textendash}\(^20\) Cofer and Economy speculated that more porous or turbostratic BN samples, which exhibit larger interlayer spacing, could be more susceptible to hydrolytic attack.\(^21\) Interestingly, hydrolytic reaction was also reported for fully crystalline \(h\)-BN, as a mechanism for “cutting” the sheets by producing hydroxyl-functionalized BN sheets.\(^22\) The possibility of completely decomposing the material was however not mentioned. In fact, the process was not
referred to as a decomposition process but rather as a functionalization one. Florent and Bandosz recently conducted a stability study investigating the aqueous stability of boron carbon nitrides. The material was highly sensitive to mere traces of water or humidity, and adsorption of water resulted in a clear loss of surface area and porosity. The B-C bonds within the nanosheets were identified as the primary site for hydrolytic attack.

Today a number of studies are reported on the use of porous boron nitride for water purification purposes. Yet, only the water stability of crystalline BN (h-BN) and non-porous turbostratic BN has been investigated. This study is meant to shed light on the water stability of porous BN and provide a mitigation strategy should water stability be an issue. The materials in this study were synthesized using a bottom-up synthesis approach and subsequently exposed to a range of aqueous environments. The resulting physical-chemical properties of the materials were mapped against the reaction conditions. The discussion focuses on the effect of water/moisture exposure on the chemistry, crystalline structure and structural parameters (i.e. specific surface area and porosity) of the materials. These findings have key implications in enhancing the performance and longevity of porous BN in a wide range of applications.

2. Experimental section

2.1 Materials synthesis

In this study, we employed two separate synthesis routes to produce two distinct porous BN samples, with one sample having a significantly higher surface area and total pore volume than the other. The two samples are simply named: ‘high surface area BN’ and ‘low surface area BN’. This approach was adopted to investigate whether the initial surface area, porosity and chemistry of the sample have an impact on the resulting stability of the material upon hydrolysis. Details of the synthesis steps are provided below.
Precursors preparation for high surface area BN sample

The synthesis of this material is based on the previous work of Marchesini et al. In a typical synthesis, boric acid (H\textsubscript{3}BO\textsubscript{3}, ACS reagent, 99.0 %, Sigma-Aldrich), urea (CH\textsubscript{4}N\textsubscript{2}O, molecular biology grade, Sigma-Aldrich), and melamine (C\textsubscript{3}H\textsubscript{6}N\textsubscript{6}, ACS reagent, 99.0 %, Sigma-Aldrich), with a 1:1 molar ratio of boric acid to melamine and 1:5 molar ratio of boric acid to urea were mechanically mixed together and finely ground for 5 minutes in an agate mortar to form a homogeneous powder.

Precursors preparation for low surface area BN sample

In a typical synthesis, boron oxide (B\textsubscript{2}O\textsubscript{3}, 98.0 %, -40 mesh, Acros Organics) and urea (CH\textsubscript{4}N\textsubscript{2}O, molecular biology grade, Sigma-Aldrich) with a 1:2 molar ratio were mechanically mixed together and finely ground for 5 minutes in an agate mortar to form a homogeneous powder.

Porous BN synthesis

The finely ground powders were subsequently transferred to an alumina boat crucible, which was placed in a horizontal tubular furnace. The samples were initially degassed at ambient temperature for 2 hours under an inert nitrogen atmosphere (flow rate of 250 cm\textsuperscript{3} min\textsuperscript{-1}). Once the degas was complete, the nitrogen flow rate was decreased to 50 cm\textsuperscript{3} min\textsuperscript{-1}, and the sample was heated from ambient temperature to 1050 °C with a ramp rate of 10 °C min\textsuperscript{-1}. This steady-state temperature was maintained for 3.5 hours, after which the samples were allowed to naturally cool to room temperature, whilst maintaining the same nitrogen flow rate. The same procedure was used to synthesize BN at higher temperatures with the key difference being the synthesis temperature of 1500 °C (using melamine, urea and boric acid like the high surface area sample) instead of 1050 °C. Upon completion of the synthesis, a porous white powder was obtained.

2.2 Water exposure routes

The BN samples were each subjected to different reactions involving water exposure. The duration of exposure to the aqueous solutions was chosen as the independent variable in the procedure to evaluate the time taken for the samples to lose stability, with a constant temperature maintained...
throughout all the runs. In addition, further water stability was measured with humidity tests, in which the samples were separately subjected to a humid environment in a closed system for two contrasting time durations. More details on the exposure to the aqueous solutions are provided below:

**Acid wash**

In the acid wash procedure, the samples (~200 mg) were stirred in solutions of 0.1 m HCl (aq) (100 mL) at 30 °C, using a reflux condenser set-up, for 1 hour and 24 hours individually. The treated samples were then washed and centrifuged twice at 10000 rpm for 10 minutes at 7 °C with deionized water to achieve a neutral pH. Upon removing the supernatant, the samples were dried overnight at 120 °C under vacuum.

**Water wash**

In a similar fashion, the second washing procedure, conducted independently from the acid treatment, entailed washing the samples (~200 mg) by stirring them in deionized water (100 mL) at 30 °C, using a reflux condenser set-up, for 1 hour and 24 hours individually. The resulting dispersion was centrifuged twice at 10000 rpm for 10 minutes at 7 °C. Upon removing the supernatant, the samples were dried overnight at 120 °C under vacuum.

**Humidity test**

The BN samples were exposed to a closed, humid environment for 8 h and 1 week individually (humidity level: > 90 %). The tests were conducted to verify whether exposure to water vapour alone was sufficient to cause decomposition of porous BN. The durations of the test were chosen to examine the extent of decomposition, in terms of surface area and porosity, during short and prolonged exposure to moisture. The sample (~100 mg) was held in a closed wire mesh, which itself was suspended above a beaker. The beaker contained of deionized water (400 mL) maintained at 30 °C. A lid was placed over the beaker and sample, and sealed to generate a closed humid system. At the end of the test, the samples were removed and dried overnight in a vacuum oven at 120 °C prior to further characterization and analysis.
2.3 Materials characterization

2.3.1 Chemical properties

The samples were initially characterized using spectroscopic techniques, namely Fourier Transform Infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). For FT-IR analysis, the samples were first ground to a powder using an agate mortar. Subsequently, the spectra were obtained in the wavenumber range of 500-4000 cm\(^{-1}\) using a Perkin-Elmer Spectrum 100 FT-IR spectrometer equipped with an attenuated total reflectance (ATR) accessory.

X-ray photoelectron spectroscopy (XPS) to determine the relative elemental composition of the samples, as well as the chemical states of the elements, was conducted using a Thermo Scientific K-Alpha\(^+\) X-ray Photoelectron Spectrometer equipped with a MXR3 Al K\(\alpha\) monochromated X-ray source (\(h\nu = 1486.6\) eV). The samples were initially ground and mounted onto an XPS sample holder using a small rectangular piece of conductive carbon tape. The X-ray gun power was set to 72 W (6 mA and 12 kV). Survey scans were acquired using 200 eV pass energy, 0.5 eV step size and 100 ms (50 ms x 2 scans) dwell times. All of the high resolution spectra (B 1s, N 1s, C 1s, and O 1s) were obtained using a 20 eV pass energy and 0.1 eV step size. The results were analyzed using the Thermo Avantage data analysis program.

The thermal stability of the samples was evaluated using a Netzch-Libra thermogravimetric analyzer. In a typical analysis, the samples were loaded into an alumina crucible, and subsequently heated under nitrogen atmosphere (flow rate of 100 mL min\(^{-1}\)) from 25 °C to 1000 °C with a ramp rate of 10 °C min\(^{-1}\).

2.3.2 Structural properties and morphology

Powder X-ray diffraction (XRD) was performed using a PANalytical X’Pert Pro X-ray diffractometer in reflection-transmission mode with a spinning stage (2 revolutions/second). An anode voltage of 40 kV and emission current of 20 mA were chosen as the operating conditions.
using a monochromatic Cu-Kα radiation source ($\lambda = 1.54178$ Å). The X’Celerator silicon strip detector was used in the diffractometer.

Nitrogen sorption isotherms and water vapour isotherms were measured using a porosity and surface area analyzer (Micrometrics 3 Flex) at -196 °C. The samples were initially degassed overnight at 120 °C at approximately 0.2 mbar pressure. Subsequently, prior to the sorption isotherm measurement, the samples were degassed in-situ for 4 hours at 120 °C. The equivalent specific surface areas of the samples were determined using the Brunauer-Emmett-Teller (BET) method. The total pore volume was ascertained from the volume of N₂ adsorbed at a relative pressure ($P/P_0$) of 0.97. The micropore volume was determined using the Dubnina-Radushkevich model. When used for water vapour sorption, the instrument was equipped with a liquid container, which has been subjected to purification prior to the analysis. Transmission Electron Microscopy (TEM) images were collected on a JEOL 2100Plus with 200 kV acceleration voltage. The samples were previously dispersed in ethanol and deposited on a carbon holey grid. The d(002)-spacing was estimated from TEM images by using the software ImageJ to produce a grey-scale profile. SEM-EDX analysis was performed on an Auriga Zeiss microscope at 5 keV for both imaging and EDX analysis. The powder samples were compressed on a carbon tape and coated with 10 nm of gold.

3. Results and discussion

To understand the effect of structural features on porous BN interactions with water, porous BN with distinct porosities were prepared and are referred to as ‘high surface area BN’ and ‘low surface area BN’. The two samples were initially characterized in terms of their structure, morphology and surface composition prior to water exposure (Figure 1). To understand the effect of the initial structure of the material on its resulting water/moisture stability, the textural properties of the two samples were analyzed using N₂ sorption analyses at -196 °C (Figure 1a, Table S1). The stark difference in surface areas between the two pristine BN samples (1666 m² g⁻¹ vs 43 m² g⁻¹) is highlighted in the inset of Figure 1a. The high surface area sample exhibited a type I/IV isotherm,
with a H3/H4 hysteresis loop, indicating the presence of both micropores and mesopores, while the low surface area sample showed a typical isotherm for a non-porous material.\textsuperscript{35} The difference in surface areas of the two starting materials comes from the synthesis methods, which involves a large excess of nitrogen-containing precursor for the high surface area BN compared to the low surface area BN sample. The excess of nitrogen precursor results in the release of larger quantities of ammonia and other gases during the reaction, which assured both the complete transformation of boron oxide into boron nitride, as well as the formation of a larger amount of pores. In the case of the low surface area BN on the other hand, the low porosity is attributed to the presence of unreacted boron oxide, blocking the pores and accounting for “dead weight”. Elemental mapping was conducted using SEM EDX analysis: the materials display a homogeneous distribution of boron, carbon, nitrogen, and oxygen (Figure S1).

Both samples contain more boron than nitrogen, as seen from XPS analysis (Figure 1b). The samples also exhibit O atoms, which, based on a prior study, is at least partially assigned to boron oxynitride, \textit{i.e.} O incorporated in the BN structure.\textsuperscript{6, 8, 36} Noticeably though, low surface area BN contains more oxygen than high surface area BN (Figure 1b). We hypothesized that part of the oxygen atoms (\textit{i.e.} non boron oxynitride) come from the residual unreacted boron oxide resulting from the particular synthesis. In comparison, the high surface area BN sample was synthesized with a large excess of nitrogen precursor, whose decomposition resulted in a large release of ammonia, which reacted with boric acid to form BN, and hence a lower residual quantity of boron oxide is present in the final material. Further support for this hypothesis is provided later. SEM images of the high and low surface area BN samples were taken to gain insight into the differences in morphology (Figures 1c and 1d, respectively). The particle morphologies of the two samples vary with the high surface area sample exhibiting a densely packed structure whereas the low surface area sample displays a flake-like morphology. We have previously reported differences in the morphology of porous BN based on the number and type of precursors used.\textsuperscript{8} We additionally investigated the thermal stability of our porous BN sample under N\textsubscript{2} and air. The results are
provided in Figure S2, indicating good stability under inert atmosphere and resistance to oxygen up to ~800 °C.

**Figure 1.** Structure, morphology and surface composition of the high and low surface area BN samples before water exposure. (a) N$_2$ sorption isotherms obtained at -196 °C for the high and low surface area BN samples. The inset in (a) shows the BET equivalent surface areas, total volume of pores, and micropore volume for the high and low surface area BN samples before water exposure. (b) XPS relative atomic percentages of the high and low surface area BN samples before water exposure. (c, d) SEM images of the high surface area BN sample (left) and low surface area BN sample (right).

Having confirmed the chemical and structural profiles of the two initial samples, we now provide an in-depth investigation of any changes observed upon exposure to water/moisture. The typical XRD patterns for the high and low surface area BN samples before and after hydrolysis are shown in Figures 2a and 2b, respectively. The XRD patterns for the high and low surface area BN samples after various degrees of exposure to aqueous solutions are presented in Figure S3. The diffraction patterns show that turbostratic/amorphous BN was obtained through both synthesis routes as confirmed by the two broad characteristic peaks at 2θ values of 26° and 44° corresponding to the
(002) and (100) planes, respectively. The low surface area BN sample exhibits an additional shoulder peak at a $2\theta$ values of $\sim 27^\circ$, which is attributed to the presence of residual boron oxide, and supports the aforementioned hypothesis. The two characteristic BN peaks are also maintained after exposure to water, with the key differences being a shift in the (002) peak position to slightly higher angles, as well as a decrease in the full width half maximum of the same peak. This is attributed to the decomposition of the most amorphous component of porous BN, leaving a residual BN product with higher crystallinity (most resembling $h$-BN).

Figures 2c and 2d illustrate the influence of varying exposure times in aqueous solutions on the textural parameters of the samples, namely the BET equivalent surface areas, total volume of pores, and micropore volume. The high surface area BN sample shows a drastic loss of porosity and surface area after water exposure (with or without acid present). The results in Figure 2c indicate that short-term exposure to aqueous solutions, even for 1 hour, drives the decomposition of porous BN and results in a virtually complete loss in surface area and porosity. In addition, the humidity tests reveal that exposing porous BN to water vapour, is sufficient to achieve the same degree of decomposition and surface area/porosity loss (Table S1).

However, it is interesting to note that the low surface area BN sample exhibits the opposite behaviour. This difference is attributed to the unreacted boron oxide in this sample, which initially blocked the pores and then dissolved as water was added to the material, thereby leading to an increased porosity. Interestingly, for that sample, prolonged exposure to water is required to achieve a similar increase in surface area and porosity as measured with exposure to acid. Figure 2d indicates that a prolonged water wash for 1-week results in a fivefold increase in porosity which, although significantly higher than the unwashed sample, is still lower than those after the 24-hour acid wash. Hence, the acid seems to catalyse the dissolution of boron oxide reaction. To clarify whether the resulting BN after the 24-hour acid hydrolysis exhibited increased hydrolytic stability, the resulting material was subjected to a subsequent 24-hour water wash. However, the sample had lost a considerable proportion of the surface area and porosity that had been increased after the first
acid wash step (Table S1). Therefore, it could be concluded that despite the increase in surface area and porosity, as well as relative crystallinity after acid hydrolysis, the resulting product remains unstable in the presence of water. Another explanation is the product that was formed, being closer in nature to \( h \)-BN (\textit{i.e.} stacked layers), was intrinsically poorly porous.

**Figure 2.** Comparison of the structure and morphology of the high and low surface area BN samples before and after a 24-hour water exposure. (a, b) XRD spectra of the high (a) and low (b) surface area BN samples before and after water exposure. (c, d) Bar plots showing the BET equivalent surface areas, total volume of pores, and micropore volume for the high (c) and low (d) surface area BN samples after varying exposure times in aqueous and acidic environments.

Following from the analysis of the structure of the materials, the influence of water exposure on their chemistry was also investigated. FT-IR spectra for the pristine and treated samples are shown in Figure 3 and S4. Prior to water exposure, both samples exhibited the two characteristic bands for
boron nitride at ~1360 cm\(^{-1}\) (B-N in-plane transverse stretching mode) and at ~800 cm\(^{-1}\) (B-N-B out-of-plane bending mode).\(^{39}\) Further, a small band at ~1000 cm\(^{-1}\), assigned to the B-O bending mode, was observed and is assigned to boron oxynitride.\(^{36}\) In addition, the band at 1360 cm\(^{-1}\) of low surface area BN exhibited a broad shoulder, indicating the presence of boron oxide in the starting material, as initially hypothesized. Like for the structural features, the two BN materials behave in very different ways in terms of their chemistry after water exposure. For the high surface area, the B-O bending mode at ~1000 cm\(^{-1}\) broadened after water exposure, indicating decomposition and formation of boron oxide. In addition, the broad band at ~3400 cm\(^{-1}\) after water exposure suggests the presence of edge conjugated hydroxyl groups, arising from nanosheet edge functionalization (Figure 3a).\(^{40-41}\) In comparison, the low surface area BN sample after water exposure still displayed the two typical BN bands at ~1360 cm\(^{-1}\) and ~800 cm\(^{-1}\). Neither the broad hydroxide peak nor the enlarged B-O band is seen in the spectrum after water exposure indicating that no decomposition happened at this point. This is in line with the textural parameters previously observed.
Figure 3. Chemistry and surface composition of the high and low surface area BN samples before and after water exposure. (a, b) FT-IR spectra of the high (a) and low (b) surface area BN samples before and after water exposure with the key characteristic bands indicated. (c, d) High resolution B1s XPS core level spectra for the high (c) and low (d) surface area BN samples before and after water exposure. (e, f) XPS relative atomic percentages of the high (e) and low (f) surface area BN samples before and after water exposure.
High resolution B 1s core level XPS spectra for the high and low surface area samples before and after water exposure are presented in Figures 3c and 3d, respectively. Unlike the pristine sample, the high surface area sample exhibited a prominent shoulder peak in the B 1s spectrum at 192.8 eV after exposure to water related to boron oxide (Figure 3c). This result is concordant with the observations made in Figures 2 and 3, and further confirms the decomposition of the amorphous part of the high surface area BN. This result is in agreement with the reaction previously described in literature for non-porous BN, where boron nitride reacts with water to form boron oxide and ammonia.21, 42 Further evidence of the decomposition is shown in Figure 3e, not only by the increase in the oxygen content, but also by the relative percentage of nitrogen decreasing, which is line with the formation of ammonia. In contrast, the low surface area sample initially displayed a shoulder peak, which is slightly shifted to higher binding energies. This shoulder can be deconvoluted into two peaks consisting of a surface oxynitride and residual unreacted boron oxide as a separate phase remaining in the sample. This shoulder peak disappeared after water exposure, which, coupled with the decrease in relative oxygen content (Figure 3f), supports the claim that the residual boron oxide dissolves into solution and subsequently increases the surface area by unblocking the pores.

From the analyses above, it is apparent that the disordered nature of porous BN, i.e. its turbostratic to amorphous arrangement which comes with the presence of O-containing functionalities, is responsible for the low water stability of the material. From this, it becomes clear that a way to address this weakness, while still having porous BN, would be to have large BN nanosheets, with a low number of defect sites, randomly arranged i.e. forming a house of card (to provide porosity). Such a structure has never been reported. Taking into account this vision, we attempted to improve the water stability of BN by decreasing the amount of defect sites and oxygen content of the material using a higher synthesis temperature.

Specifically, a high temperature BN sample was synthesized at 1500 °C (denoted as high temperature BN) instead of 1050 °C (denoted as low temperature BN). Both samples were prepared
using the mixture of melamine, urea and boric acid. In order to understand the increased water stability and hydrophobicity of the high temperature BN sample, the material was analyzed using a range of techniques and the features were compared to those of low temperature BN. To gain insight into the crystallinity of the materials, we collected TEM images of the two materials (Figures 4a and 4b). By comparing the TEM images, it can be seen that the degree of stacking increased when porous BN was synthesized at 1500 °C, with a larger number of stacked layers and wider crystalline areas in high temperature BN compared to low temperature BN. However, there was only little change in the XRD patterns for the high and low temperature BN samples (Figure S5). This is line with the fact that the material maintained overall an amorphous nature, and therefore likely porous nature, upon heating. We further took SEM images of the two samples (Figures 4c and 4d) and did not observe significant change at that scale.

**Figure 4.** Morphology and structure of the low and high temperature BN samples before water exposure. (a, b) TEM images of the low (left) and high (right) temperature BN samples before water exposure. (c, d) SEM images of the low (left) and high (right) temperature BN samples before water exposure.
exposure and (c, d) SEM images of the low (left) and high (right) temperature BN samples before water exposure.

The chemistries of the high and low temperature BN materials were also compared using FT-IR and XPS (Figure 5). The FTIR spectrum for porous BN synthesized at high temperature shows much sharper and more symmetrical vibrations corresponding to $h$-BN. This is in contrast with the broad asymmetrical peaks, which are usually recorded at low temperature (see Figure 3). This may be linked to a smaller amount of oxygen impurities in samples synthesized at higher temperature. Indeed, XPS further confirms that the relative oxygen content in high temperature BN is lower than that in low temperature BN. This suggests that the high temperature synthesis lowered the amount of defect sites, which implies that there are fewer points of hydrolytic attack when synthesizing BN at higher temperature.

**Figure 5:** (a) FT-IR spectra of the high- and low temperature BN samples, together with a reference spectrum measured for boron oxide. (b) XPS relative atomic percentages of the high and low temperature BN samples before water exposure.

Based on the findings from the high temperature synthesis, the interactions of BN with water were studied. Water vapour isotherms at 30 °C were collected for porous BN samples synthesized at low
and high temperatures (Figures 6a and 6b). The former sample displayed a hydrophilic character at low relative pressures, adsorbing a large amount of water, as illustrated by the steep isotherm gradient up to \( \sim 0.3 \ P/P_0 \). In comparison, the latter sample behaved as a hydrophobic material, as seen as by the shallower isotherm gradient, showing little/no water uptake up to \( \sim 0.3 \ P/P_0 \), indicating that the high thermal treatment was successful in creating hydrophobic regions in the materials as suggested by the TEM images. At higher relative pressures though, water adsorption occurred, with a total water uptake per surface area similar to the porous BN synthesized at low temperature. In both samples, desorption did not result in the full removal of water vapour, indicating that either chemisorption occurred, or that BN structure was modified from the exposure to water vapour. The latter is most likely given the reactivity of the material as evidenced in the first part of this study.

\( \text{N}_2 \) sorption isotherms for the samples synthesized at different temperatures are shown in Figures 6c and 6d, respectively. The material remained porous, though a decrease in surface area was noted upon thermal treatment (from \( \sim 1600 \) to \( \sim 1000 \ \text{m}^2 \ \text{g}^{-1} \)). This suggests that full crystallisation to a \( h \)-BN form did not occur. Upon exposure to water, the high temperature BN sample exhibited a much higher degree of water stability, characterized by a smaller decrease in surface area. Whilst the low temperature BN sample loses virtually all of the original high surface area and porosity, the high temperature BN still exhibits a surface area of \( \sim 300 \ \text{m}^2 \ \text{g}^{-1} \) after 24 hour water exposure (Figures 6c and 6d). Our findings suggest that the thermal treatment leads to the formation of more crystalline regions. These regions being more hydrophobic in nature limit the points of hydrolytic attack and enhance the water stability.
Figure 6. Comparison of the water stability of the low and high temperature BN samples. (a, b) \( \text{N}_2 \) sorption isotherms obtained at -196 °C for the high and low temperature BN samples before and after water exposure for 24 hours. (c, d) Water vapour isotherms at 30 °C for the low and high temperature BN samples.

4. Conclusions

A detailed investigation was conducted to identify clear links between the structural and chemical features of porous BN and its stability upon exposure to water. This was done in an attempt to control/enhance this stability, given the many applications foreseen for this material that involve moisture/water. We showed that like non-porous turbostratic boron nitride, porous boron nitride is unstable in water. We hypothesized the combination of a large surface area/porosity, low crystallinity, presence of oxygen atoms and defect sites renders the material susceptible to
hydrolytic attack. Through a systematic study involving a range of spectroscopic, imaging and analytical techniques, we showed that porous BN samples that possess an amorphous, turbostratic character, and exhibit larger specific surface areas and porosities, undergo virtually complete decomposition when exposed to water/moisture.

A facile strategy to enhance the hydrolytic stability of porous BN in aqueous environments, and hence overcome this issue, is presented in this study. The underlying advantage of this method is that it only entails varying the reaction temperature as the control parameter in a single-step, template-free pyrolytic synthesis. In doing so, our approach allows for the production of a BN material with an improved hydrophobicity through lower oxygen content and defect sites as well as the creation of crystalline $h$-BN domains.

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX.

Textural parameters for the various samples derived from $N_2$ sorption isotherms at 77 K, SEM images and EDX spectra, XRD patterns for all samples (including high temperature BN), FTIR spectra for all samples, SEM images for the various porous boron nitride samples and TGA graphs for porous boron nitride.

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Declaration

The authors declare that there is no competing financial interest.

References


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Faster defect sites and oxygen atoms