Modification of TiO₂ with hBN: high temperature anatase phase stabilisation and photocatalytic degradation of 1,4-dioxane

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Abstract
This paper examines the modification of anatase TiO₂ with hexagonal boron nitride (hBN) and the impact this coupling has on the temperature of the anatase to rutile phase transition and photocatalytic activity. All samples were 100% anatase when calcined up to 500 °C. At 600 °C, all BN-modified samples contain mixed rutile and anatase phases, with 8% and 16% BN–TiO₂ showing the highest anatase contents of 64.4% and 65.5% respectively. The control sample converted fully to rutile at 600 °C while the BN modified sample converted to rutile only at 650 °C. In addition to TiO₂ phase composition, XRD also showed the presence of bulk boron nitride peaks, with the peak at 26° indicating the graphite-like hBN structure. Density functional theory calculations of hBN-rings adsorbed at the anatase (101) surface show strong binding at the interface; new interfacial bonds are formed with key interfacial features being formation of B–O–Ti and N–Ti bonds. Models of extended hBN sheets at the anatase (101) surface show that formation of B–O and N–Ti bonds along the edge of the hBN sheet anchor it to the anatase surface. 16% BN–TiO₂ at 500 °C showed a significant increase in the photocatalytic degradation of 1,4-dioxane when compared with pure anatase TiO₂ at 500 °C. This arises from the effect of hBN on anatase. The computed density of states (DOS) plots show that interfacing anatase with BN results in a red shift in the TiO₂ energy gap; N–p states extend the valence band maximum (VBM) to higher energies. This facilitates transitions from high lying N–p states to the Ti–d conduction band. A simple photoexcited state model shows separation of electrons and holes onto TiO₂ and BN, respectively, which promotes the photocatalytic activity.

1. Introduction

For the past five decades, titanium dioxide (TiO₂) based materials have been widely studied as photocatalysts. This is mainly due to its low cost, photoactivity, non-toxicity, chemical stability and ease of preparation[1–7] but there is still the need of increasing its photocatalytic activity[8–13]. The anatase polymorph (tetragonal, a = b = 3.785 Å, c = 9.54 Å) is widely reported as the most photoactive phase of titania[14, 15]. However, anatase TiO₂ has a wide energy band gap (3.2 eV) which results in a high electron-hole recombination rate and absorbance in only the UV light region[5, 16, 17]. Additionally, anatase is metastable and irreversibly transforms

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into the thermodynamically stable rutile phase \((a = b = 4.593 \, \text{Å}, c = 2.959 \, \text{Å})\) from 600 °C–700 °C\cite{18, 19}. Therefore it is required to produce a high temperature (≥800 °C), UV and visible light (250–700 nm) active stable anatase phase which can significantly enhance the photocatalytic activity and provide a benefit for industrial applications and building materials\cite{20}.

The use of chemical modifiers/dopants is one method of addressing the low transition temperature and issues regarding photocatalysis in TiO\(_2\). One type of doping involves the use of metal dopants such as iron\cite{21–24}, silver\cite{15, 25}, chromium\cite{26}, copper\cite{22, 27, 28}, and manganese\cite{29–31} or metal oxides such as Al\(_2\)O\(_3\), SiO\(_2\), and ZnO\cite{11, 14, 32–34}. However, as noted by Byrne et al the use of metal dopants can result in the formation of impurities at elevated temperatures which can have a negative impact on the transition temperature and photocatalytic activity\cite{14, 20, 35}. Consequently, the use of non-metal (anion) doping, which is the second type of chemical modifiers/dopants, has been studied\cite{36, 37}, as for example carbon\cite{35, 38–41}, nitrogen\cite{42–45}, sulphur\cite{11, 22}, and fluorne\cite{46, 47}, or co-doping of these\cite{37, 48–54}.

Boron nitride (BN) modification of titania has also been investigated in recent years in a means to modify the properties of TiO\(_2\)\cite{55–60}. For example Fu et al used the ball milling method to prepare hexagonal-BN\cite(hBN)/TiO\(_2\) composites and examined the photodegradation of rhodamine B and methylene blue with a 375 W medium pressure mercury lamp (which had a maximum emission at about 365 nm)\cite{58}. The study examined the effect of various wt% BN and ball milling times. They found that the optimum sample was 0.5 wt% hBN which had been milled for 30 min. This photocatalyst showed a 15 times higher rate of removal for rhodamine B and an increase of a factor of 8 in the removal of methylene blue\cite{58}.

Lui et al examined porous BN/TiO\(_2\) hybrid nanosheets for photocatalytic degradation of Rhodamine B and phenol under simulated solar and visible light\cite{56}. The study found that 38 wt% porous BN/TiO\(_2\) hybrid nanosheets exhibited visible light photodegradation of both phenol and rhodamine B\cite{56}. In the same year, Singh et al used an ice bath method to synthesise BN–TiO\(_2\) photocatalyst with a large pore size\cite{61}. The study found the BN–TiO\(_2\) composite showed a 79% removal of methylene blue after 200 min under visible light, while bare titania removed only 32% of the methylene blue. They stated that BN-modified titania could be used for practical environmental purification\cite{61}. Both Fu et al and Lui et al used commerical mixed phased titania during their studies (90% anatase and 80% anatase respectively) while Singh et al synthesized samples containing 100% anatase.

However, to date there have been no comprehensive systematic studies on the effect of the concentrations of BN and calcination temperatures on the anatase to rutile phase transition and the resulting photocatalytic activity of BN-modified TiO\(_2\). For the latter, we chose removal of 1,4-dioxane as a model system.

This synthetic cyclic ether was chosen because it is commonly present in industrial effluents since it is widely used as solvent and it can be produced as by-product in different chemical processes\cite{62, 63}. The impact on human health of 1,4-dioxane is of growing interest as it has been classified in Group 2B (as a probable human carcinogen) by the US Environmental Protection Agency (EPA)\cite{62, 64–68}. Conventional solvent removal method and biodegradation treatments are not enough to remove 1,4-dioxane from waste water due to its properties such as high volatility in its pure form but high water solubility\cite{64, 65, 69–71}. In order to compensate for this inadequacy of removal, a combination of different processes are used, e.g. biodegradation and photochemical methods\cite{62, 64, 70–74}. The improvement of the photodegradation of 1,4-dioxane will represent an important environmental benefit that will be applicable to many other organic contaminants.

Thus, the primary materials advance in this work is the comprehensive examination of the impact that BN-modification has on the anatase to rutile transition and on the photocatalytic activity of TiO\(_2\) for 1,4-dioxane removal. TiO\(_2\) was interfaced with BN at five different concentrations (0%–16% BN–TiO\(_2\)) and samples were calcined at four temperatures (300 °C–700 °C). These interfacial materials were characterized using x-ray diffraction (XRD), Raman Spectroscopy and x-ray photoelectron spectroscopy (XPS). The ability of the samples to act as a photocatalyst was determined by examining the photodegradation of 1,4-dioxane. Density functional theory (DFT) studies were also undertaken to provide detailed insights into the bonding of BN with anatase and the origin of the enhanced photocatalytic activity.

2. Method

2.1. Density functional theory calculations

DFT calculations were performed using the VASP5.4\cite{75, 76} code with the core-valence interaction described by projector augmented wave\cite{77, 78} (PAW) potentials. Titanium (Ti) is described with 12 valence electrons, oxygen (O) with six, nitrogen (N) with five and boron (B) with three valence electrons. The plane wave energy cut-off for the basis set is 396 eV and the convergence threshold for electronic relaxations is 10\(^{-4}\) eV. The exchange-correlation functional is approximated by the Perdew–Wang (PW91)\cite{79} functional and aspherical gradient corrections are applied throughout.
Comparisons are made between the DFT-D2 [80] and vdW-DF [81, 82] approaches to account for vdW interactions. In general, these approaches yielded qualitatively consistent results. Quantitative differences only arose in computed adsorption energies and interfacial bond lengths while computed density of states and charge localisation were not affected by choice of approach. Throughout the text, the results relevant to the DFT-D2 setup will be presented in detail, with reference made to those computed within vdW-DF where appropriate.

All structures were relaxed until forces were less than 0.02 eV Å⁻¹. Calculations were spin-polarized and no symmetry constraints were imposed. The calculations include an on-site Hubbard correction (DFT + U) [83, 84] to describe the partially filled Ti 3d state; U = 4.5 eV is applied to Ti 3d states, with this choice for U informed by previous studies [85–89]. Additional corrections are applied to O and N 2p states, with U = 5.5 eV, for calculations in the model for photoexcitation.

The bulk lattice parameters of the anatase unit cell were computed as: \( a = 3.791 \) Å and \( c = 9.584 \) Å. The bulk lattice parameters for the hBN unit cell were computed as: \( a = 2.511 \) Å and \( c = 7.744 \) Å; with the inclusion of vdW forces these parameters were revised to: \( a = 2.507 \) Å and \( c = 6.116 \) Å. The unit cells were optimised with a \((8 \times 8 \times 8)\) \( k \)-point sampling grid.

BN-modified anatase TiO₂ is modelled as one, two and three hBN rings in intimate contact with the anatase (101) surface, denoted \( 1-(\text{BN})_3-a101 \), \( 2-(\text{BN})_3-a101 \) and \( 3-(\text{BN})_3-a101 \). The TiO₂ substrate is modelled as a 12-layer slab with a \( \Gamma \)-point. The adsorption energies are calculated using:

\[
E_{\text{ads}} = E(x - (\text{BN})_3-a101) - E(a101) - xE((\text{BN})_3),
\]

where \( E(x - (\text{BN})_3-a101) \) is the total energy of the modified surface, \( x \) is the number of BN rings, \( E(a101) \) is the total energy of the unmodified surface and \( E((\text{BN})_3) \) is the energy of a single BN ring in the gas phase.

Two additional models consist of hBN ribbons, of compositions \((\text{BN})_{24}\) and \((\text{BN})_{42}\), at \((1 \times 6)\) and \((3 \times 2)\) expansions of the anatase (101) surface, respectively. These models are denoted \((\text{BN})_{24-a101}\) and \((\text{BN})_{42-a101}\) and more details about their construction are provided in the supporting information available online at stacks.iop.org/JPMATER/3/015009/mmedia. In each model the hBN layer is continuous at the periodic boundary along [101], but discontinuous along [010] due to a mismatch between the lattice parameters of the hBN layer and the anatase (101) surface. Thus, the hBN layers resemble 1D periodic ribbons. For \((\text{BN})_{24-a101}\), one edge is terminated by B ions and the other by N ions and these edges are separated by 12 Å across the periodic boundary along [010]. For \((\text{BN})_{42-a101}\), the ribbon edges are terminated by alternating B and N ions, with these edges separated by 5.5 Å across the periodic boundary along [010]. For these ribbon models, the adsorption energy is computed as:

\[
E_{\text{ads}} = E((\text{BN})_x-a101) - E(a101) - E((\text{BN})_x),
\]

where \( x \) denotes the number of BN units per ribbon.

The computed Bader charges of Ti ions in the unmodified surfaces are in the range 9.6–9.7 electrons. Bridging oxygen ions (\( \text{O}_{\text{br}} \)) of the surface have Bader charges of 7.1 electrons, while all other O ions have Bader charges of 7.2 electrons. Bader charges for B and N ions in bulk hBN are computed as 0.0 and 8.0 electrons, respectively.

To model photoexcitation, a triplet electronic state was imposed on the system; this forces an electron from the filled valence band (VB) to the empty conduction band (CB), leaving a hole in the VB. More details of this model are presented in the supporting information and in [90–94]. Charge localization is assessed via analysis of computed Bader charges [95], spin magnetizations and excess spin density plots.

2.2. Materials

The chemicals used in this study were titanium tetraisopropoxide (97%), boron nitride and isopropanol (≥99.5%), all of them purchased from Sigma-Aldrich and used without any treatment. 1,4-dioxane (>99%) was purchase from Merck.

2.3. Preparation of nanomaterials

TiO₂ was modified with BN at five different concentrations (0% BN–TiO₂, 2% BN–TiO₂, 4% BN–TiO₂, 8% BN–TiO₂ and 16% BN–TiO₂). For the 2 mol% sample, 55.4 ml of TTIP was added to 200 ml of IPA and was stirred for 15 min (Solution A). 0.0948 g BN was added to 200 ml of deionized water, this was stirred for 15 min (Solution B). Solution B was added to Solution A and this was stirred for 30 min. The resulting sol-gel was dried in the oven at 100 °C for 12 h. The resulting powder was annealed at 500 °C, 600 °C, 650 °C and 700 °C at a ramp rate of 10 °C min⁻¹ and was held for 2 h. This method was repeated for the 0%, 4%, 8% and 16% BN samples by changing the volume of TTIP and grams of BN (0%—56.6 ml and 0 g; 4%—54.2 ml and 0.1897 g; 8%—52.2 ml and 0.3793 g; 16%—47.6 ml and 0.7587 g).
2.4. Characterization of nanomaterials

A Siemens D500 x-ray powder diffractometer was used for the XRD characterization, using Cu Kα radiation ($\lambda = 0.15418$ nm). The diffraction range examined was between $2\theta = 10^\circ$ – $80^\circ$. To determine the fraction of rutile in the samples, the Spurr equation was used (equation (1)) [96]

$$F_R = \frac{1}{1 + 0.8[I_A(101)/I_R(110)]},$$

where $F_R$ is the quantity of rutile in mixed sample, $I_A(101)$ and $I_R(110)$ are the intensities of the main anatase and rutile peaks. XRD data were also used for determining the size of the crystalline structures in each sample; this was determined using the Scherrer equation (equation (2)) [97]

$$\Phi = \frac{K\lambda}{\beta \cos \theta},$$

where $\Phi$ is the crystallite size, $K$ is the shape factor, $\lambda$ is the x-ray wavelength, $\beta$ is the full line width at the half-maximum height of the main intensity peak and $\theta$ is the Bragg angle.

The Horiba Jobin Yvon LabRAM HR 800 with a grating of 300 gr mm$^{-1}$ was used for Raman analysis. A 660 nm solid state diode laser standard bandwidth version with double edge filter upgrade was the laser used. The acquisition time was 3 s. When focusing onto the sample, a X50 lens was used.

A ThermoFisher Scientific Instruments (East Grinstead, UK) K-Alpha$^+$ spectrometer was employed for the XPS analysis of samples. A monochromatic Al Kα x-ray source ($h\nu = 1486.6$ eV) with a spot radius of $\sim400$ μm was used to obtain the XPS spectra. A Pass Energy of 200 eV was used for acquiring survey spectra, while a Pass Energy of 50 eV was employed for producing core level spectra with high resolution for all elements. C1s (285 eV) was used as a reference peak to correct for charging effects during acquisition. After accounting for the removal of a nonlinear (Shirley) background, the core level spectra were used in calculating the quantitative surface chemical composition. In order to correct for electron energy analyser transmission function and integrate the applicable sensitivity factors the manufacturers software (Avantage) was used.

Measurements of 1,4-dioxane were performed by a gas liquid chromatography–flame ionization detector (GLC-FID) (Agilent 7980 A, Palo Alto, CA). Samples of 2 μl were injected with a split ratio of 5:1 at 310 °C and analysed in a Teknokroma capillary column TRB-FFAP 30 m × 0.25 mm ID × 0.25 μm film thickness (Teknokroma, Spain). Carrier gas was He, 43 psi. After 9 min initial hold, the temperature was increased at 15 °C min$^{-1}$ from 80 °C to 240 °C. A FID detector was used, detection temperature was 280 °C. GC-ChemStation software Rev. B.04.02 (96) from Agilent was used for quantification based on corrected peak areas. 60 ppm of 1-butanol was used as internal standard.

2.5. Photocatalysis

Photocatalytic analysis was performed using a total volume of 50 ml of synthetic solution, which was comprised of 1,4-dioxane (100 mg l$^{-1}$) dissolved in deionized water and TiO$_2$ catalyser (1 g l$^{-1}$). The concentration of 1,4-dioxane is similar or even lower than the concentration that may be found in industrial wastewater [64, 65]. A sample was taken every 30 min, with a total reaction time of 240 min. There were three types of control experiments preformed: (1) without presence of UV radiation, (2) without any photocatalyst present, and (3) with photocatalyst not containing BN. All experiments were repeated in triplicate.

A solar simulator equipped with a 300 W Xenon lamp (from Newport, USA) was used as UV light source. An ASTM E490–73a correction filter was used to obtain the solar spectrum. A total photon flux of $6.8 \cdot 10^{19}$ photon s$^{-1}$ was calculated to flow inside the photochemical reactor using the methodology described by Liang et al (2011). Light intensity between 315 to 400 nm resulted of 50 W m$^{-2}$ at 3 cm from the light source on a total surface of 0.0104 cm$^{-2}$. A UV–vis Radiometer RM-21 (Elektronik, Germany) was used to record the light intensity.

3. Results

3.1. DFT results

The relaxed geometries of the anatase TiO$_2$ surface modified with one, two and three hBN rings are shown in figure 1 and the adsorption energies are included in the insets. The large, negative adsorption energies indicate that the interaction between the hBN rings and the surface is favourable and the magnitude of the energies increases approximately linearly with the number of adsorbed rings. For the anatase surface modified with one and two hBN rings, multiple starting geometries were considered. Those presented in figure 1 correspond to the most stable structures of those sampled and the other interfacial structures are described in the supporting information. However, it was found that key properties of the interfacial system are not dependent on the precise orientation of the hBN rings at the anatase (101) surface.
The geometries presented herein were computed with the DFT-D2 approach to account for vdW interactions. The geometries computed within vdW-DF are qualitatively equivalent with the exception that interfacial bonds are slightly elongated (<0.01 Å) in the latter scheme. The adsorption energies are moderated in the vdW-DF calculations; the difference between the computed adsorption energies is at most 0.3 eV per hBN ring.

For 1-(BN)\textsubscript{3}-a101, shown in figure 1(a), five interfacial bonds are established between the hBN ring and the titania surface. There are two Ti–N bonds, each of length 2.00 Å, and the interaction draws the Ti ions out from the surface by 0.1 Å. There are three B–O bonds; of these, two involve bridging O ions (O\textsubscript{br}), with B–O distances of 1.44 Å, and the third involves an in-plane O ion (O\textsubscript{ip}), with a B–O distance of 1.48 Å. B–N distances elongate from 1.36 Å in the gas-phase and are in the range 1.42–1.47 Å. The computed Bader charges for the two N ions which bind to Ti decrease from 8.0 electrons, in the gas-phase, to 7.5 electrons. The computed Bader charge for the third N ion decreases from 8.0 to 7.8 electrons. This charge is distributed over the TiO\textsubscript{2} surface. In particular, the computed Bader charge for the O\textsubscript{ip} bonded to B increases from 7.2 to 7.5 electrons.

In the 2-(BN)\textsubscript{3}-a101 system, shown in figure 1(b), a second hBN ring is adsorbed at the surface, neighbouring the first. The geometry of the first ring at the surface is consistent with that described for 1-(BN)\textsubscript{3}-a101, while the second hBN ring is adsorbed edgewise, forming two bonds with the surface, B–O\textsubscript{br} and Ti–N, of lengths 1.46 and 1.87 Å. A third bond is established between the hBN rings with a B–N distance of 1.51 Å. The Bader charges for the three N ions which bind to Ti of the surface decrease by 0.5–0.6 electrons and an O\textsubscript{ip} ion and O\textsubscript{br} ion gain 0.3 and 0.6 electrons, respectively.

Figure 1(c) shows the relaxed structure of 3-(BN)\textsubscript{3}-a101, in which the three hBN rings adsorbed at the surface are not in direct interaction. The geometry of the rings at the surface is similar to that described for 1-(BN)\textsubscript{3}-a101, above. However, N ions of the rings labelled 2 and 3 in figure 1(c) bind to the same Ti ion; this Ti ion moves out from the surface by 0.9 Å. This distortion shortens the bond length to the N ion of ring 2–1.97 Å and the Ti ion binds to the third N ion of ring 3 with a bond length of 2.14 Å. The Bader charges for the N ions decrease by 0.2–0.5 electrons, and correspondingly, 10 O ions of the surface gain between 0.1 and 0.6 electrons.

![Figure 1. Relaxed structures of (a) 1-(BN)\textsubscript{3}-a101, (b) 2-(BN)\textsubscript{3}-a101 and (c) 3-(BN)\textsubscript{3}-a101. The adsorption energies, computed within the DFT-D2 (vdW-DF) approach, are included in the insets of the panels on the left. The panels on the right show the top view of the modified surface. In this and subsequent figures, Ti are represented by grey spheres, O by red, B by pink and N by blue.](image-url)
The relaxed structure of (BN)$_{24}$-a$_{101}$ is shown in panels (a)–(d) of figure 2. Adsorption energies of $-13.71$ and $-13.60$ eV are computed within the DFT-D2 and vdW-DF frameworks; in each case this corresponds to adsorption energies of $-0.57$ eV per BN unit. The relaxed geometries are qualitatively consistent but computed bond lengths are elongated by 0.01–0.02 Å in the vdW-DF set-up relative to those computed in DFT-D2. One side of the hBN strip has B ions at the outermost edge (figure 2(a)), while the other consists of N ions (figure 2(c)). At the B-terminated edge, three B–O bonds are formed of lengths in the range 1.35–1.42 Å. Two bonds involve Obr and the third involves Oip; these ions migrate out from the surface by 0.3–0.5 Å. At the N–terminated edge there are three interfacial bonds, two Ti–N bonds of length 2.04 Å and the distance of edge N to the nearest surface O is 1.43 Å. The Ti ions move out from the surface by 0.2–0.3 Å. The hBN-layer is anchored at the surface by the interfacial bonds at the B– and N-terminated edges and bows towards the centre of the strip to a maximum distance of 3.3 Å.

The Bader charges for two surface Ti ions along the B-terminated edge increase to 10.0 electrons and the computed spin magnetizations are 0.9 $\mu_B$; these values are typical of reduction to Ti$^{3+}$. A third Ti ion in the vicinity of the B-terminated edge has a computed Bader charge of 9.8 electrons and a spin magnetization of
0.3 $\mu_B$, indicating partial reduction. The reduction of these cations along the B-terminated edge results from charge transfer along the B–O–Ti bond, which is established to maintain the oxidation state of the B ions. This is further confirmed by increased Bader charges of 7.7 electrons for those surface O ions which bind to the B sites of the hBN ribbon. Along the N-terminated edge, the N ion which does not bind to the surface has a computed Bader charge of 7.1 electrons and a spin magnetization of 0.6 $\mu_B$, indicating a localized hole state, due to under-coordination. The N and O ions which share a bond each have a Bader charge of 6.8 electrons. These results indicate a considerable reorganization of charge at the interface; in total, two electrons are transferred from the hBN ribbon to the TiO$_2$ surface.

The relaxed geometry of the second ribbon model, (BN)$_{12}$–a101, is shown in panels (e)–(g) of figure 2. Adsorption energies of $-15.04$ and $-14.74$ eV are computed within DFT–D2 and vdW–DF, respectively, corresponding to adsorption energies of $-0.36$ and $-0.35$ eV per BN unit. Six interfacial bonds are established along each edge of the ribbon (figures 2(c) and (f)). Of these interfacial bonds, six are B–O$_{hr}$ bonds with lengths in the range 1.40–1.45 Å. The six Ti–N bonds have lengths of 2.02–2.17 Å. Once again, these bond lengths are elongated by 0.01–0.02 Å, in the vdW-DF set-up.

Those ions of the ribbon which bind to the surface neighbour each other along their shared edge, as shown in figure 2(e), and the ions of the edge opposite this binding site are not bound to the surface. Hence, the ribbon is twisted at the surface in this binding configuration.

For (BN)$_{12}$–a101, there is no interfacial charge transfer, although there is some redistribution of charge. The computed Bader charges for those O$_{hr}$ ions which bind to B increase from 7.1 to 7.6 electrons, while the Bader charges for N sites which bind to the surface decrease from 8.0 to 7.5 electrons. For (BN)$_{12}$–a101, 12 of the 28 edge sites bind to the surface; this compares with six of eight edge sites binding to the surface in (BN)$_{24}$–a101. This is reflected in the adsorption energies per BN-unit, which are $-0.35$ and $-0.57$ eV for (BN)$_{24}$–a101 and (BN)$_{12}$–a101, respectively.

The computed projected electronic density of states (PEDOS) plots for BN-modified TiO$_2$ are shown in figure 3. For 1-(BN)$_{3}$–a101 (figure 3(a)), N–p derived peaks emerge at 0.5, 0.8 and 1.7 eV above the valence band maximum (VBM) of the titania support. For 2-(BN)$_{3}$–a101 (figure 3(b)), N–p derived peaks emerge at 0.4 and 1.8 eV, with additional peaks extending from 0.8 to 1.3 eV, above the VBM. For 3-(BN)$_{3}$–a101, shown in figure 3(c), N–p states extend to 1.4 eV above the O–p derived VBM. Figure 3(d) shows the PEDOS for (BN)$_{32}$–a101 and we see that N–p states extend to 1.5 eV above the titania VBM. Reduced Ti$^{3+}$ states emerge in the titania energy gap at 1.0 and 1.3 eV above the VBM, as indicated by the dashed peaks in figure 3(d). In addition, the N ion at which the hole localizes, as described previously, contributes an empty state just below the CBM. For (BN)$_{12}$–a101 (figure 3(e)), N–p states extend to 1.8 eV above the VBM.

The PEDOS plots computed for hBN-modified anatase TiO$_2$ show that modification has a significant impact on the energy gap. In particular, for the hBN ring models, modification enhances the DOS at the VBM while having little or no effect on the titania CBM. For the hBN ribbon model, the features of the DOS depend on the nature of the bonds formed at the interface. Under-coordinated B ions will bind to O sites of the surface and transfer charge across the interface, reducing surface Ti ions to Ti$^{3+}$ and these occupied states will emerge in the
The impact of the modified anatase support so that the modified anatase (101) surface has been included for reference. Values computed for the unmodified TiO$_2$ anatase (101) surface have been included for reference.

| Composite structure | $E_{\text{vertical}}$ (eV) | $E_{\text{excite}}$ (eV) | $E_{\text{relax}}$ (eV) |
|---------------------|-----------------------------|--------------------------|-------------------------|
| Anatase (101)       | 2.72                        | 2.19                     | 0.53                    |
| 1-(BN)$_3$-a101     | 1.63                        | 0.31                     | 1.32                    |
| 2-(BN)$_3$-a101     | 1.64                        | 0.51                     | 1.13                    |
| 3-(BN)$_3$-a101     | 1.47                        | 0.31                     | 1.17                    |
| (BN)$_{24}$-a101    | 0.98                        | 0.20                     | 0.79                    |

The extent of the impact on the DOS is coverage dependent. At low coverages, N-p peaks emerge in the energy gap, as shown in figures 3(a) and (b), while at higher coverages a continuum of states extend the VBM to higher energies. These features suggest facile charge transfer from the hBN modifiers to the TiO$_2$ support, with consequences for the photocatalytic activity.

To examine charge carrier separation and localization we implement a model for photoexcitation, as described in the Supporting Information. The model is applied only to the hBN ring modified surfaces and (BN)$_{24}$-a101 as the accumulation of charge at the interface of (BN)$_{24}$-a101 complicates implementation of the model with this system. Within this model, three energies are computed: the vertical single-triplet energy ($E_{\text{vertical}}$), which is analogous to the optical band gap; the singlet-triplet energy ($E_{\text{excite}}$), which is the difference in energy between the singlet ground state and the fully relaxed triplet state; and the relaxation, or trapping energy ($E_{\text{relax}}$). The latter energy represents the energy gained by the system after relaxing in response to the imposition of the triplet state and relates to the trapping energy of the photoexcited electron and hole. These relevant computed energies are presented in table 1.

From the values for $E_{\text{vertical}}$ in table 1 it is clear that the underestimation of the band gap, which is inherent in approximate DFT, persists in the current computational setup. While the $U + V$ correction can be tuned to reproduce the experimental energy gap this can have a detrimental effect on other material properties. In the current computational setup, DFT + $U$ is implemented to yield solutions in which charges are localized, rather than delocalized over the entire system, as in standard DFT. Despite these shortcomings, inferences regarding the impact of the modification may be drawn by comparing the energies computed in the photoexcitation model across the different systems and, in particular, with reference to the unmodified anatase (101) surface [91–93].

The values for $E_{\text{vertical}}$ indicate that modification with hBN results in a reduction of the optical band gap. This is expected from analysis of the DOS plots which show N-p states lying higher in energy than O-p states of the anatase support so that the modified energy gap involves transitions from the occupied N-p states to the Ti-d dominated CBM. Values for $E_{\text{vertical}}$ of 1.63 eV, 1.64 eV, 1.47 eV, and 0.98 eV are computed for 1-(BN)$_3$-a101, 2-(BN)$_3$-a101, 3-(BN)$_3$-a101 and (BN)$_{24}$-a101, which can be compared with a computed value of 2.72 eV for the unmodified surface.

In addition to decreases in the values for $E_{\text{vertical}}$, the modification also enhances the stability of the photoexcited electrons and holes. The values for $E_{\text{excite}}$ between 0.2–0.5 eV indicate that the stability of the triplet electronic state is significantly enhanced with respect to the unmodified surface and suggest a facile transfer of charge across the hBN–TiO$_2$ interface. Further evidence for the stability of the charges is given by the values for $E_{\text{relax}}$ which are larger for the ring-modified surfaces by 0.6–0.8 eV and for (BN)$_{24}$-a101 by 0.2 eV, relative to bare anatase (101).

Localization of electrons and holes is shown in the excess spin density plots in figure 4 for the hBN-modified anatase surfaces. For each of the surfaces the electron localizes at a surface Ti site; the computed Bader charge increases from 9.6 to 9.9 electrons for Ti in 1-(BN)$_3$-a101, 2-(BN)$_3$-a101 and (BN)$_{24}$-a101, and from 9.7 to 10.0 electrons for 3-(BN)$_3$-a101. For each system the spin magnetization computed for the Ti ion at which the electron localizes is 0.9 $\mu_B$. These results correspond to reduction of Ti to Ti$^{3+}$. The hole predominantly localizes at a two-fold coordinated N site for 1-(BN)$_3$-a101 (figure 4(a)), 3-(BN)$_3$-a101 (figure 4(c)) and (BN)$_{24}$-a101 (figure 4(d)). For these sites the Bader charges decrease from 7.8 to 7.1 electrons and the computed spin magnetizations are 0.6 $\mu_B$. For 2-(BN)$_3$-a101 (figure 4(b)), the hole is distributed over two doubly-coordinated N ions; for these sites the Bader charges decrease from 7.9 to 7.5 electrons and the spin magnetizations are 0.3 $\mu_B$. Holes localize at low-coordinated N ions and these results in empty states below the titania CBM. Consistent across all models are N-p states that extend into the energy gap and we predict that modification of TiO$_2$ with hBN will yield a red-shift in the light absorption edge.
3.2. Phase composition of BN–TiO₂ samples

XRD was used to determine the phase of each sample and from this analysis the impact on the transition temperature can also be concluded. The main anatase (25°) and rutile (27°) peaks were used with Spurr equation (equation (1)) when examining mixed samples to denote the % of anatase/rutile present (figures 5 and S1). Additionally, figure 5 shows the presence of bulk boron nitride peaks, with the peak at 26° indicating the graphite-like hBN structure [98–101]. All samples were 100% anatase when calcined up to 500 °C. At 600 °C, 0% BN–TiO₂ had converted to 100% rutile, while the BN-modified samples with 2%, 4%, 8% and 16% BN show anatase contents of 13.2%, 25.9%, 64.4% and 65.5%, respectively. All samples convert to the rutile phase when calcined at 650 °C and 700 °C (figure S1), irrespective of BN concentration. The peak at 26° is only present for 16% BN–TiO₂ when calcined at 650 °C and 700 °C.

In addition to phase composition, XRD was also used to determine the particle size of all samples. Table S1 shows that there are significant variations in particle size that depend on the calcination temperature and the concentration of BN. When the samples were calcined at 500 °C, the smallest particle size was 9.09 nm, which is seen from 8% BN while 2% BN showed the largest particle size at this temperature (10.86 nm). The 4% BN sample showed the lowest anatase particle size and 2% BN displayed the lowest rutile particle size when calcined at 600 °C, 16.28 nm and 24.67 nm respectively. Once calcined at 650 °C and 700 °C, 2% BN showed the smallest particle size.

Raman spectroscopy was used as a complementary tool to XRD and confirmed the phase composition of the titania samples. Figure 6 (a) shows peaks at 147, 197, 396, 516 and 638 cm⁻¹ which relate to the A₁g, 2B₁g and 3Eg active modes and indicate the anatase phase [14, 102–106]. Spectra showing the presence of anatase and
rutile peaks indicate mixed phased samples. The intensity of these peaks is dependent on the % of each of the phases present; this can be seen in figure 6(b). Figure 6(c) shows peaks at 144, 238, 446, 612 and 827 cm$^{-1}$ which relate to the $A_{1g}$, $B_{1g}$, $B_{2g}$ and $3E_g$ active modes and indicates the presence of the rutile phase [14, 102–106]. Very low intensity BN peaks can also be seen in figure 6(c).
3.3. Surface chemical/elemental composition of nanomaterials

XPS analysis was employed to determine the elemental composition and oxidation states of elements that were found on or close to the surface of the pure and BN-modified TiO₂ calcined at 500 °C, 600 °C and 700 °C. The elements found present in the samples were carbon, boron, nitrogen, oxygen and titanium; the atomic (at) % varied depending on the samples (see table S2). 0% BN–TiO₂ showed the presence of N 1s peaks, however these N 1s peaks are considered as contamination as the atomic % for all three samples is under 0.41% (table S2). The 0% and 16% BN–TiO₂ spectra and data were used as examples for deconvoluted peaks.

Table S2 shows that the at% of B 1s and N 1s increases in the composite samples as the concentration of BN increases. However, the at% of boron remains higher than nitrogen in all modified samples. In contrast, the at% of Ti 2p and O 1s present decreases as the concentration of BN increases. The amount of carbon present varies throughout all twelve samples, from 6.87 to 14.24 at%.

Figures S2 and S3 show the binding energy for O 1s and Ti 2p₃/₂ (Ti–O). The increase in temperature does not have a significant impact on the binding energy of the Ti 2p peaks. A decrease in the Ti 2p binding energy is indicative of oxygen vacancy formation and the reduction of Ti⁴⁺ to Ti³⁺ [20]. However, the peaks in figure S2 only shows a decrease of 0.2 eV in binding energy indicating that Ti⁴⁺ has not converted to Ti³⁺ and oxygen vacancies have not formed [107].

Analysis of the O 1s spectra (figure S3) show two fitted peaks, at ~530.2 eV and 531.48–531.97 eV. The main fitted peak at ~530.2 eV (pink) is attributed to oxygen bound within the Ti lattice [20]. A decrease in the O 1s binding energy (~530.2) denotes oxygen vacancies forming in TiO₂ [20]. As with the Ti 2p, the O 1s binding energy only shows a 0.2 eV decrease. The second fitted peak (green) in the O 1s spectra is at 531.48–531.97 eV (figure S3) can be indicative of the O–Ti bond. As seen in figure 5, these peaks broaden and increase in intensity as the temperature increases for the 16% BN–TiO₂ samples.

The composite samples (2%–16% BN–TiO₂) also contained B 1s and N 1s peaks, the spectra for 16% BN–TiO₂ can be seen in figure 7. The B 1s spectra (figure 7) show the presence of two peaks, the first at 190.68–190.78 eV and second at 191.36–191.83 eV. The fitted peaks at ~190 eV (pink) show the presence of elemental boron when examining boron doped TiO₂ [108]. The second fitted peak at ~191 eV (green) has a significantly lower intensity and indicates the presence of doping with B⁵⁺ ions in interstitial modes [108]. Liu et al (2017) suggests that this peak could also be a result of ‘edge/interfacial boron dangling bonds’ which are linked with –OH [56]. It is important to note that the XPS analysis does not show the presence of Ti–B bonds (187 eV) or boron being incorporated into TiO₂ and its environment (Ti–B–O at 192 eV) [109]. Finally, the N 1s peaks that are present in the 16% BN–TiO₂ range from 398.28–398.48 eV, which relate to the B–N bonding and refer

![Figure 7. XPS spectra of B1s and N1s for 16% BN–TiO₂ calcined at 500 °C, 600 °C and 700 °C.](image-url)
to the trigonal units of BN layers (BN3 and NB3) [56]. The peak which indicates Ti–N interactions (∼396 eV) is not present in the N 1s spectra [37, 110].

C 1s peaks were present in all samples at all temperatures. The eV for all C 1s peaks remained largely unchanged. Peaks at ∼285 eV and ∼288–289 eV were initially seen (figure S4). However, after deconvolution of the spectra showed a third peak at ∼286 eV (figure S4). The peaks are attributed to adventitious carbon (284.6–285 eV = hydrocarbon, 286.2–286.6 eV = C–OH and 289 = C(=O)OH) which can arise due to contamination during synthesis/calcination and/or the standard used for XPS analysis [12, 20, 40, 102, 103, 111, 112]. This can be confirmed by the absence of the characteristic peak for Ti–C (281.5 eV) [14, 102, 113]. Any surface of samples exposed to the atmosphere will contain contamination from air, including carbon. As XPS is a surface analysis method, there is almost always a C 1s peak present. Additionally, the C 1s peak is used as a charge correction reference for energy calibration purposes. These account for C 1s peaks found in the BN–TiO2 samples. XPS spectra of C 1s for 0% and 16% BN–TiO2 calcined at 500 °C, 600 °C and 700 °C are seen in figure S4.

3.4. Photocatalytic degradation of 1,4-dioxane
The photocatalytic activity of 16% BN–TiO2 materials was determined by examining the photodegradation of 1,4-dioxane and was compared to pure TiO2. The reduction of 1,4-dioxane under solar light without any photocatalyst present (TiO2 = 0) was also examined and this showed the removal of 15.8% of 1,4-dioxane after 4 h (figure 8).

At 500 °C and 700 °C, the 16% BN–TiO2 photocatalysts showed a removal rate of 86.3% and 73.4%, respectively, after 4 h (figure 8). However, 100% anatase of pure TiO2, calcined at 500 °C, showed 60.5% removal (figure 8), while after calcination to 700 °C (100% rutile), only 17.9% of 1,4-dioxane was removed after 4 h, which is not significantly different from the activity without any catalyst. Therefore, the 16% BN–TiO2 at given temperatures showed a significant improvement in the photocatalytic activity compared to pure anatase and rutile.

4. Discussion
Traditionally the anatase to rutile transition is considered to occur between 600 °C and 700 °C. The BN–TiO2 samples only showed an increased transition temperature when compared with the control (0% BN–TiO2). The control is 100% rutile from 600 °C, while the doped samples were mixed phased sample at this temperature and only converted to 100% rutile at 650 °C. In addition to TiO2 peaks, XRD also showed the presence of hexagonal BN. This structure was determined based on its characteristic peak at 26°, which the other structures do not have. XRD was also used in calculating the particle size of the nanomaterials. The particle size increased as the temperature increased, which occurs due to the formation of rutile. Raman spectroscopy further confirmed the TiO2 phase composition, very small BN peaks could also be seen in some of the Raman spectra. Due to Ti-B or Ti–B–O not being present in the XPS analysis, it can be concluded that the BN doped on the surface of the TiO2.
and it has not been doped within the TiO$_2$ crystal lattice structure. These results confirm the DFT calculations suggestion that hBN rings are absorbed onto the TiO$_2$ surface. DFT calculations also suggest the presence of Ti–N bonds at the interface, however XPS analysis did not show the presence of Ti–N peaks in Ti 2p ($\sim$457 eV) or N 1s (396 eV) spectra [110].

The photocatalytic activity of the 0% and 16% BN–TiO$_2$ were evaluated by examining the photocatalytic oxidation of 1,4-dioxane (figure 8). The absence of anatase phase of the catalyst at 700 °C produces a total reduction of the efficiency of the catalyst, hence the values are not significantly different to the values obtained after the treatment without catalyst. On the other hand, TiO$_2$ at 500 °C without the presence of BN removes part of the 1,4 dioxane at 240 min (≈60%). The removal of 1,4 dioxane has been already tested using immobilized NF-TiO$_2$ composite with monodisperse TiO$_2$ nanoparticles and Aeroxide® P25-TiO$_2$ photocatalyst obtaining slightly better removal kinetic [64, 114]. The 16% BN–TiO$_2$ samples calcined at 500 °C and 600 °C both showed a significant improvement compared to the 0% BN–TiO$_2$ at 500 °C. The 16% BN–TiO$_2$ at 500 °C obtained the best removal efficiency probably due to the higher presence of anatase phase (100% versus 65.5% in the 16% BN–TiO$_2$ at 600 °C) and the presence of BN. They are even better than the obtained with other NF doped catalysts, although they were immobilized [64]. The particle size of 16% BN–TiO$_2$ at 500 °C is lower than that of the 16% BN–TiO$_2$ at 600 °C, but quite similar to the 0% BN–TiO$_2$ at 500 °C. Although 16% BN–TiO$_2$ at 500 °C and 0% BN–TiO$_2$ at 500 °C have 100% anatase phase and similar particle size the presence of BN clearly increase the removal efficiency and kinetics (figure 8). This could be due to the better efficiency of BN–TiO$_2$ materials in the visible region in comparison to the undoped TiO$_2$ [56, 61]. Different authors affirm the formation of B–O–Ti bonding extends the wavelength range from UV to the visible range being clearly of relevance during the treatment under solar conditions [56, 61].

Lui et al and Singh et al propose that the TiO$_2$ nanoparticles are bonded onto the hBN sheets and suggest that this is done via a B–O–Ti bond [56, 61]. Sheng et al further confirmed this during their examination of the BN–TiO$_2$ nanocomposites for the photocatalytic degradation of Rhodamine B and methylene blue [60].

Figure 9 shows the proposed photocatalytic mechanism that occurs between hBN and TiO$_2$. The photogenerated electrons transfer across the B–O–Ti bond from the TiO$_2$ CB to BN, seen in figure 9 [56, 61]. The electrons are not in a fixed position within the $\pi$–$\pi$ conjugate system of BN [61]. As a result of this, there is a slower rate of recombination of the electron–hole pair. This results in an increased rate of photocatalysis for TiO$_2$ [61].

5. Conclusion

The photocatalytic activity of TiO$_2$ has been successfully increased by interfacing titania with BN. DFT calculations reveal that, at low coverages, hBN rings adsorb strongly at the surface with the formation of B–O and Ti–N bonds at the interface. For higher coverages, hBN layers are anchored at the surface by bonds between B- and N-terminated edge sites and the TiO$_2$ surface. For the hBN ribbon model, adsorption at the anatase surface led to electron transfer from the hBN modifier to the TiO$_2$ support. For each system, modification has a significant effect on the energy gap. Occupied N$p$ states extend the VBM to higher energies which should produce a red shift in light absorption. Application of the photoexcitation model corroborated analysis of the computed PEDOS plots and showed electron excitation from high-lying N$p$ states to the TiO$_2$ conduction
band, with hole localized on the hBN modifier. Along with preservation of the anatase phase, the red shift in light absorption and promotion of charge carrier separation, which arise due to hBN modification, contribute to the observed enhancements in photocatalytic performance.

This comprehensive study shows that BN-modified TiO$_2$ samples exhibited an improvement in the % anatase present at 600 °C compared to 0% BN–TiO$_2$. From 600 °C, unmodified TiO$_2$ had transitioned to 100% rutile while all composite samples comprised of both anatase and rutile phases. The highest content of anatase phase was obtained for 16% BN–TiO$_2$, containing 63.5% at 600 °C, closely followed by 8% BN–TiO$_2$, containing 64.4% at 600 °C. XPS determined that the BN forms an interface at the TiO$_2$ surface. When examining the photocatalytic degradation 1,4-dioxane, 16% BN–TiO$_2$ at 500 °C (100% anatase) showed over a 25% improvement in the removal rate compared to pure TiO$_2$ (86.3% and 60.5% removal respectively), in spite of the similar anatase phase contents. In conclusion, interfacing with BN increases the anatase to rutile transition temperature and enhances photocatalytic activity under solar conditions in comparison to bare TiO$_2$.

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