Supplementary material:

Defect engineering in Boron Nitride for catalysis

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**SEM flake analysis of the ball-milled samples**

Higher resolution SEM images of the ball-milled and heat-treated flakes are presented in Fig. S1. This clearly depicts the effect of ball milling on reducing the size of the flakes compared to heat treatment for which the flakes maintain their initial dimensions.

|  |  |
| --- | --- |
| **C:\Users\yding\Documents\[] Research\[1] SEM\20180524-SEM\pristine on cu\dh-bn-43k.tif** | **C:\Users\yding\Documents\[] Research\[1] SEM\20180524-SEM\pristine on cu\h-BN_11k.tif** |

**Fig. S1.** SEM image of the powder obtained after 2 h of ball milling with ZrO2 (left) and of the powder heat treated at 950˚C for 2 h (right). Both treatments were carries out under argon atmosphere.

SEM images acquired at 5000x magnification were selected for flake size analysis. We assigned three size category (> 5 μm, 2-5 μm, < 2 μm) for which the number of the flakes was estimated. The percentage of the number of flake in the image belonging to each category was calculated.

**Table S1.** Summary of the flake size distribution percentage for the different ball-milled dh-BN powders

|  |  |  |  |
| --- | --- | --- | --- |
|  | **>5 μm** | **2-5 μm** | **<2 μm** |
| **ZrO2 30 min** | **17.9** | **52.2** | **29.9** |
| **ZrO2 60 min** | **12.2** | **76.4** | **11.4** |
| **ZrO2 90 min** | **13.5** | **18.9** | **67.6** |
| **ZrO2 120 min** | **0** | **15.8** | **84.2** |
| **WC 120 min** | **4.8** | **47.6** | **47.6** |

**IR spectroscopy analysis of the ball-milled samples**

FTIR spectra obtained for dh-BN indicated a change in the relative intensity of the A2u and E1u modes. We extracted the intensity of each band and we present their ratio below.

**Table S2.** Absorption(A2u)/ Absorption(E1u) ratio in the IR spectrum of pristine *h-*BNand ball-milled *dh-*BN

|  |  |
| --- | --- |
|  | **Absorption(A2u)/ Absorption(E1u)** |
| **Pristine** | **1.36** |
| **ZrO2 30 min** | **0.81** |
| **ZrO2 60 min** | **0.58** |
| **ZrO2 90 min** | **0.55** |
| **ZrO2 120 min** | **0.55** |
| **WC 120 min** | **0.84** |

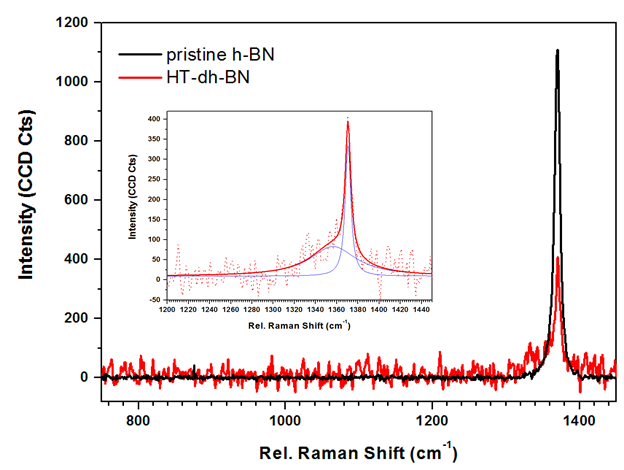
Raman spectra obtained for dh-BN indicated a change in the relative intensity of the band at 1371 cm-1, making it difficult to compare the width of the band. We fitted the band with a Lorentzian function and extracted the position and FWHM for each powder. The results are summarized in the table below.

**Table S3.** Summary of the position and FWHM of the E2g band in heat treated *dh-*BN

|  |  |  |
| --- | --- | --- |
| **Sample** | **Position (cm-1)** | **FWHM (cm-1)** |
| **800˚C 2 h** | **1371** | **8.2** |
| **850˚C 2 h** | **1371** | **8.4** |
| **850˚C 12 h** | **1371** | **8.3** |
| **850˚C 24 h** | **1371** | **8.3** |
| **900˚C 2 h** | **1371** | **8.4** |
| **900˚C 12 h** | **1371** | **7.9** |
| **900˚C 24 h** | **1371** | **8.1** |
| **950˚C 2 h** | **1371** | **8.4** |

**Raman spectrum of the *dh-*BN obtained by heat treatment of 950˚C for 2h under Argon atmosphere in the glove box**

The effect of heat treatment on h-BN was investigated. As it required long hours of high temperature in the furnace, for security considerations, optimization was carried out in air. We identified a treatment at 950˚C for 2 h to be a good condition to reproduce the treatment under argon atmosphere in the glovebox. The Raman spectrum of the *dh-*BN obtained under argon is presented in Fig. S2. Using a deconvolution algorithm with two Lorentzian fits, we assigned the position of the E2g band at 1371 cm-1 with a FWHM of ~7 cm-1. A secondary broader band (FWHM of ~ 53 cm-1) at 1356 cm-1 was observed in the spectrum, likely resulting from defects in the lattice. This band has previously been assigned to h-BN with 5:5:8 N-N grain boundaries 1 of BN. Further studies will be performed to pinpoint the nature of the sub-band. However, the measurement allows us to confirm that oxidation in the 800-900 cm-1 range disappeared.



**Fig. S2.** Raman spectrum of the powder heat treated at 950˚C for 2 h under argon atmosphere. No sign of oxidation was observed in the 800-900 cm-1 region. The E2g band and secondary band at 1356 cm-1 are identified with deconvolution as shown in the inset.

1. R.C.N. Rao and W.U. Vasudeo: 2d Inorganic Materials Beyond Graphene, (World Scientific Publishing Company 2017).