Supplementary Information

Large-scale Mechanical Peeling of Boron Nitride Nanosheets by Low-Energy Ball Milling

Lu Hua Li,*[a] Ying Chen,[a] Gavin Behan,[b] Hongzhou Zhang,[b] Mladen Petravic[c] and Alexey M. Glushenkov[a]

[a] *Institute for Technology Research and Innovation, Deakin University, Geelong Waurn Ponds Campus, VIC 3216, Australia. E-mail: luhua.li@deakin.edu.au*

[b] *School of Physics and CRANN, Trinity College Dublin, College Green, Dublin 2, Republic of Ireland*

[c] *Department of Physics, University of Rijeka, Omladinska 14, Rijeka 51000, Croatia*

1. Helium Ion Microscope (HeIM) and TEM study of the initial hBN particles

Fig. S1a shows a scanning helium ion microscope (Orion, Carl Zeiss) image of the initial particles without charging artifacts. Fig. S1b shows a TEM image of the initial particles at low magnification. This image also shows that the un-milled hBN particles have no obvious preferential orientation. A higher magnification TEM edge-on image of the particles shows that some of the disks are closely attached to each other (Fig. S1c). Fig. S1c shows a HRTEM image of a stack of the particles, which have nearly identical crystalline orientation with (002) plane parallel to the particle top surface.

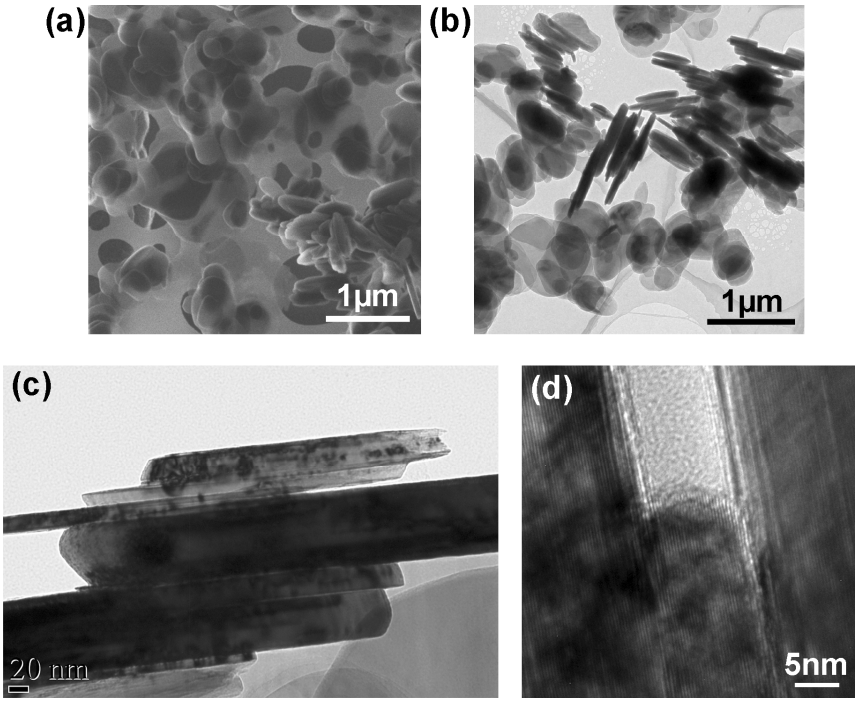

Fig. S1 *(a) Helium ion microscope image of the initial hBN particles; (b) low magnification TEM image of the hBN particles without milling; (c) edge view of a stack of hBN plates; (d) high magnification TEM image of the stack.*

2. hBN sheets centrifuged at low *g* force

Fig. S2 shows a SEM image (on Si) and a helium ion microscope image (on a carbon coated TEM grid) of hBN sheets produced by ball milling in benzyl benzoate for 15 h and then centrifuged in benzyl benzoate at 376 *g* (2000 rpm) for 1 h.

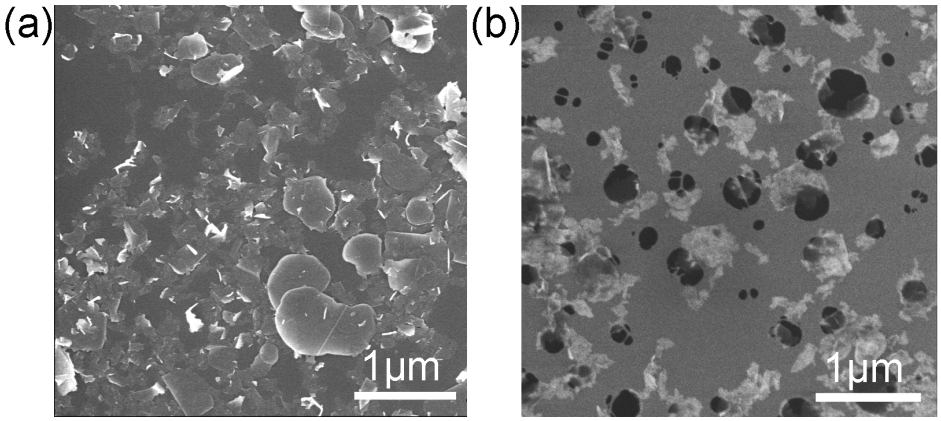

Fig. S2 *(a) SEM image, and (b) scanning helium ion microscope image, of the hBN sheets produced by ball milling in benzyl benzoate for 15 h and centrifugation at 376 g for 1 h.*

3. Production yields

To precisely estimate the yields of BN nanosheets produced by ball milling, the following method was used. More benzyl benzoate was added to the BN particles ball milled for 15 h. The diluted solution was bath sonicated for 0.5 h and then centrifuged at 376 *g* (2000 rpm) for 1 h or 9391 *g* (10000 rpm) for 0.5 h. After centrifugation, the suspension and the sediment were separated and vacuum filtered to remove most of the benzyl benzoate. The filter papers with the solid residues were then immersed in acetone and mildly sonicated to wash the solid residues off into the acetone. Heating at 290 °C evaporated the acetone and the small amount of benzyl benzoate and left the solids only. The BN sheets in the suspension and the sediments were able to be weighted. The production yield was calculated by dividing the weight of the sheets in suspension by the total weight (the sum of the sheets in suspension and the sediments).

4. Dry milling

The addition of a liquid controlling agent is essential for retaining the BN structure during ball milling. When the hBN particles were dry ball milled (the other milling parameters the same), only round-shaped BN particles were obtained (Fig. S3a). The XRD spectra (Fig. S3b) clearly show that the dry

milled sample were semi-amorphous and had a high level of steel contamination, but the particles milled in benzyl benzoate still retained their hexagonal structure.

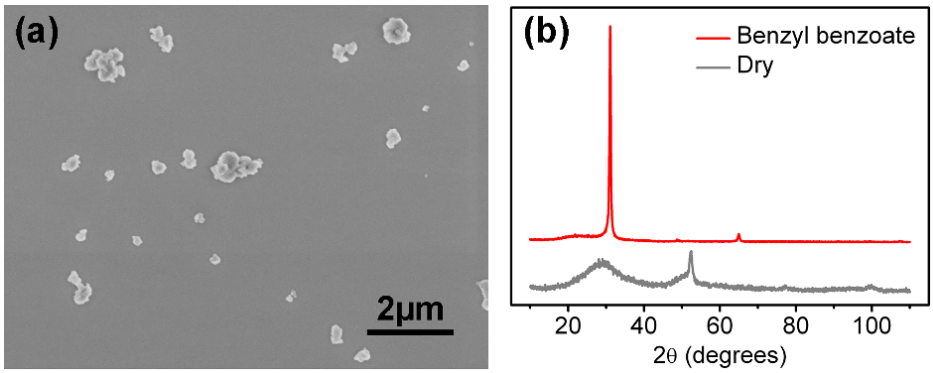

Fig. S3 *(a) SEM image showing the round-shaped BN particles after dry planetary milling for 15 h; (b) XRD spectra showing that the hBN milled in benzyl benzoate for 15 h still has a strong (002) diffraction peak, but the dry 15 h milled sample only shows a broad peak centred at 29.3˚ and a strong peak at 52.4˚ corresponding to steel contamination.*

5. Exfoliation from 0.5 h sonication

To evaluate the exfoliation effect solely from the short time sonication, the initial hBN particles were sonicated in benzyl benzoate for 0.5 h and centrifuged at 9391 *g* (10000 rpm) for 0.5 h or 376 *g* (2000 rpm) for 1 h. The SEM images (Fig. S4) show that the short time sonication did have exfoliation effect, however the short time sonicated BN sheets are much thicker than the milled ones (for comparison, see Fig. 1b). Because under the same imaging accelerating voltage (3 kV) and working distance, the sheets produced by milling are transparent but the sheets produced by 0.5 h sonication are not. This proves that the short time sonication itself is not enough to exfoliate such thin BN nanosheets and ball milling is the main reason for the observed exfoliation in our case.

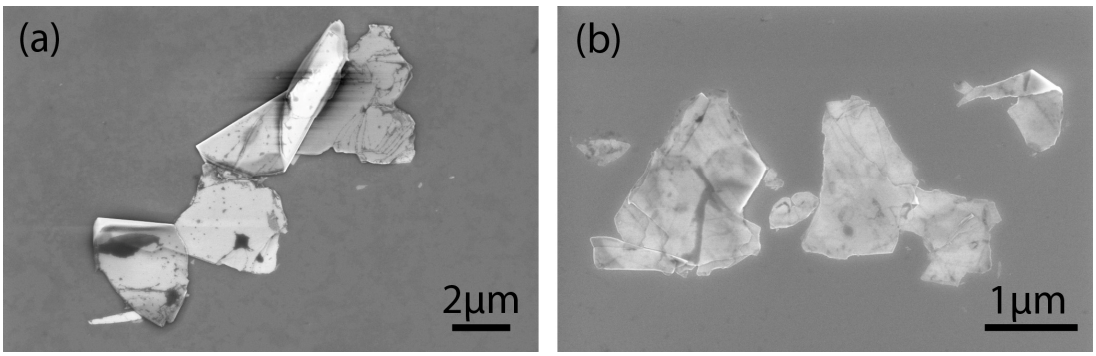

Fig. S4 *Typical SEM images of a cluster of BN sheets produced by (a) sonication in benzyl benzoate for 0.5 h and centrifuged at 376 g for 1 h; (b) sonication in benzyl benzoate for 0.5 h and centrifuged at 9391 g for 0.5 h.*