Supporting Information

Scalable Exfoliation for Large-Size Boron Nitride Nanosheets by Thermal Expansion-Assisted Ultrasonic Exfoliation

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Preparation of BN-OH

Fig. S1 Raman spectra of the pristine h-BN and BN-OH

Raman spectra of the h-BN and BN-OH both show a dominant peak at 1367.6 cm$^{-1}$, which is related to the high frequency $E_{2g}$ mode (Fig. S1). Compared with the Raman spectrum of pristine h-BN, the BN-OH has no new features, suggesting that the alkaline treatment process brings no damage to the hexagonal structure.$^{1}$
**H₂ induced low temperature thermal expansion of BN-OH**

![TGA curves of the raw h-BN, BN-OH and BN-200 under nitrogen atmosphere with a heating speed of 10 °C min⁻¹.](image)

**Fig. S2** TGA curves of the raw h-BN, BN-OH and BN-200 under nitrogen atmosphere with a heating speed of 10 °C min⁻¹.

Fig. S2 shows the TGA curves of the raw h-BN, BN-OH and BN-200, it observes that the BN-200 exhibits significantly improved thermal stability as compared to BN-OH, and the mass loss is only 0.44% at 800 °C, which is comparable to the value of the pristine h-BN (0.32% at 800 °C), but much lower than 2.09 % for BH-OH at 800 °C. This further confirms the occurrence of thermal reduction of BN-OH during the H₂-assisted low temperature thermal treatment.
Fig. S3 XRD patterns of the pristine h-BN and the sample (h-BN-200) left after the direct thermal treatment of pristine h-BN powders.

For comparison, the raw h-BN powders were also subjected to thermal treatment according to the process done to BN-OH. It can be seen that the XRD spectrum of h-BN-200 matches well with that of the pristine h-BN, and the (002) plane peak shows no any shift, suggesting that the h-BN-200 fails to be expanded during \( \text{H}_2 \) assisted low temperature thermal treatment.
Preparation of BNNS by sonication

Fig. S4 (a-c) AFM topography images and the corresponding height of BNNSs with different atomic layers (a) a BNNS with three layers. (b) a BNNS with two layers. (c) a mono-layer BNNS.
The Raman spectrum of the bulk h-BN shows a peak at 1367.6 cm\(^{-1}\), which corresponds to the E\(_{2g}\) phonon mode (Fig. S5). The peak of E\(_{2g}\) phonon mode can show a red shift or blue shift when the number of layer decreases.\(^2\) For bilayers or few layers, a red shift can be observed, since the B-N bonds can be slightly elongated to soften the phonon mode. Whereas, for monolayer, the peak will show a blue shift of 2-4 cm\(^{-1}\), which is attributed to the hardening of the phonon mode caused by a slightly shorter B-N bond. As can be seen, the resultant BNNSs show the E\(_{2g}\) phonon mode at 1365.5 cm\(^{-1}\), corresponding to a red shift of \(~2\) cm\(^{-1}\). The results reveal the successful preparation of few-layer BNNSs.
The yield of BNNSs

In order to demonstrate that the precipitate removed by centrifugation is reusable, we firstly treated the precipitate with fresh NaOH solution, and then H$_2$-induced thermal expansion and sonication once again under the same experimental conditions. After separation by centrifugation and vacuum drying, it was found that additional 0.12 g of bulk materials were peeled off to BNNSs, giving a yield of 6%. AFM result shows the successful exfoliation of few-layer BNNSs from the sediment, as shown in Fig.S6.

**Fig. S6** AFM image of the recycled BNNSs and the corresponding height profile along the line.
Thermal conductivity of the TPU/BNNSs composites

Fig. S7 (a) Low-magnification TEM image of BNNSs-2. (b) Statistical analyses on the lateral size over a sample set of 45 pieces of BNNSs-2. (c) Low-magnification TEM image of BNNSs-10. (d) Statistical analyses on the lateral size over a sample set of 45 pieces of BNNSs-10.

Reference