Electronic Supporting Information (ESI)

Facile One-Step and High-Yield Synthesis of Few-Layered and Hierarchically Porous Boron Nitride Nanosheets

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1. XRD of CaB_6 crystals

Fig. S1 shows the XRD pattern of the commercial CaB_6 crystals that was used as the starting material to synthesize BNNSs. The ten peaks at *d*-spacings of 4.153, 2.932, 2.392, 2.071, 1.854, 1.690, 1.462, 1.385, 1.308, and 1.247 Å can be indexed as cubic phase CaB_6 ((100), (110), (111), (200), (210), (211), (220), (221), (310), and (311)). The lattice constant a = 4.141 Å, in good agreement with a = 4.145 Å in JCPDS card no. 89-4304 (space group Pm-3m, no. 221). No impurities were observed in the XRD pattern. Inset in Fig. S1 reveals the multilayered structures of the CaB_6 crystals.

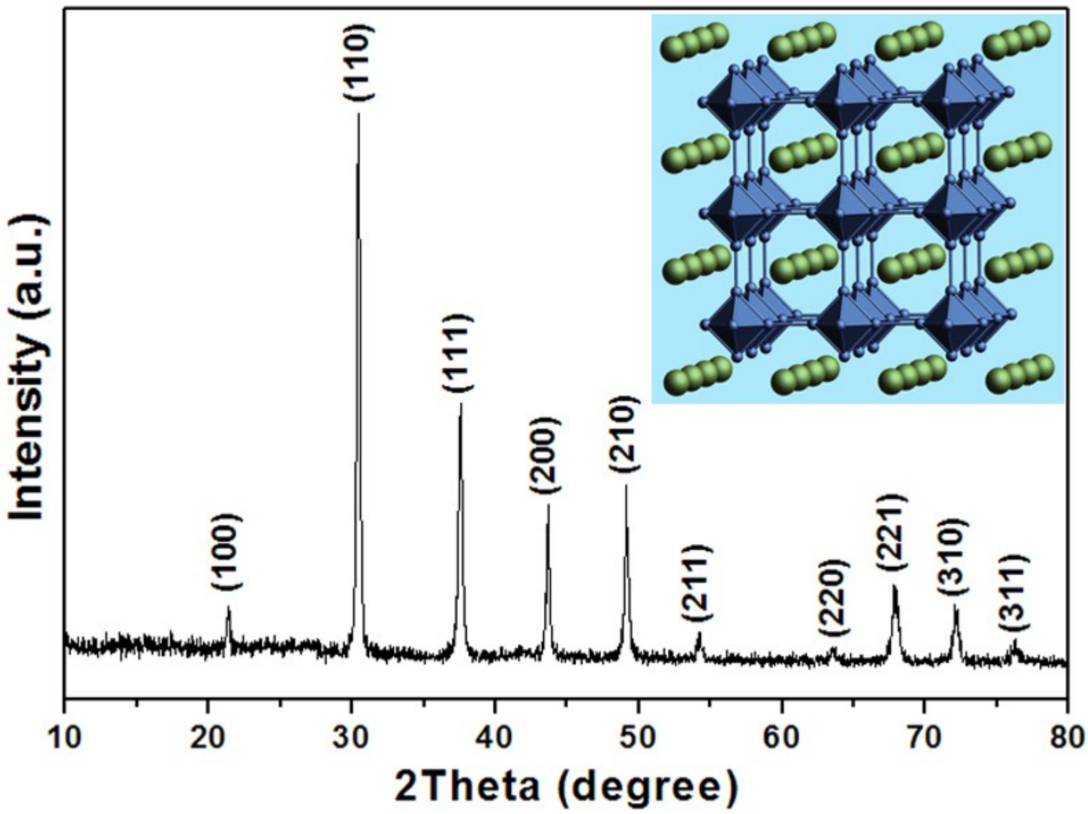

Fig. S1 XRD pattern of commercial CaB6 crystals employed as boron precursor in the present work.

2. Chemical composition of the few-layered BNNSs

Fig. S2a is the corresponding energy dispersive X-ray spectrum (EDS) of the sample in Fig.1, which was also prepared by nitriding the CaB_6 at 600˚C for 24 hours with the CaB_6:NH_4Cl molar ratio of 1:12. In the EDS spectrum, boron and nitrogen signals exist, and have a B:N molar ratio of 1.05:1, approximately equal to that of boron nitride, indicating the product was BN. Slightly rich boron may be resulted from surface hydrolysis during purification which could result a small amount loss of nitrogen. The additional signals of carbon, copper and oxygen are mainly due to the sample grid (copper grids coated with carbon film) used in the transmission electron microscopy. K-edges characteristic of boron and nitrogen can be observed (Fig. S2b) in the EELS spectrum with peaks at about 190, and 400 eV, respectively. The π^* peak on the left side of the B-K and N-K edges and the shapes of the σ^* bands on the right side are typical of the sp^2-bonded layered BN. The XPS survey of the BNNSs-600-24 sample is shown in Fig. S3. The calculated atomic content was 34.76 and 33.92 at% for B and N, respectively. Carbon and oxygen were also detected with 30.93, and 0.39 at %, respectively. XPS results of the BNNSs sample lead to a B/N ratio of 1.02:1 with an error of about 0.05 at %.

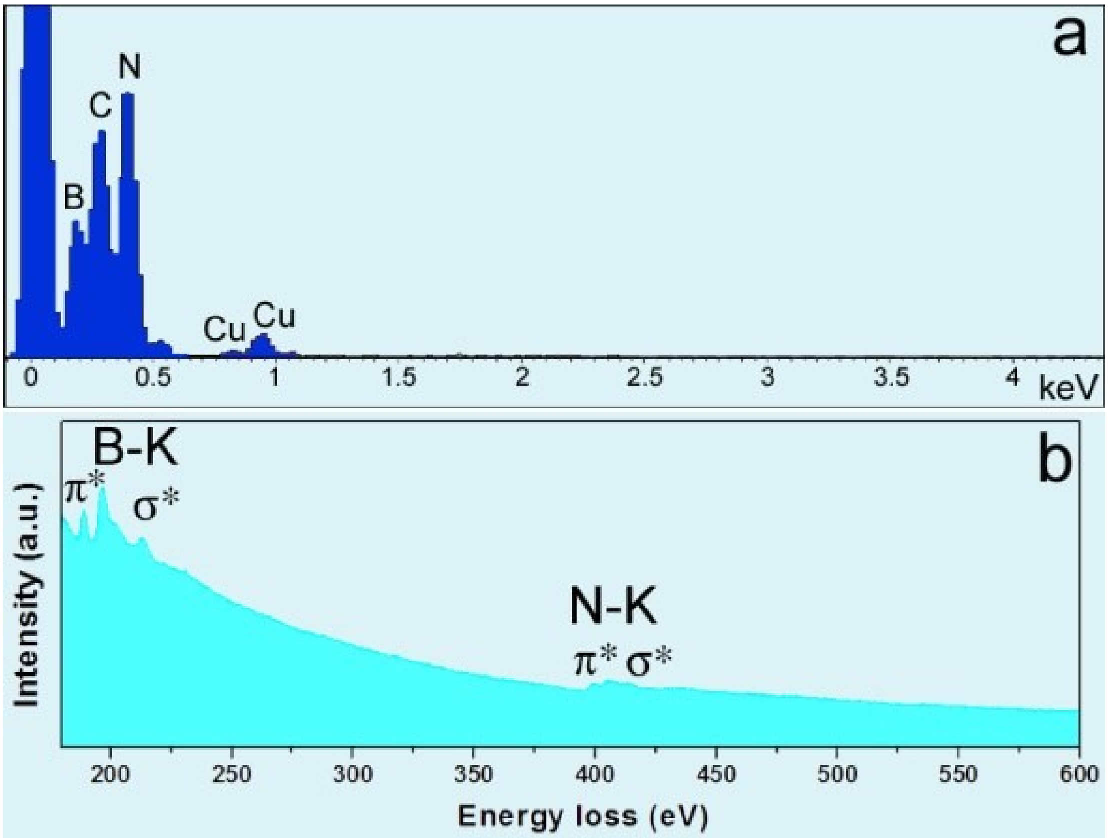

Fig. S2 EDS (a) and EELS (b) spectra of the as-prepared BNNSs-600-24 sample.

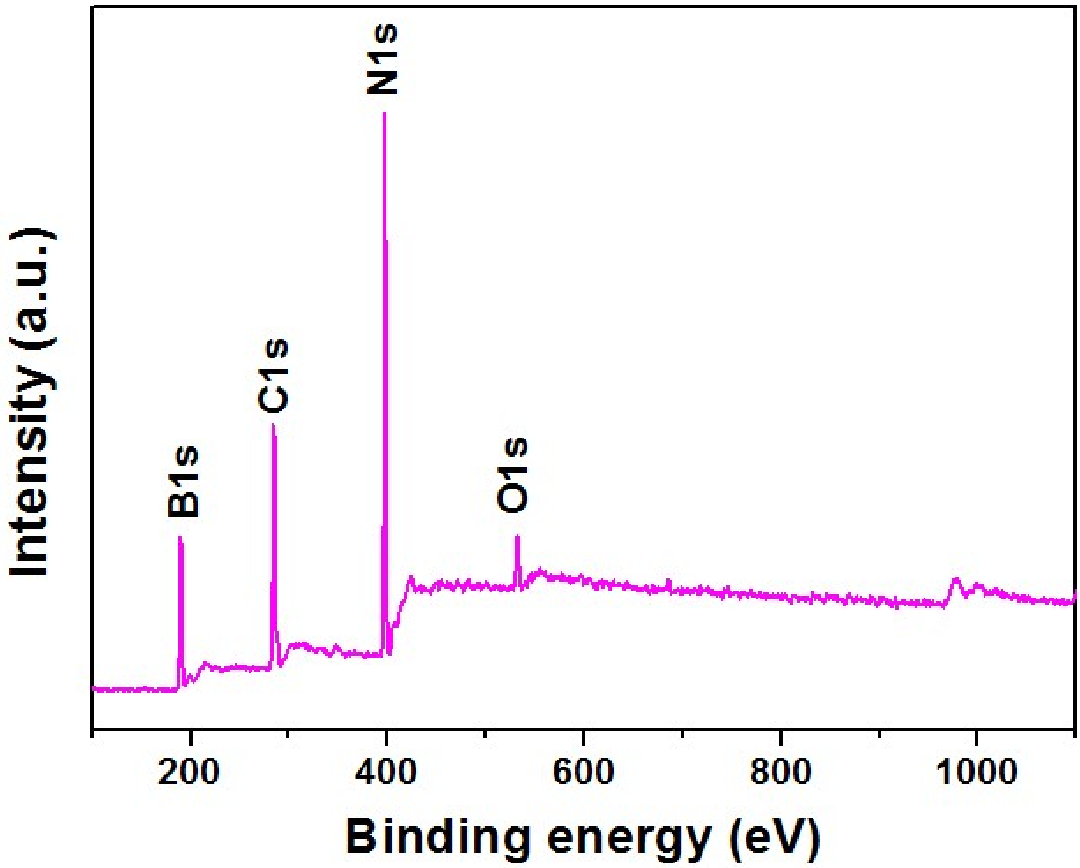

Fig. S3 The XPS survey of the BNNSs-600-24 sample.

3. Porosity and H_2 uptakes of the as-resulted BNNSs

Table S1 Textural characteristics and H_2 uptakes of the BNNS samples

Samples	BET SSA (m^2 g^{-1})[a]	Micropore area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})[b]	Micropore volume (cm^3 g^{-1})	Meso + macro pore volume (cm^3 g^{-1})[c]	H_2 uptake (wt %)[d]
BNNSs-600-6	492	367	0.33	0.16	0.17	1.48
BNNSs-600-12	561	438	0.34	0.18	0.16	1.75
BNNSs-600-24	795	644	0.50	0.27	0.23	2.18
BNNSs-600-48	745	460	0.47	0.19	0.28	1.80

[a] The total pore volume is calculated at a relative pressure of 0.99.

[b] The micropore volume and width are calculated by NLDFT method applied to nitrogen adsorption isotherm.

[c] Meso- and macropore volumes are evaluated by subtracting the micropore volume from the total pore volume.

[d] H_2 uptake capacities are measured volumetrically at 77 K and 1.0 MPa.