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Supplementary Material

Surface-controlled Regeneration of Ammonia Borane from Boron Nitride

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This supporting information shows;

1. ^{11}B solution NMR spectra of N_2H_4/NH_3 treated neat BN, treated BN-NH_x, and mixture of authentic AB and treated BNH_x.
2. ^{1}H solution NMR spectra of BNH_x before and after the treatment.
3. XRD profiles of BNH_x before and after the treatment.
4. FT-IR spectra of BNH_x and N_2H_4/NH_3 treated BNH_x without AB

1. ^{11}B Solution NMR Spectra

Figure S1 shows 1H-decoupled ^{11}B solution NMR profiles of neat hexagonal boron nitride (h-BN) after the hydrazine/ammonia treatment (Hz/NH_3) and mixture of authentic ammonia borane (AB) and treated BNH_x. No AB was detected in the ammonia/NH_3 treated neat h-BN (Figure S1a) and BN-NH_x (Figure S1c), whereas the mixture of authentic AB and treated BNH_x shows single peak (−20.4 ppm) as mentioned in the main manuscript (Figure S1b).

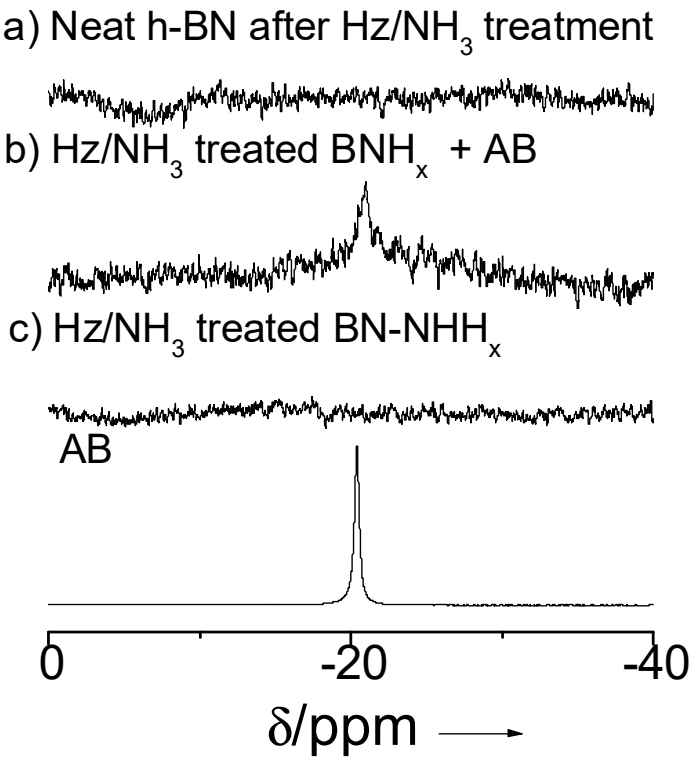

Figure S1. ^{1}H-decoupled ^{11}B solution NMR profiles of (**a**) Hz/NH_3 treated neat h-BN, (**b**) mixture of AB and Hz/NH_3 BNH_x, and (**c**) treated BN-NH_x together with that of AB as a reference.

2. ^{1}H Solution NMR Profiles

Figure S2 illustrates ^{1}H NMR spectra of BNH_x before and after Hz/NH_3 treatment. The dashed lines in Figure S2 are corresponding to NH_3 signals of AB. Although BH_3 signals at 0.5–1 ppm are unclear due to a lot of peaks, NH_3 peaks in treated BNH_x locate the same position and pattern as those of the authentic AB (Figure S2a). The NMR spectrum is dominated by the residual protons in d-8 THF and non-deuterated THF used for filtering (The strong peak at 0 ppm in inset of Figure S2 is insoluble impurity in THF used for filtering). The simple BNH_x extracted shows same signals as solvent due only to THF and impurity peaks in the spectrum, indicating no soluble H species in BNH_x (Figure S2b). Above results are consistent with the results from ^{11}B solution NMR in the main manuscript.

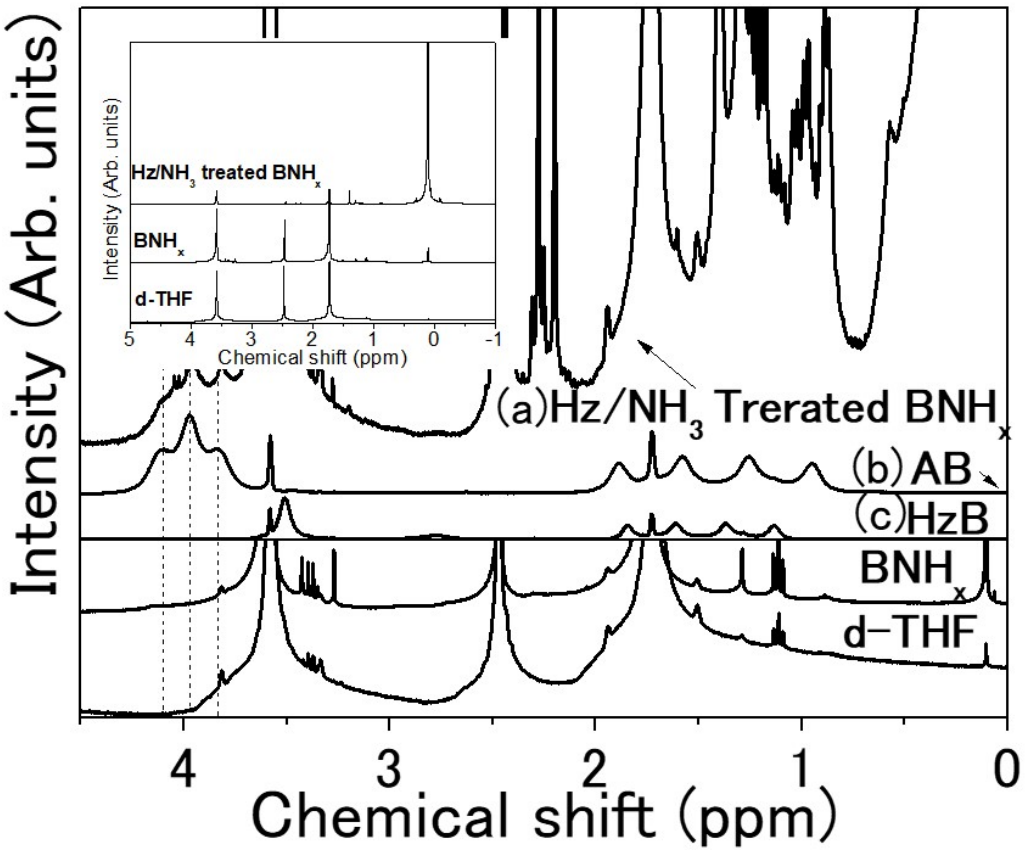

Figure S2. ^{1}H solution NMR of BNH_x spectra (**a**) after and (**b**) before the Hz/NH_3 treatment together with AB, hydrazine borane (HzB), and d-THF as references. Inset shows the full scale of BNH_x before and after the treatment spectra with d-THF spectrum.

3. XRD Profiles

XRD profiles of BNH_x before and after Hz/NH_3 treatment are shown in Figure S3. A peak corresponding to B_3N_3 ring structure (*hklm* = 0002) of h-BN at 27° marked by arrow is observed in both profiles. All broad peaks in both profiles are background of protections from air ((a) polyimide film at 12–30° and (b) Be doom at 20–30°).

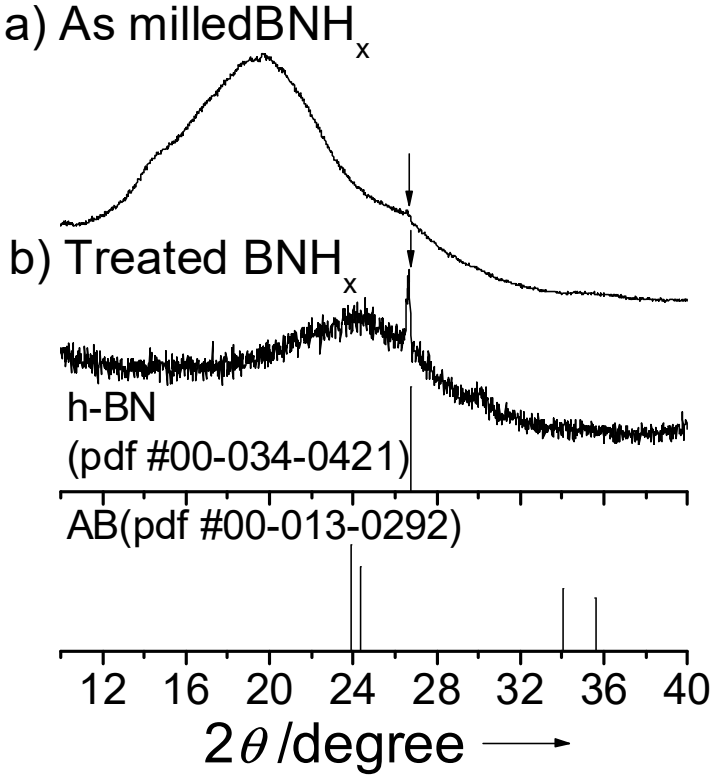

Figure S3. XRD profiles of BNH_x (**a**) before and (**b**) after the Hz/NH_3 treatment together with h-BN and AB patterns.

4. FT-IR Spectra

FT-IR spectra of BNH_x has strong N-H (~3500 cm^{-1}), B-H (~2500 cm^{-1}), and B-N (~1500 cm^{-1}) bonds. Residue of BNH_x after the treatment increases N-H peak and decreases B-H bond.

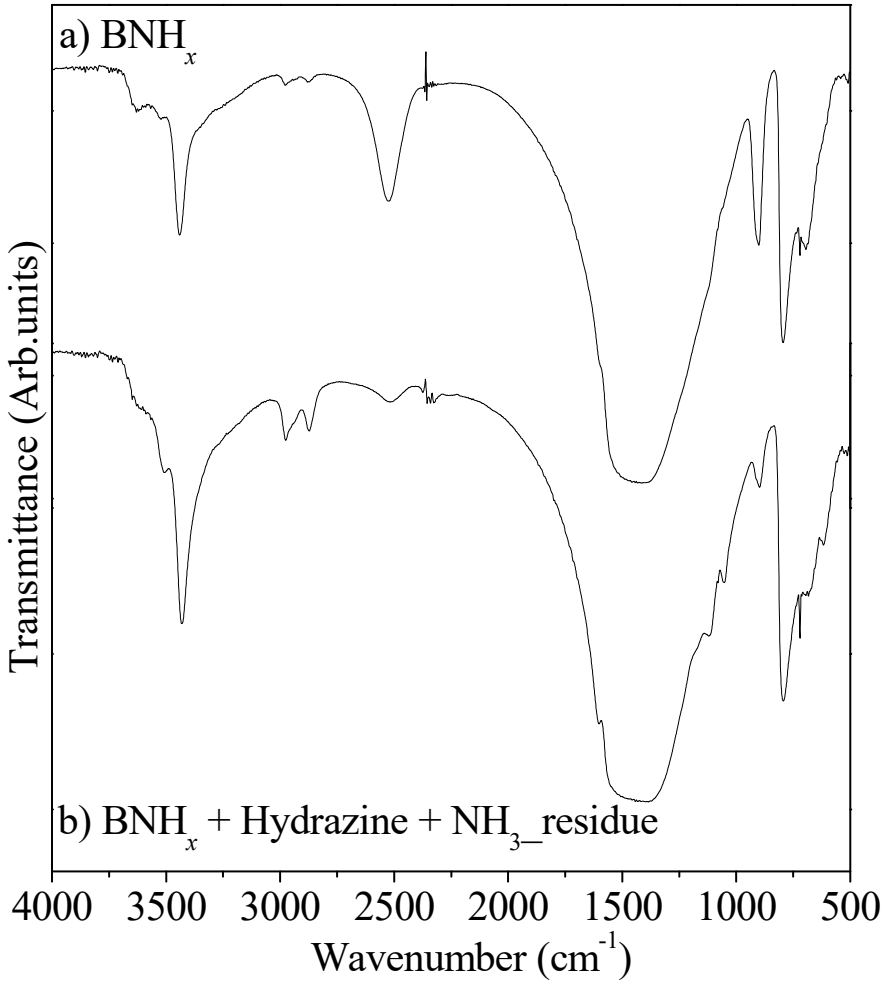

Figure S4. FT-IR spectra of BNH_x and N_2H_4/NH_3 treated BNH_x without AB.