

Electronic Supplementary Information

## Simulations of synthesis of the boron-nitride nanostructures in a hot, high pressure gas volume

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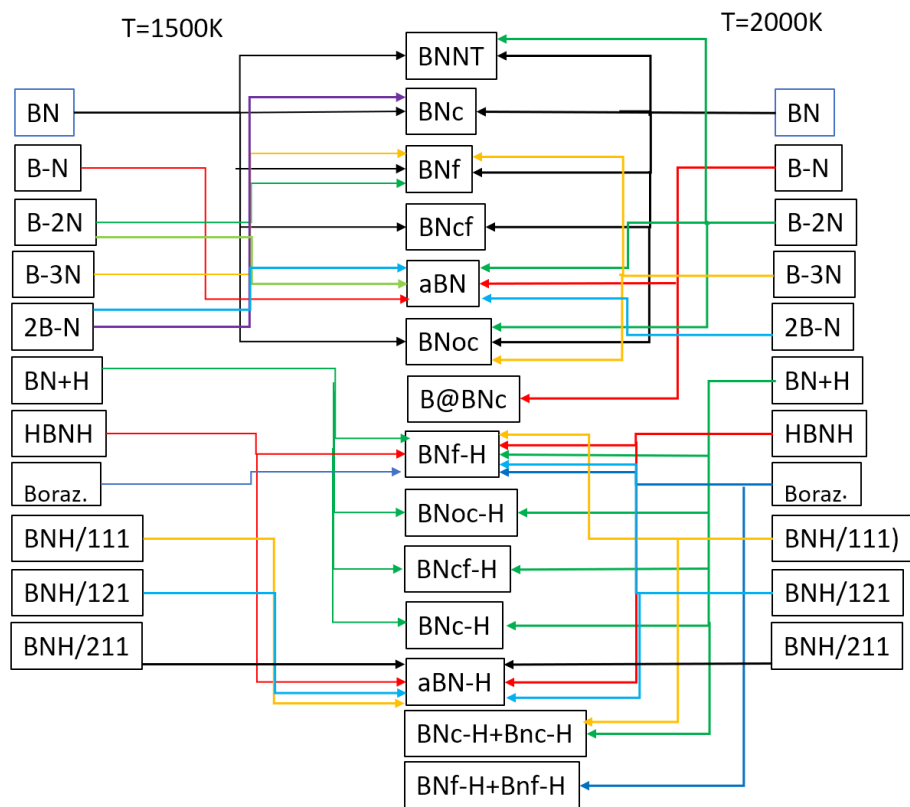
### Table of contents

**Fig. S1** Precursor - product map of the nanosynthesis products from various precursor configurations, at T=1500 K and T=2000 K.

**Fig. S2** Evolution of diatomic molecules from initial mixture of BN molecules and H atoms (in ratio of 4:1) at 2000 K and 6000 K.

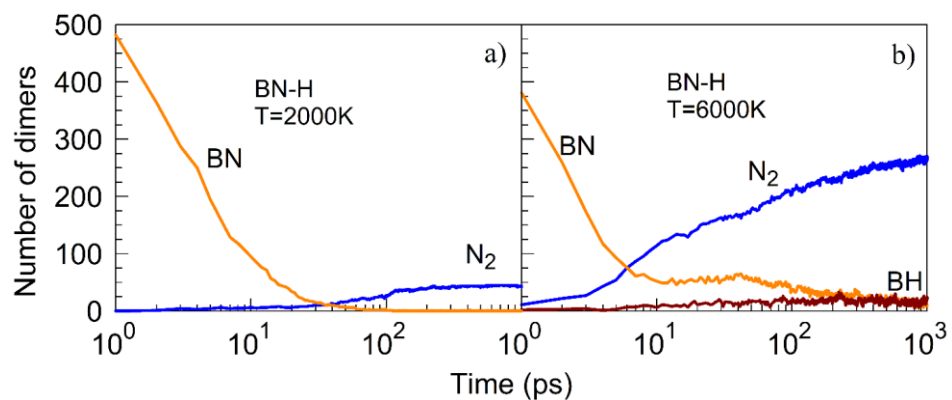
**Fig. S3** Size distribution and atomic content of the clusters, larger than 10 atoms, formed by BN-H precursors at various temperatures, after 1 ns.

**Fig. S4** Number of ideally hybridized sp, sp<sup>2</sup> and sp<sup>3</sup> atoms for B (pink) and N (blue) at (a) 2000K and (b) 4000K, as functions of time for BN-H precursor system. Probabilities of formation of (c) sp, (d) sp<sup>2</sup> and (e) sp<sup>3</sup> B and N atoms at various temperatures, as functions of time.



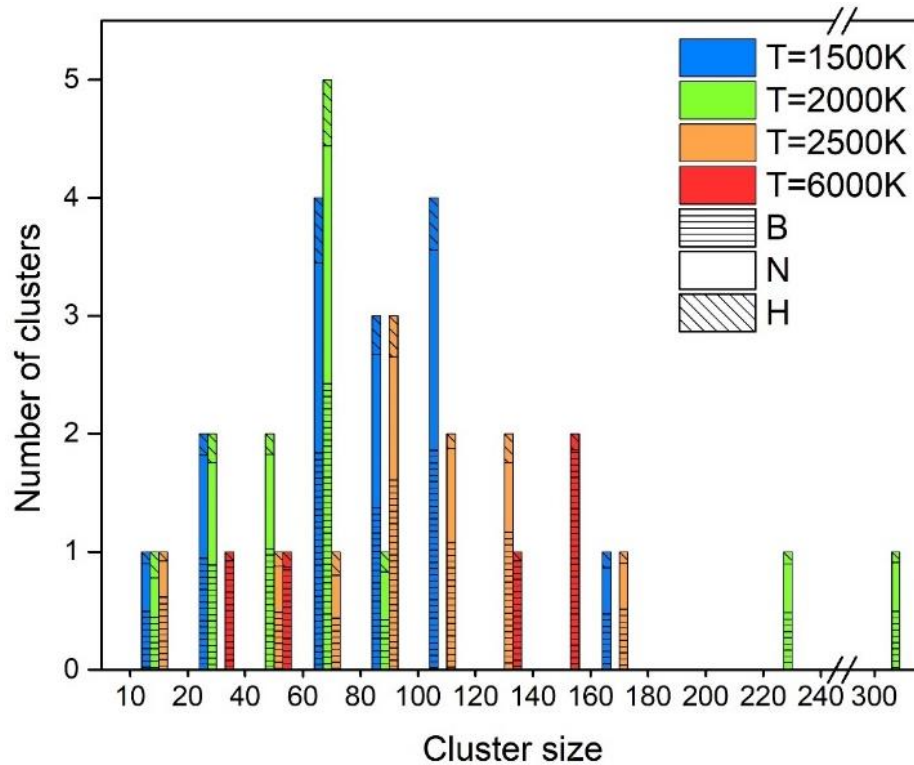
**Fig. S1** Precursor - product map of the nanosynthesis products from various precursor configurations, at  $T=1500\text{ K}$  and  $T=2000\text{ K}$ .

The precursor configurations are denoted by labels specified in Table 1, and products are in the same labels as shown in Fig. 1. Not all structures of Fig. 1 are shown here, because some of the structures only form at high temperatures, such as aB (amorphous boron cluster).



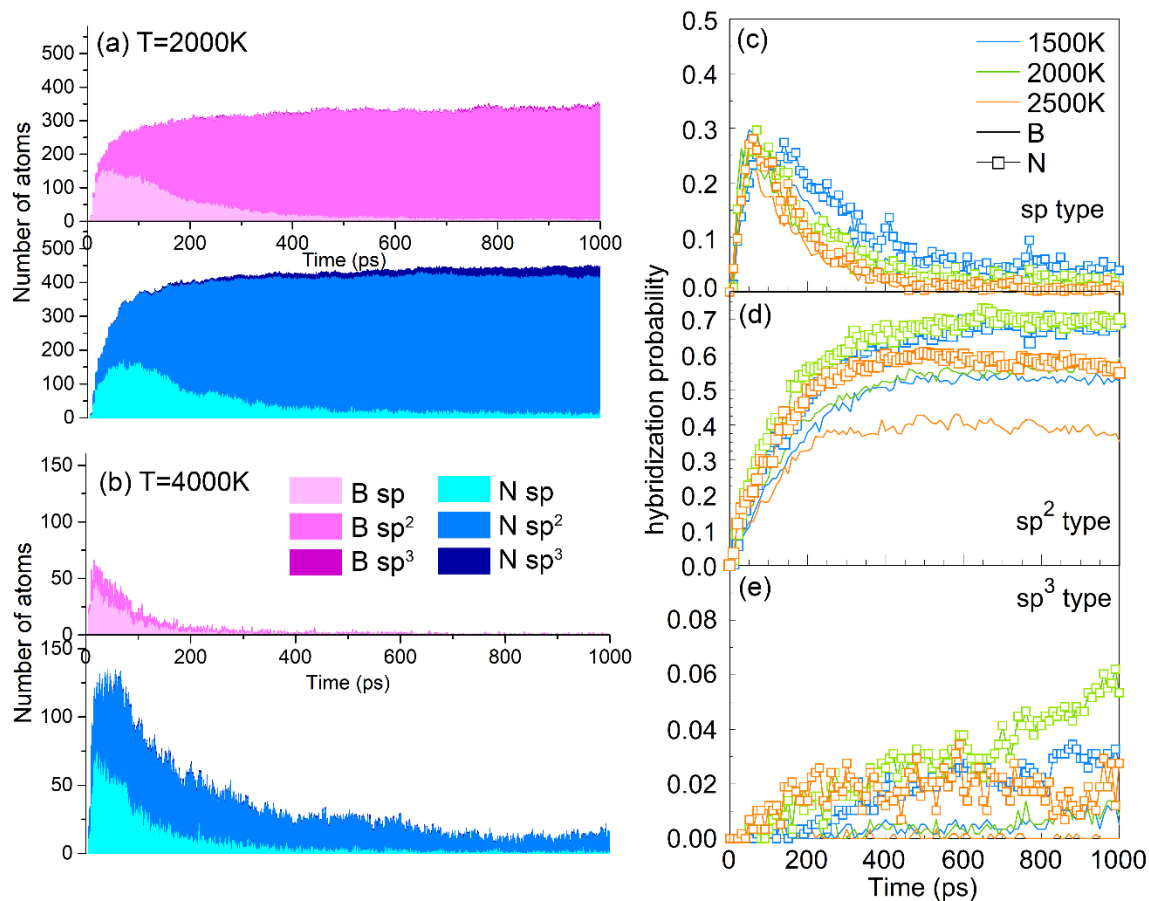
**Fig. S2** Evolution of diatomic molecules in initial mixture of BN molecules and H atoms (starting in ratio of 4:1) at 2000 K and 6000 K.

Evolution of BN and  $N_2$  molecules for BN-H precursor configuration is similar to the evolution of BN precursor configuration. At 2000 K, number of BN decreases as they are incorporated into the BNNSs. But at 6000 K, the incorporation of BN into chains and BNNSs is suppressed, and the majority of BN precursors dissociate, leading to significant association into  $N_2$  molecules. Addition of H contribute to the formation of BH dimers at 6000 K.



**Fig. S3** Size distribution and atomic content of the clusters (larger than 10 atoms), formed by BN-H precursors at various temperatures, at  $t=1$  ns.

Content of B in the clusters dominates over N and H and increases as the temperature increases. The presence of H suppresses agglomeration of small boron clusters into larger ones at 6000 K, as they adsorb on the external surface of boron clusters. This explains the smaller size of boron clusters formed by BN-H precursor configuration, as compared with those formed by BN precursor configuration at 6000 K.



**Fig. S4** Number of ideally hybridized  $sp$ ,  $sp^2$  and  $sp^3$  atoms for B (pink) and N (blue) at (a) 2000K and (b) 4000K, as functions of time for BN-H precursor system. Probabilities of formation of (c)  $sp$ , (d)  $sp^2$  and (e)  $sp^3$  hybridized B and N atoms at various temperatures, as functions of time. As indicated in the legend, lines present B atoms, while symbols (squares) are for N atoms.

The content of  $sp^2$  (in Fig. d) is by far larger than final  $sp^3$  and  $sp$  hybrids, for both B and N atoms. Difference of N and B  $sp^2$  hybrids is proportional to the number of defects in the structures. Initially large number of  $sp$  hybrids indicates evolution of the structures by initially forming the chains, which branch and reorganize into flake and cage structures.