Cui, Wang et al., J. Mater. Chem., 2010, DOI: 10.1039/b920881j

Supplementary Information

S-1 Verifying the reaction mechanism by examining the solid and gaseous byproducts

In order to examine the proposed mechanism of the solid state metathesis reaction, we have examined the unwashed solid product by XRD, and the gaseous byproducts were tested by FTIR. When NH_4BF_4 and NaN_3 reacted at 300 ˚C without adding sulfur, no other solid products can be detected by XRD except hBN and NaF (see Fig. S-1(a)). Besides, among the gaseous byproducts, only NH_3 was found from the FTIR spectrum (see Fig. S-2(b)), thus no other gases with polar molecules formed during the reaction process. Considering these facts and the related literatures, the overall reaction process should be:

$$2NH_4BF_4+8NaN_3 \rightarrow 2BN+8NaF+11N_2+2NH_3+H_2$$

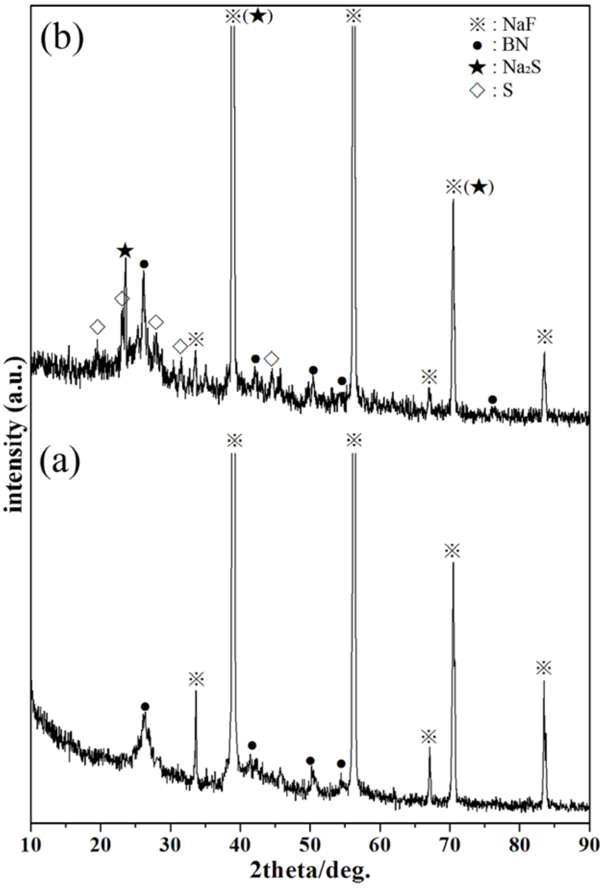

Fig. S-1 XRD patterns of unwashed solid product. (a) Product prepared by reacting NH_4BF_4 and NaN_3 at 300 ˚C for 1 h without sulfur. (b) The product obtained by reacting NH_4BF_4, NaN_3 and S at 250 ˚C for 20 h. (BN, JCPDS, No. 45-0896; NaF, JCPDS, No. 36-1455; Na_2S, JCPDS, No. 65-2995; S, JCPDS, No. 83-2285).

However, when sulfur was introduced into the reactants, it should react with NaN_3 to form Na_2S at first, releasing large amount of heat. Then the reaction between NH_4BF_4 and NaN_3 was driven by the released heat and BN formed, although the apparent reaction temperature (250 ˚C) was lower than the decomposing temperature of NH_4BF_4 (>307 ˚C) [S-1] and NaN_3 (>283 ˚C) [S-2]. As a result, all the hBN, NaF, Na_2S and S were detected by XRD in the unwashed solid product (Fig. S-1(b)). Furthermore, NH_3 was the only gaseous byproduct detected by FTIR (Fig. S-2(c)). So, it should be reasonable to believe that the overall reaction process when sulfur was introduced is as follows:

$$S+2NaN_3 \longrightarrow Na_2S+3N_2+\mathit{heat}$$

$$2NH_4BF_4+8NaN_3 \xrightarrow{heat} 2BN+8NaF+NH_3+H_2+11N_2$$

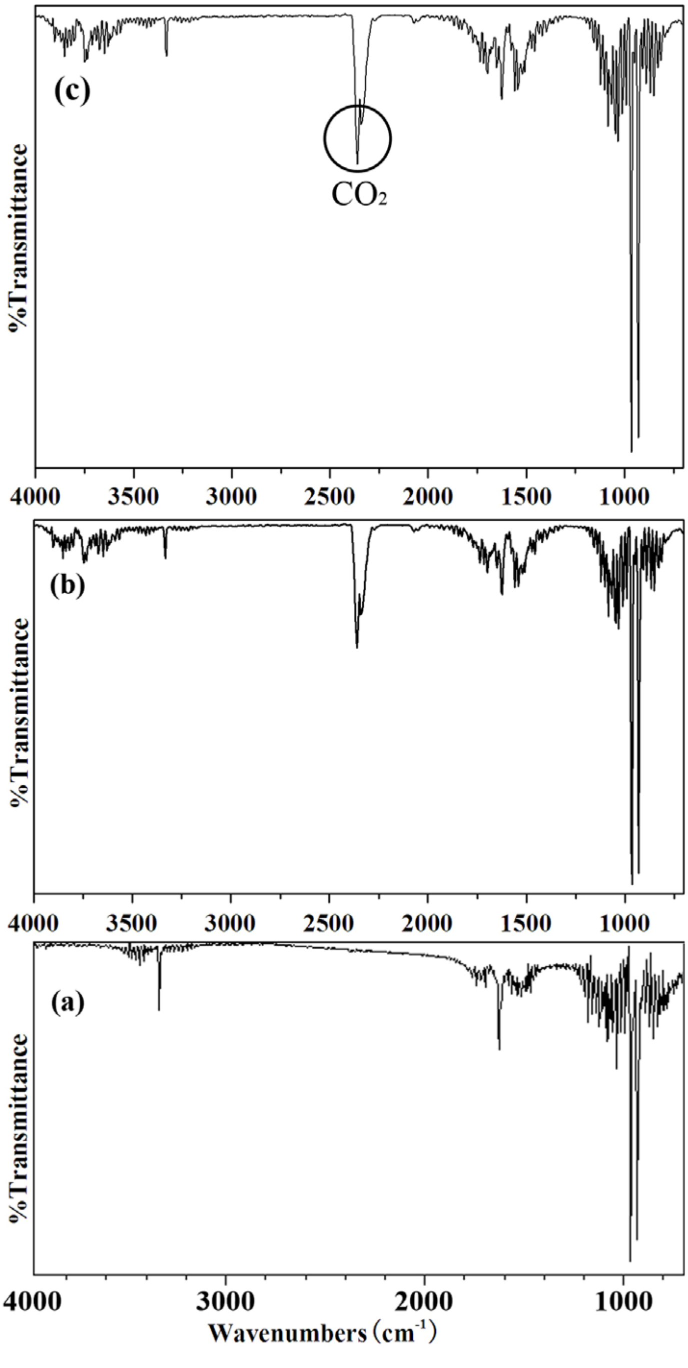

Fig. S-2 FTIR spectra of gaseous byproducts formed during the reaction. (a) FTIR spectrum of pure NH_3 [S-3]. (b) Gaseous byproduct formed by reacting NH_4BF_4 and NaN_3 at 300 °C for 1 h without sulfur. (c) Gaseous byproduct formed by reacting NH_4BF_4, NaN_3 and S at 250 °C for 20 h. Only NH_3 gas can be detected by FTIR, and H_2O and CO_2 come from the atmosphere.

S-2 Raman spectrum of sample S12 (Table 1)

Fig. S-3 presents the Raman spectrum of sample S12. In this figure, the sharp peak at 1365 cm^{-1} with a full-width at half maximum (FWHM) of ~10 cm^{-1}, can be indexed to the E_{2g} mode of hBN [S-4]. In contrast, tBN is a sp^2-like BN with low-ordering degree, and its Raman spectrum has not been reported up to now. So, it is generally believed that Raman spectrum can be used to distinguish hBN and tBN.

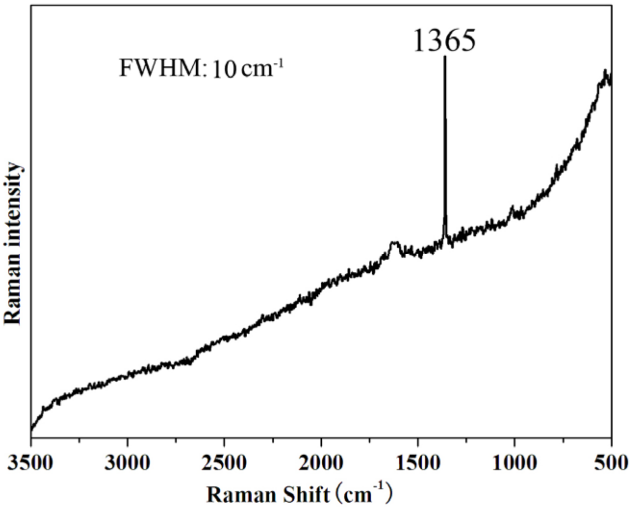

Fig. S-3 Raman spectrum of BN sample S12.

S-3 Synthesizing hBN nanoparticles using $NaBF_4$ and $NaBH_4$ as the boron sources

1. Experimental

10 mmol $NaBF_4$ (or $NaBH_4$), 30 mmol NaN_3 and 20 mmol S were mixed together and ground thoroughly, then the mixture was pressed into pellets under a pressure of 450 MPa. Whereafter, the pellets were placed in an N_2-flowing glove box (the concentration of both moisture and oxygen was less than 1 ppm) for 24 h to eliminate the adsorbed water and oxygen, followed by sealing the pellets into an autoclave. Afterwards, the autoclave was heated at a rate of 3 ˚C/min to 300 ˚C / 350 ˚C and kept constant for 24 h, and then cooled to room temperature naturally. Finally, the product was rinsed with hydrochloric acid (HCl) to eliminate the iron-containing impurities, and the resultant solid products were further washed with benzene and deionized water successively to remove the remaining sulfur and water soluble salts. After heating the product at 80 ˚C for 8 h, white hBN powder can be obtained.

2. Characterization of the samples

The samples were mainly characterized by FTIR and SEM. On the FTIR spectra in Fig. S-4, only the characteristic absorption peaks of hBN (1382~1387 cm^{-1} and 813~816 cm^{-1}) can be observed, which reveals that all the samples should be composed of pure hBN. On the other hand, the SEM and TEM images of the samples (Fig. S-5) indicated that the BN nanoparticles are in spherical shape and they are quite uniform in size.

The investigation of synthesizing BN nanoparticles using different boron- and nitrogen- sources via the modified solid state reaction route is still under way.

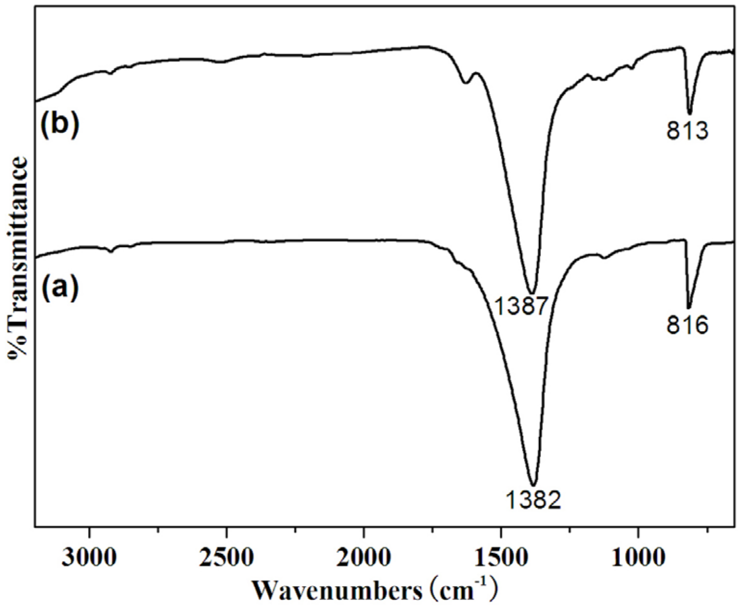

Fig. S-4 FTIR spectra of BN samples. (a) reaction of $NaBF_4$, NaN_3 and S at 300 ˚C. (b) reaction of $NaBH_4$, NaN_3 and S at 350 ˚C.

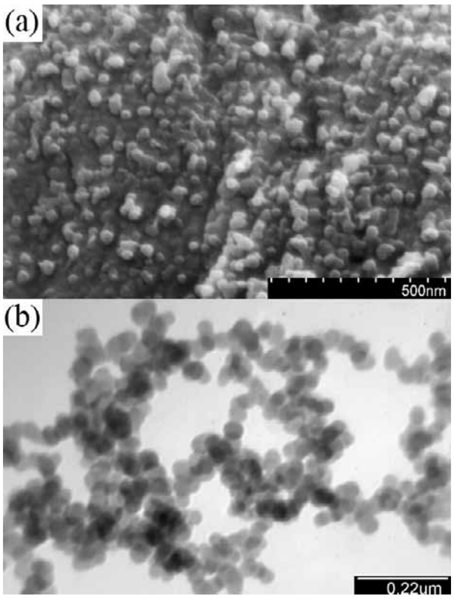

Fig. S-5 SEM and TEM images of BN nanoparticles prepared using different boron sources. (a) prepared by reacting $NaBF_4$, NaN_3 and S at 300 ˚C, (b) prepared by reacting $NaBH_4$, NaN_3 and S at 350 ˚C.

References:

S-1. D. Göbbels, G. Meyer, *Z. Anorg. Allg. Chem.*, 2002, **628**, 1799-1805.

S-2. B. E. Douglas, D. H. McDaniel, J. J. Alexander, *Concepts and Model of Inorganic Chemistry, 2nd Edition*, Wiley, New York 1983.

S-3. NIST Chemistry WebBook (http://webbook.nist.gov/chemistry/).

S-4. Y. Kubota, K. Watanabe, O. Tsuda, T. Taniguchi, *Science*, 2007, 317, 932-934.