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Supplementary Information

Few-atomic-layer boron nitride nanosheets synthesized in solid thermal waves

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1. Thermochemical analysis:

Prior to the combustion experiments, a preliminary thermochemical analysis was conducted to calculate the composition of the equilibrium products for the $B_2O_3+(3+0.5k)Mg+kNH_4Cl$ system for k=5 as a function of the temperature. The calculation of the equilibrium concentrations of all reaction species was performed using the commercially available HSC Chemistry 6.0 Windows software package (Outokumpu HSC Chemistry for Windows). The phases present and their quantities were then calculated by the software, based on the Gibbs free energy minimization rationale. As a typical example, the results of the calculation for k=5 are shown in Fig. 1Sa,b (here, to show the concentration of the reaction species, b is the magnified part of Fig. 1Sa). The main solid reaction species involved in the activated NH₄Cl activated are BN, MgCl₂, and MgO. A small amount of Mg₃N₂ phase can also be detected in Fig. 1S,b. Above 1000 °C the concentration of BN shows a decreasing tendency, giving rise to the Mg₃N₂ phase. The gas phase contains H₂, N₂, and NH₃ species; however, at elevated temperatures (>700 °C) NH₃ is decomposed into H₂ and N₂. Since MgO is soluble in HCl, after acid leaching and water purification, single phase BN is expected to be obtained from the given system.



Fig. 1S. Thermochemical analysis of $B_2O_3+(3+0.5k)Mg+kNH_4Cl$ system for k=5.

2. Photoluminescence characteristics of BN sheets

The high quality of the combustion synthesized *h*-BN nanosheets makes them an excellent candidate for both optoelectronic and electronic applications. To investigate the optical properties, the emission spectra of BN nanosheets were determined under the excitation of UV light. The photoluminescence spectra (excitation and emission) of h-BN nanoplates (for different excitation energies), measured at room temperature, are shown in Fig. 2S. The excitation energy for each curve is listed in the inset. The strongest emission, located at around 319 nm in the PL spectrum, indicates the fine multi-phonon features at 307.7, 319, 331, and 350 nm. The phonon frequencies involved in this transition are 1366.4 cm⁻¹ and 1379 cm⁻¹, consistent with the B-N E_{2g} vibration mode, which was measured by Raman and FTIR spectroscopy (Figs. 6 and 7). The intensity of the spectra gradually changes due to the excitation energy. The highest emission intensity was recorded under 230 nm excitation. However, there is no change in the peak position versus excitation wavelength. A broad band at 319 nm often appeared in the BN samples, for instance in the BN nanotubes, nanorods, and whiskers. This broad band was attributed to either impurity and vacancy defect centres or to radiative excitonic dark state; however, its detailed origin is still unclear.¹⁻⁵ According to the excitation spectrum shown in Fig. 2S,b ($\lambda em=320$ nm), only one adsorption band located at 230 nm can be found. Moreover, the strength of this band was found to slightly decrease with increasing NH₄Cl concentration.



Fig. 2S. Photoluminescence spectra of h-BN powder measured at room temperature under the respective excitation energies listed in the inset.

3. FE-SEM images and EDX analysis

Fig. 3 shows high resolution FE-SEM images of h-BN sheets synthesized for k=3, 5, and 7. One can see that with the increase of the value of k from 3 to 7 mol, the lateral dimension of the individual nanosheets decreases from several micrometers to submicrometer size. BN nanosheets are well dispersed, with very small thickness and smooth surface. The sheets show good crystallinity and perfect B and N stoichiometry, as confirmed by electron dispersive X-ray spectroscopy (EDX).



Fig. 3S. SEM morphology of h-BN sheets according to the concentration of NH_4Cl in the initial mixture (*k*).

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