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## COMMUNICATION

## Supercritical Fluids Processing: A Rapid, One-Pot Exfoliation for Surfactant-Free Hexagonal Boron Nitride Nanosheets

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**We demonstrate a simple, rapid, one-pot exfoliation of *h*-boron nitride for generating surfactant-free nanosheets from a supercritical mixture of *iso*-propanol and water. The product was characterized by powder X-ray diffraction, UV-visible, FT-IR, Field-emission scanning electron microscope and Raman spectroscopy. That the sample comprised few-layer BN nanosheets was confirmed by AFM and TEM analyses.**

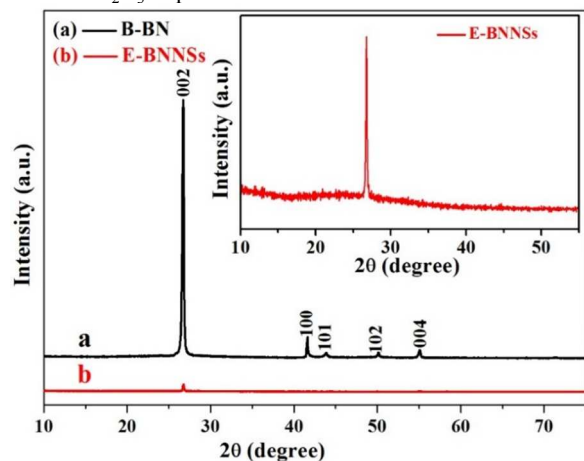
Boron nitride (BN), a fascinating two-dimensional layered material such as graphene, MoS<sub>2</sub> and WS<sub>2</sub>, exists in two major forms, hexagonal boron nitride (*h*-BN) and cubic boron nitride (*c*-BN). The structure of single layer *h*-BN nanosheets is analogous to that of graphene, and is often referred to as 'white graphene'. In this structure, boron and nitrogen atoms are arranged alternatively in a honey-comb lattice with *sp*<sup>2</sup> bonding.<sup>1</sup> *c*-BN, on the other hand, has a diamond-like structure and is the second hardest known material to date. Within the *h*-BN layer, boron and nitrogen atoms are bound by strong covalent bonding while the adjacent layers are held together by van der Waals forces. The interlayer spacing between the layers in graphite is 3.33~3.35Å,<sup>2</sup> whereas in *h*-BN it is 3.30~3.33Å.<sup>3</sup> Electrostatic attraction between oppositely charged atomic centres in adjacent *h*-BN layers results in a reduction in the interlayer distance in *h*-BN. Such polarity an interaction is absent in than graphite is attributed to polarity changes in the B-N bond in *h*-BN. The *h*-BN is an insulator owing to the wide band gap of 5.9 eV and exhibits many unique properties such as high thermal stability, low dielectric constant, high mechanical strength, high thermal conductivity, high hardness, and high corrosion resistance. These features can be utilized in various fields such as optoelectronic technologies,<sup>4</sup> tunnel devices and field effect transistors.<sup>5</sup> The properties of BN nanosheets can be altered by doping with other elements, thereby it becomes semiconductor and performs similar to graphene on the fabrication of nano-electronic and nano-photonics devices. Recently, the developments on the synthesis of single or few-layered two dimensional inorganic materials has attracted much attention.<sup>6</sup> So

far, there are several methods including mechanical exfoliation,<sup>7,8</sup> liquid exfoliation by sonication, chemical exfoliation, surface segregation of catalyst alloy and chemical vapour deposition (CVD) has been reported.<sup>9</sup> The surfactant-free liquid exfoliation of layered materials of inorganic graphene analogous (IGAs) in volatile solvents is a very challenging task. Thus, preparation of few layer BN nanosheets has gathered much attention, recently. Coleman *et al* succeeded in the preparation of IGAs in various organic solvents with the assistance of bath sonication including non-volatile solvents.<sup>10</sup> Recently, there is a growing interest to find new methods for the preparation of good quality *h*-BN layers. Here, we report rapid one-pot exfoliation of surfactant-free *h*-BN by supercritical fluids processing. When the temperature and pressure of the solvent is increased above its supercritical temperature and pressure, the density of solvent diminishes very rapidly that renders gas-like diffusion with liquid-like solvent properties to the fluids. Supercritical fluids processing has several advantages like, short reaction time, homogeneous medium. It has been successfully utilized for the synthesis of several metal oxides, sulphides and mixed metal oxides.<sup>11</sup> However, it has not been explored for 2D layered materials except the direct exfoliation of graphene from graphite flakes and its functionalization.<sup>12</sup> Recent attempts for the preparation of 2D layered materials and several selected attempts for the preparation of metal oxide nanoparticles have been provided in Table S1 (Supporting information). To the best of our knowledge, the direct exfoliation of BN nanosheets using supercritical fluids processing is not yet attempted. The short reaction time (15 min) and surfactant-free exfoliation makes this method as unique and promising for scaling-up for viable applications compared to other methods. The advantages of this method over other methods have been compared in Table S2 (Supporting information). Here we have used isopropanol-water mixture for the exfoliation and dispersion of BN nanosheets based on the previous experimental report on mixed solvent strategy for the better the exfoliation and dispersion of inorganic graphene analogues.<sup>13</sup>

In a typical exfoliation process, 200 mg of BN powder (Merck, 99.5%) was dispersed in 25 mL isopropanol-water (1:1vol %)

mixture by 5 min sonication. The resulting solution was poured into stainless steel reactor vessel (35 mL capacity) and sealed. Then, the sealed reactor was placed in a pre-heated (400 °C) vertical tubular furnace for 15 min followed by quenching in an ice cold water bath. The exfoliated solution containing the BN nanosheets was collected and subjected to centrifugation at 2000 rpm for 20 min. The resulting supernatant solution containing the E-BNNSs was collected for further studies.

Fig. 1 shows the PXRD pattern of pristine BN and E-BNNSs measured using PAN analytical X-ray diffractometer with CuK $\alpha$  radiation (1.5418 Å). For the pristine BN powder, the observed diffraction lines at  $2\theta = 26.72^\circ$ ,  $41.61^\circ$ ,  $43.87^\circ$ ,  $50.16^\circ$  and  $55.11^\circ$  with lattice parameters  $a = b = 2.5040$  and  $c = 6.6612$  Å are readily indexed to (002), (100), (101), (102) and (004) planes of *h*-BN (JCPDS Card No: 01-073-2095), respectively. Whereas, the E-BNNSs shows only one line with very low intensity at  $2\theta = 26.72^\circ$  corresponding to 002 plane and a *d* spacing of 3.33 Å (Fig. 1, Inset). The absence of the other diffraction lines indicates the formation of few layers E-BNNSs with defect free i.e., no surface oxidation. When the heating temperature and reaction time increased further, the surface oxidation takes place on the *h*-BN nanosheets and the formation of B<sub>2</sub>O<sub>3</sub> impurities was observed.

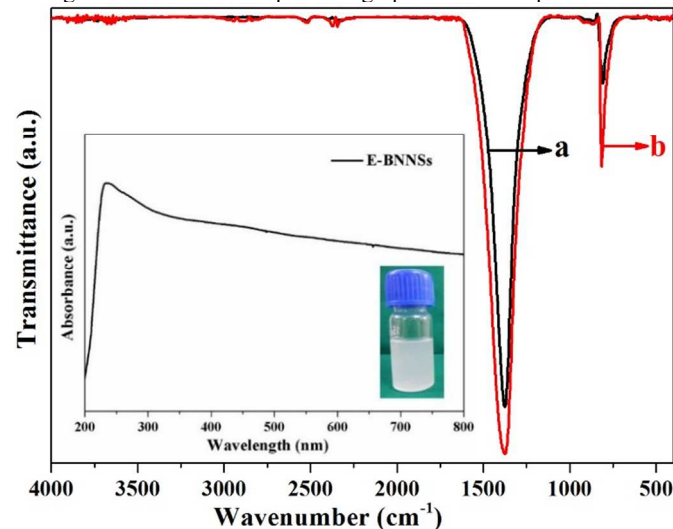


**Fig. 1** XRD patterns of (a) pristine BN powder and (b) E-BNNSs. XRD profile of E-BNNSs (inset)

FT-IR spectroscopy was used as a primary tool to determine the surface functional groups and bonding nature in *h*-BN. In Fig. 2, FT-IR spectra of *h*-BN powder and E-BNNSs were compared from 400-4000 cm<sup>-1</sup> region. The pristine *h*-BN powder exhibits two sharp absorption peaks at 1377 and 810 cm<sup>-1</sup> corresponding to in-plane B-N stretching vibration of sp<sup>2</sup>-bonded *h*-BN and out of plane B-N-B bending vibration, respectively. The E-BNNSs also shows two sharp absorption peaks at 1375 and 816 cm<sup>-1</sup> but the relative peak intensity of in-plane B-N stretching to out of plane B-N-B bending vibration is decreased significantly for the E-BNNSs compared to pristine *h*-BN powder. It could be attributed to the smaller the thickness of E-BNNSs compared to *h*-BN powder.<sup>14</sup> It should be noted that there is no additional peaks were found in the spectrum of E-BNNSs and it implies that the exfoliated BN sheets are free of foreign groups/surface functional groups. UV-visible absorption spectrum of E-BNNSs in isopropanol/water mixture and a digital photograph of E-BNNSs dispersion are shown in Fig. 2 (inset). The single absorption peak located at 236 nm corresponding to an optical band gap of ~ 5.26 eV is in good agreement with reported literature of exfoliated BN nanosheets.<sup>15</sup> It was further confirmed in solid state mode on quartz substrate (Fig S1). The dispersion of E-BNNSs solution is stable for more than few months without any significant aggregation or precipitation. It is worthy to note there that no

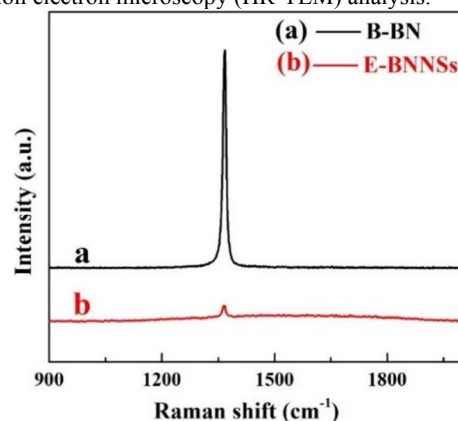
surfactants or stabilizing agents were added during the exfoliation and after the exfoliation.

Raman spectroscopy is a powerful analytical tool to determine the number of layers present in E-BNNSs. Raman spectrum of *h*-BN powder and E-BNNSs was measured using a laser wavelength ( $\lambda = 632.8$  nm) and shown in Fig. 3. The pristine *h*-BN powder shows a peak at 1367.4 cm<sup>-1</sup> with high intensity due to the E<sub>2g</sub> phonon, analogous to the G band peak in graphene.<sup>16</sup> This peak becomes



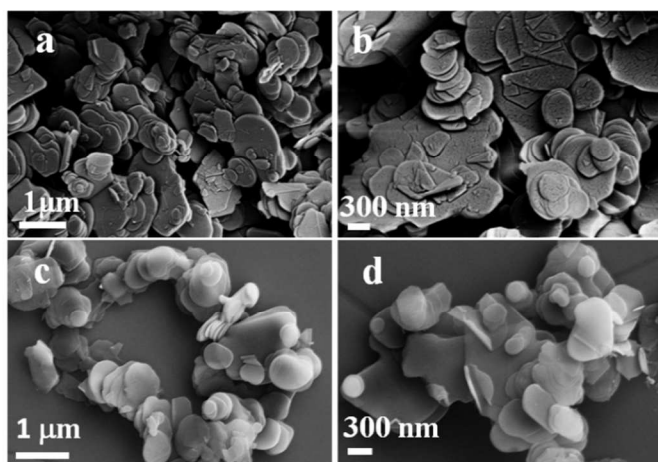
**Fig. 2** FT-IR spectra of pristine BN powder (a) and E-BNNSs (b). (inset) UV spectrum of E-BNNSs in isopropanol-water mixture.

progressively weaker when the number of layer decreases and a red shift or blue shift was observed in peak position depending upon the quality of exfoliation.<sup>17</sup> Generally, red shift was mainly observed for bilayers or few layers since the interactions between the neighbouring layers in few layered nanosheets which cause a small elongation of the B-N bonds and consequently a softening of the phonons.<sup>18</sup> Whereas, monolayer shows blue shifts typically between 2-4 cm<sup>-1</sup> which is due to a slightly shorter B-N bond in the exfoliated or isolated monolayers and therefore hardening of the phonon mode was expected.<sup>8</sup> The observed red shifted peak at 1365.5 cm<sup>-1</sup> for the E-BNNSs is in good agreement with previous reported literature and reveals the presence of few layers in E-BNNSs. In addition, the FWHM increases from 11.3 cm<sup>-1</sup> to 12.6 cm<sup>-1</sup> for the E-BNNSs compared to *h*-BN powder. This also confirmed the presence of few-layer *h*-BN nanosheets in E-BNNSs. The exfoliation of BN nanosheets by the supercritical fluids was further confirmed using FE-SEM, atomic force microscopy (AFM) and high resolution transmission electron microscopy (HR-TEM) analysis.



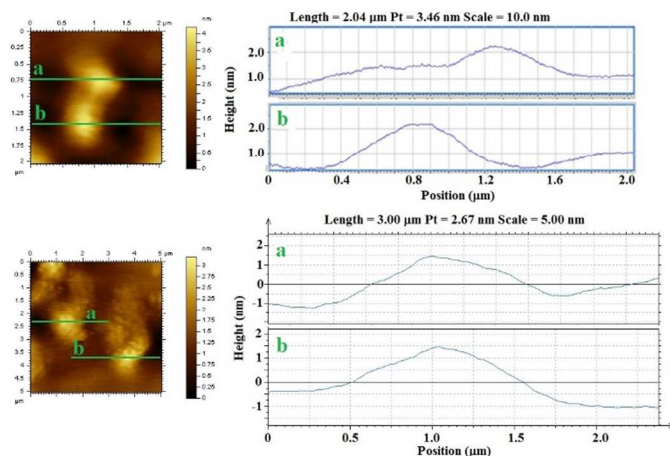
**Fig. 3** Raman spectrum of pristine BN and E-BNNSs.





**Fig. 4** FE-SEM images of the starting BN powder (a-b) and E-BNNSs (c-d).

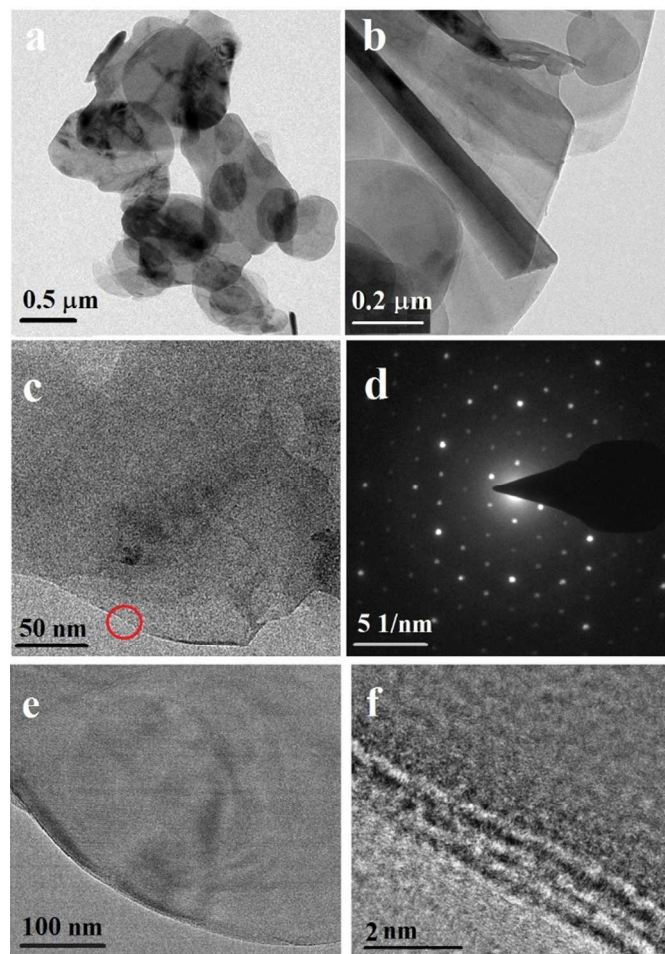
Fig. 4(a&b) and (c&d) represents the FE-SEM images of *h*-BN powder and E-BNNSs, respectively. It can be clearly seen from images that the *h*-BN powder has disk like morphology with lateral size of  $\sim 0.5$ - $1 \mu\text{m}$  and thickness of  $100$ - $200 \text{ nm}$  that are stacked together. Certainly, the thickness of E-BNNSs was considerably reduced compared to *h*-BN powder due to the exfoliation by SCFs of isopropanol-water mixture. AFM images of E-BNNSs were acquired on  $\text{SiO}_2$  substrate after dropping a small volume of the E-BNNSs dispersion on silica substrate followed by removal of solvents by gentle evaporation. AFM image and height profile of E-BNNSs are shown in Fig. 5. The existence of few layer BN nanosheets could be clearly seen from the AFM images. The height profile measurements clearly indicates the existence of  $1$ - $2 \text{ nm}$  thick E-BNNSs on the substrate. This suggests that the obtained BN nanosheets consist of  $2$ - $3$  layers of BN nanosheets. It was further confirmed from the TEM images obtained by drying E-BNNSs dispersion on a carbon coated copper grids (Fig. 6)



**Fig. 5** AFM images and corresponding height profile of E-BNNSs on silica substrate.

At low magnification images (Fig 6a&b), formation of agglomerated E-BNNSs can be seen, the highly transparent nature indicates the existence of few layers of BN monolayer in the E-BNNSs that agglomerated during the drying process in TEM sample preparation. The existence of few layers in the E-BNNSs could be

clearly seen at high magnification image (Fig 6c). The hexagonal structure of E-BNNSs was further confirmed from the selected area electron diffraction (SAED) pattern (Fig 6d), which is in good agreement with the XRD pattern analysis and literature reports. HR-TEM images of an E-BNNSs are shown in Fig 6 (e&f). Fig 6f clearly indicates that the folded site of *h*-BN nanosheet comprises of three atomic layers. It is worthy to note here that we have obtained  $\sim 10\%$  yield of few layers ( $2$ - $3$  layers) *h*-BN nanosheets in the supernatant solution.



**Fig. 6** TEM images of (a-c) E-BNNSs at different magnifications and (d) corresponding SAED pattern of the region marked in fig. c. (e-f) HR-TEM images of E-BNNSs.

Surfactant-free BN nanosheets Exfoliated from pristine BN powder was demonstrated by a simple, rapid, one-pot supercritical fluids processing. The *iso*-propanol-water mixture was used as solvent and the exfoliation was achieved in a shortest reaction time of  $15 \text{ min}$ . The FT-IR and Raman spectroscopic analysis revealed the existence of defect free BN nanosheets. Formation of few layer BN nanosheets was confirmed by the AFM and TEM analysis. The unique features of the supercritical fluids, such as low interfacial tension, excellent wetting of surfaces and high diffusion coefficients leads this method as simple, scaleable, and convenient.

## Notes and references

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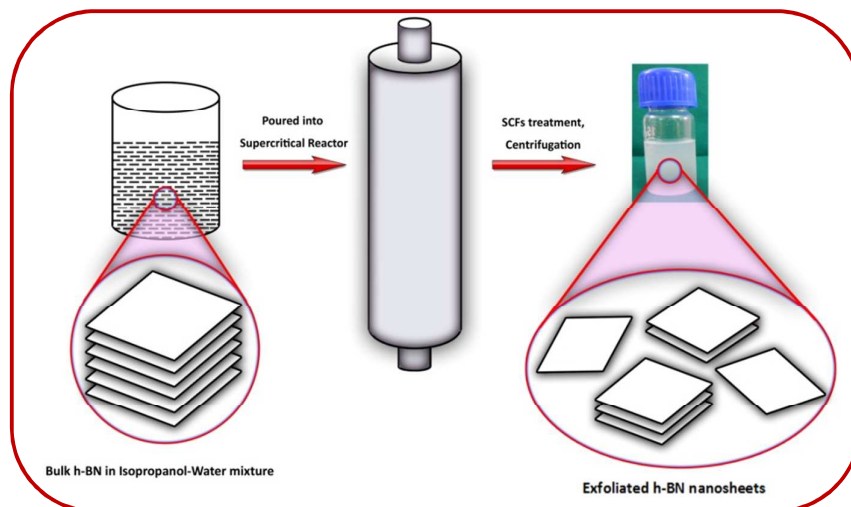
Detailed structural characterization, additional AFM images and corresponding height profile of bare silica substrate and E-BNNSs on silica substrate are available in the Electronic Supplementary Information (ESI): See DOI: 10.1039/c000000x/

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## Graphical abstract

### Supercritical Fluids Processing: A Rapid, One-Pot Exfoliation for Surfactant-Free Hexagonal Boron Nitride Nanosheets

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A simple, rapid, one-pot method for exfoliated surfactant-free few-layered *h*-boron nitride by supercritical fluid processing is demonstrated. The product was characterized by AFM, TEM and Raman analyses.