Electronic Supplementary information (ESI)

Functionality preservation with enhanced mechanical integrity in the nanocomposites of the metal-organic framework, ZIF-8, with BN nanosheets

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Experimental Section

Reagents and Chemicals: All the chemicals used in the synthesis were of high purity, and obtained from commercial sources. High purity (99.999 %) anhydrous ammonia was used for the synthesis of few-layer BN.

BN synthesis: Few layer boron nitride (BN) nanosheets were prepared by the reported procedure using boric acid and urea in 1:48 molar ratio and heating in ammonia atmosphere. (characterization is given below).[1]

Synthesis of ZIF-8 nanoparticles:ZIF-8 nanocrystals were prepared using a procedure reported by Wiebcke*et al.*[2] In a typical synthesis, 0.751 g (2.5 mmol) $Zn(NO_3)_2.6H_2O$ was dissolved in 50 ml methanol and 1.658 g (20 mmol) of 2-methylimidazole dissolved in 50 ml methanol was added to it slowly under constant stirring. The resulting solution was stirred for 12 hours. The product was centrifuged, washed properly with methanol and dried in 60 °C oven. The yield obtained was ~ 56 % based on zinc.

Synthesis of ZBN composites: Different mole ratios of BN (between 1 to 4) with respect to ZIF-8 were taken in methanol and sonicated for 90 minutes to form a uniform dispersion. Under constant stirring, $Zn(NO_3)_2.6H_2O$ was added and allowed to stir for ~10 min. 2-Methylimidazole dissolved in methanol was then added slowly. The remaining steps were similar to those employed in the synthesis of ZIF-8. The resulting composites with increasing BN content are denoted as ZBN-1, ZBN-2, ZBN-3 and ZBN-4.

Characterization: Powder X-ray diffraction (PXRD) patterns were recorded on Bruker D8 Discover using Cu-Kα radiation. FT-IR spectra were recorded on a Bruker IFS 66v/S spectrophotometer. Raman spectra of the samples were collected at several different locations in back scattering arrangement, using a 632.8 nm He-Ne laser in LabRam HR 800 spectrometer. TEM images were obtained using a JEOL JEM-3010 microscope at an accelerating voltage at 300 kV. Thermogravimetric analysis (TGA) was carried out in an oxygen atmosphere with a Metler Toledo TGA-850 at a heating rate of 3 °C/min. SEM images of samples were obtained from Nova Nano SEM 600, FEI Company. X-ray photoelectron spectra (XPS) were recorded using Omicron Nanotechnology Spectrometer with Mg Kα as the X-ray source. The high speed MAS ^{11}B solid state NMR spectra were collected at a frequency of 160.47 MHz using Bruker 500 MHz AVANCE III Solid-state FT-NMR Spectrometer at room temperature. ZrO_2 rotor and CPMG pulse sequence was used. Elemental analysis was carried out using Thermo FLASH 2000 elemental analyser.

Gas adsorption: Adsorption isotherms for N_2, and CO_2 (at 77K and 195 K) were carried out using *QUANTACHROME AUTOSORB-1C* analyser. Approximately 100 – 150 mg samples were activated at 433 K under vacuum for 12 h before the measurement.The amount of gas adsorbed was calculated from pressure difference (P_{cal} - P_{e}), where P_{cal} is the calculated pressure with no gas adsorption and P_{e} is the observed equilibrium pressure. All operations were computer-controlled and automatic.

Mechanical property measurements: As it was not possible to measure mechanical properties of powders, they were pelletized using the following procedure. 100 mg of powder was placed in a 12 mm diameter hardened stainless steel die and was heated to 160 °C where it was held for 30 min before loading to 10 kN at a rate of 1 mm/s (Zwick/Roell, Z-100). The load was held constant for 15 minutes. Subsequently, the sample was unloaded, cooled to room temperature and then the pellet was extracted from the die. The thickness of the mechanically robust pellets was approximately 0.9 mm. Before mechanical property measurements, PXRD pattern was recorded on all the pellets prepared to examine phase purity (Fig. 6). The diffraction patterns confirmed that hot-pressing procedure adopted did not alter the phases.

Mechanical properties of the nanocomposite pellets were evaluated by employing the nanoindentation technique using the Triboindenter (Hysitron, Minneapolis, USA). In these experiments, the applied load, P, and the corresponding depth of the penetration of the indenter, h,were collected evaluated. A Berkovich tip diamond indenter with the tip radius of 100 nm is used for the indentation. In all cases, the peak load, P_{max}, was maintained at 2 mN and the loading and unloading rates were 0.4 mN/s. The hold time at P_{max} was 5 s. A minimum of 30 indentations were performed on each pellet so to obtain statistically significant information. The *P-h* curves are analysed using the Oliver-Pharr method to extract the elastic modulus, *E*, and the hardness, *H*, of the samples.

References:

1 A. Nag, K. Raidongia, K. P. S. S. Hembram, R. Datta, U. V. Waghmare and C. N. R. Rao, *ACS Nano,* 2010, **4**, 1539.

2 J. Cravillon, S. Münzer, S.-J. Lohmeier, A. Feldhoff, K. Huber and M. Wiebcke, *Chem. Mater.,* 2009, **21**, 1410.

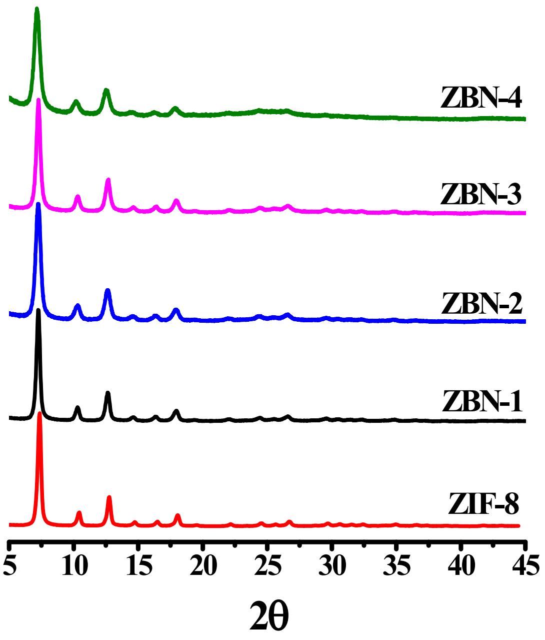

Fig. S1 PXRD patterns of ZIF-8 and the ZBN nanocomposites.

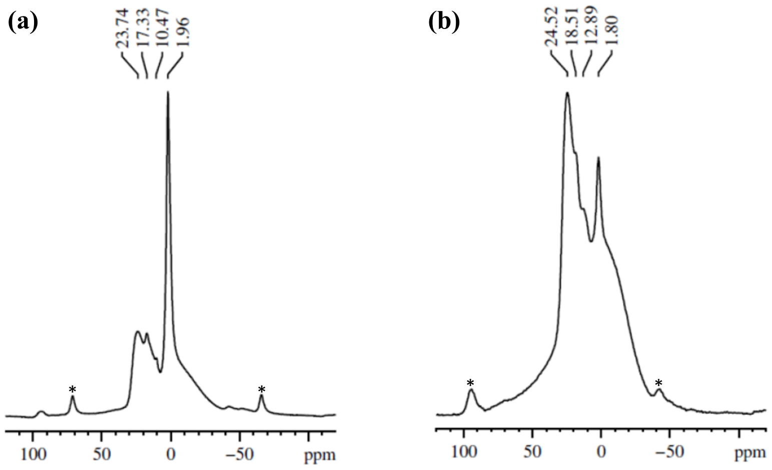

Fig. S2 160.47 MHz ^{11}B NMR spectra of (a) few layer BN and (b) ZBN-2 at 11 kHz MAS. Asterisk represents spinning sidebands.

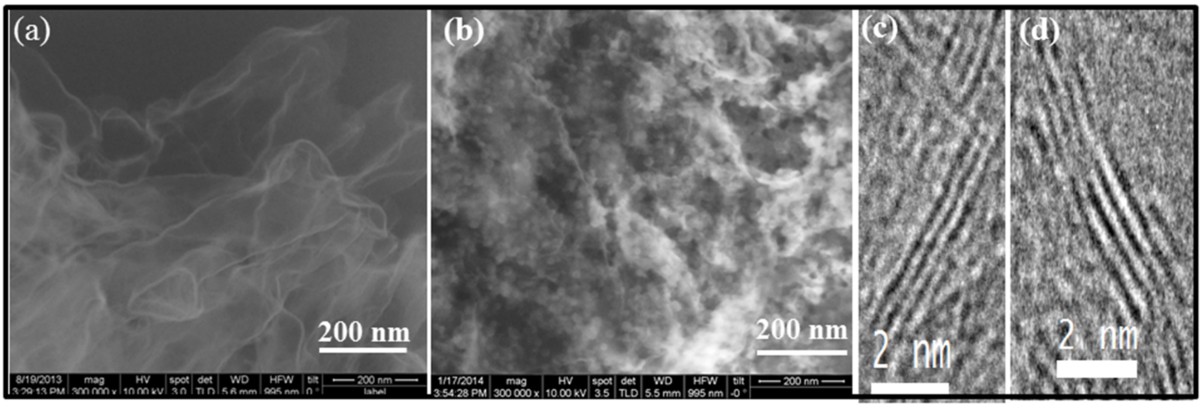

Fig. S3 (a) FESEM image of few-layer BN, (b) FESEM image of ZBN-4 and (c, d) HRTEM images of few layer-BN corresponding to the TEM image in main manuscript showing layers.

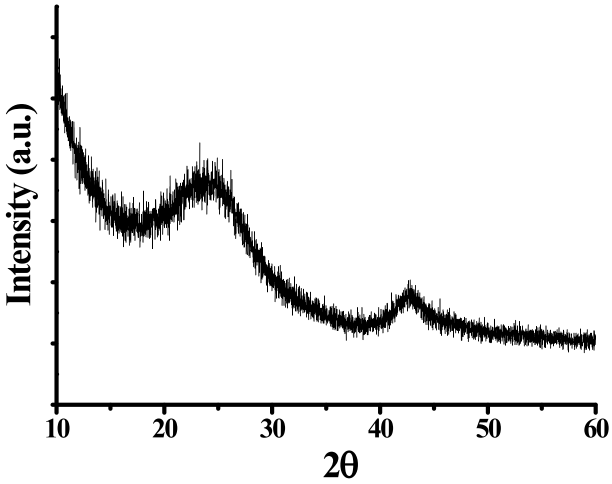

Fig. S4 PXRD pattern of few-layer BN.

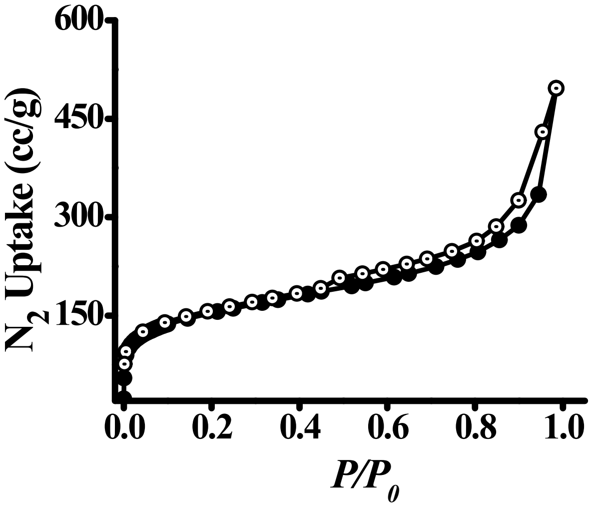

Fig. S5 N_2 adsorption profile of few-layer BN at 77 K.

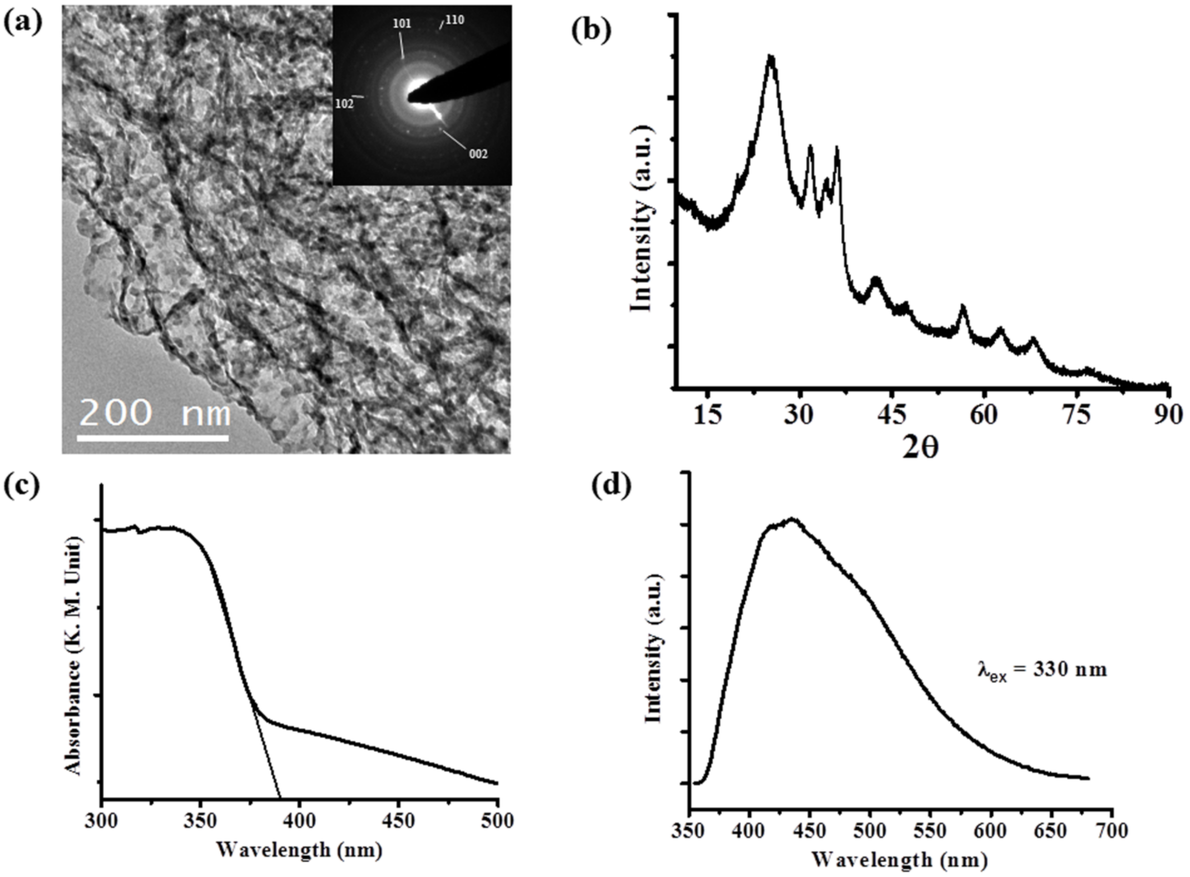

Fig. S6 BN@ZnO composite obtained on heating ZBN-2 in oxygen atmosphere. (a) TEM image; (b) PXRD pattern; (c) UV-visible absorption spectrum and (d) Photoluminescence emission spectrum of obtained BN@ZnO composite.

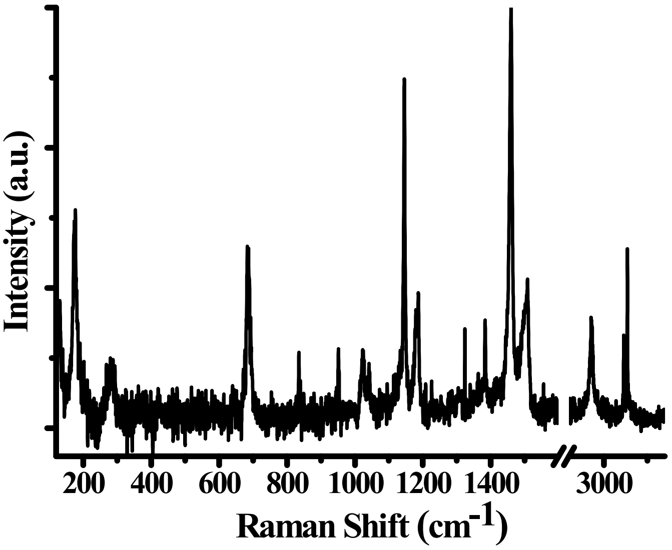

Fig. S7 Raman spectrum of ZIF-8.

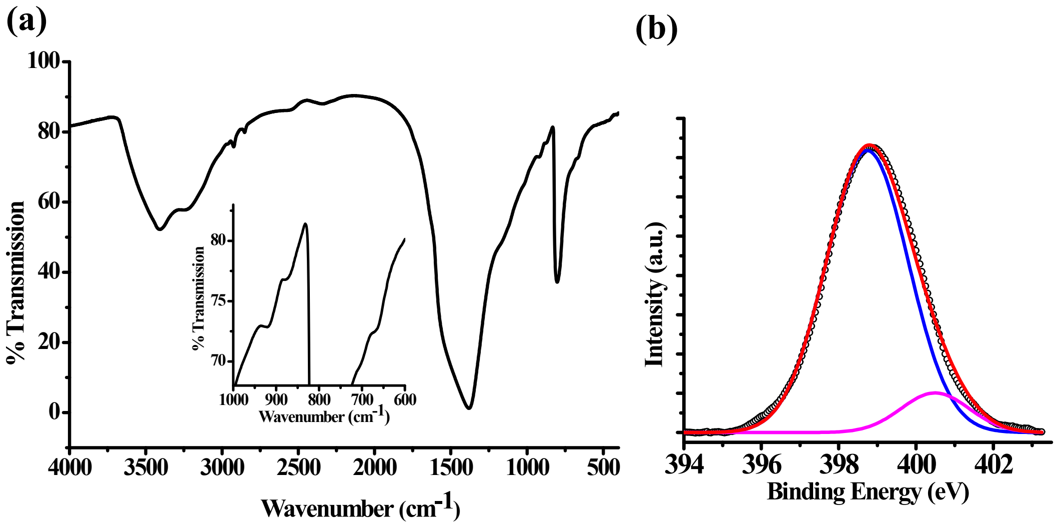

Fig. S8 (a) Infrared spectrum of amine functionalized few-layer BN prepared by urea route under ammonia atmosphere. (Inset) Enlarged view of $-NH_2$ wagging region. (b) High resolution N 1s X-ray photoelectron spectrum of BN. Black circles represents experimentally obtained N 1s spectrum whereas red line represents fitted curve.[3, 4]

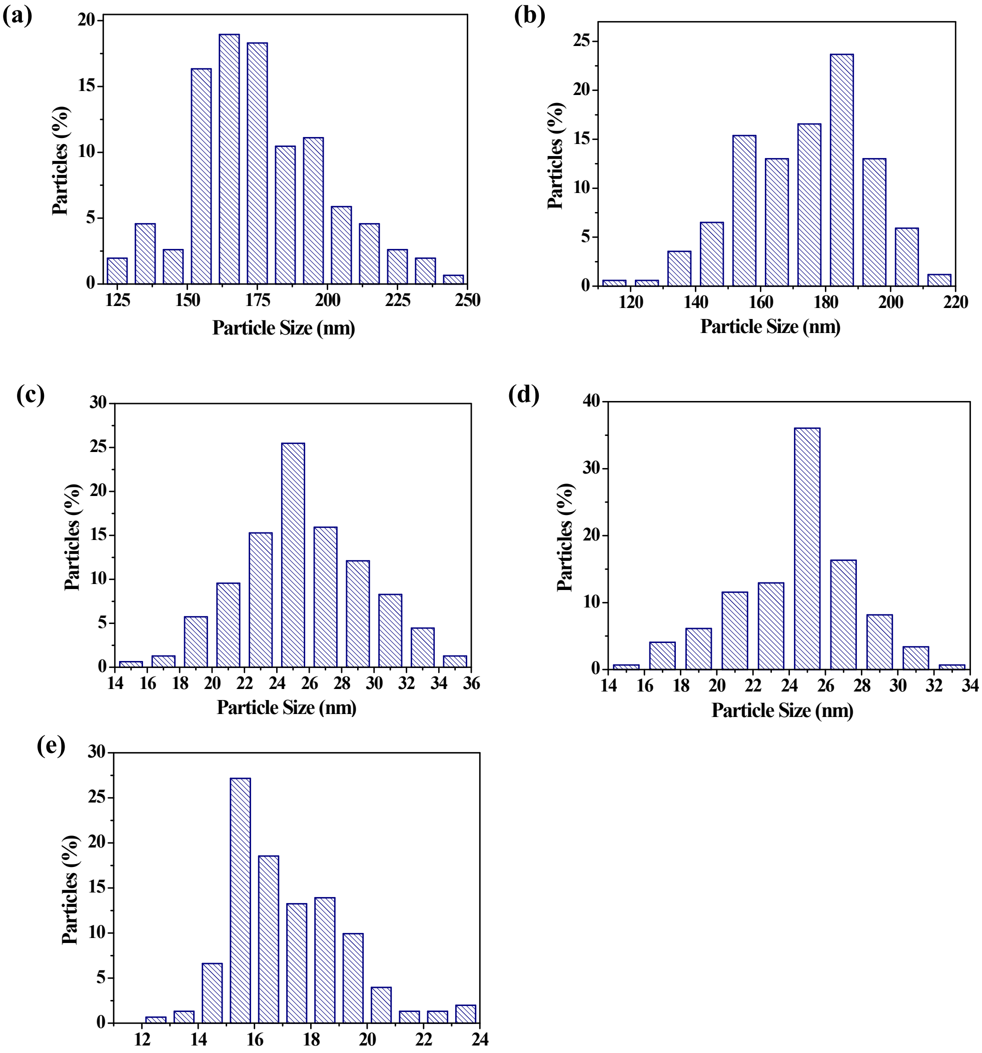

Fig. S9 Particle size distribution in (a) ZIF-8, (b) ZBN-1, (c) ZBN-2, (d) ZBN-3 and (e) ZBN-4

Sl. No.	Sample (Physical mixture)	Elastic modulus, Er (Gpa)	Standard deviation, Er (Gpa)	Hardness, H (MPa)	Standard deviation, H (Mpa)
1	BN:ZIF-8	3.08	0.85	348	156
2	2BN:ZIF-8	2.42	0.54	230	38
3	3BN:ZIF-8	3.83	1.1	575	218
4	4BN:ZIF-8	4.3	0.9	254	47

Table S1 Elastic modulus and hardness of physical mixtures containing few-layer BN and ZIF-8.

Sample	Exp. C	Calc. C	Exp. N	Calc. N	Exp. H	Calc. H
ZIF-8	41.76	42.22	24.37	24.62	4.26	4.43
ZBN-1	37.18	38.1	24.93	25.18	3.98	4.15
ZBN-2	33.86	34.71	25.52	25.65	3.71	3.93
ZBN-3	31.24	31.88	25.9	26.04	3.63	3.73
ZBN-4	28.13	29.47	26.92	26.37	3.44	3.57

Table S2 Elemental analysis data of ZIF-8 and ZBN composites.

References:

3 T. Ramanathan, F. T. Fisher, R. S. Ruoff and L. C. Brinson, *Chem. Mater.,* 2005, **17**, 1290.

4 T. Sainsbury, T. Ikuno, D. Okawa, D. Pacilé, J. M. J. Fréchet and A. Zettl, *J. Phys. Chem. C,* 2007, **111**, 12992.