

Efficient Mixed Solvent Strategy for Boron Nitride Exfoliation

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Abstract: Boron nitride (BN), a two-dimensional white solid layered material has potential applications in its exfoliated form. In the present study, a novel facile mixed solvent strategy has been introduced for the development of Boron nitride nanosheets (BNNS). The results demonstrated successive exfoliation of the bulk material in a mixed solution of Benzyl Benzoate (BB) and Dimethylformamide (DMF) as the solvent. Cetyltrimethylammonium bromide (CTAB) used as the surface modifier aided the exfoliation process. BN and CTAB has taken in the ratio of 1:1 has resulted in better exfoliation than that in the ratio 1:1.5. Prepared samples were characterized using XRD, Raman spectroscopy, SEM and TGA. The implications of the novel exfoliation strategy are discussed and interpreted.

1 INTRODUCTION

Hexagonal Boron Nitride (h-BN), a two-dimensional layered white solid material is a structural analog of carbon. h-BN takes the form of a honeycomb with boron and nitrogen atoms alternate to each other. Boron nitride (BN) is generally nontoxic, chemically inert having higher value of thermal conductivity, lower thermal expansion property, excellent thermal shock resistance, high electrical resistance, microwave transparency, low dielectric constant value etc. BN is stable in inert and reducing atmosphere up to 2000°C and in oxidizing atmospheres up to 850°C showing higher stability for BN when compared to other two-dimensional materials. Exfoliation has a high impact on material science by rendering characteristic properties seen in two-dimensional layered form that are not present in its bulk form. The present work focusses on liquid phase exfoliation of BNNS as an efficient method to obtain layers of pristine h-BN. Many solvents used have been reported for dispersion and exfoliation of BN. BB and DMF are two organic solvents. As a milling agent, BB has reported a production yield of 13.8% and BNNS of 0.5-1.5µm in diameter by exfoliation process [1]. Ball milling could create little damage to the inplane structure and hence BB in its liquid form has been used in the present work. The solvent has a major role because the energy needed for exfoliation is balanced by the solvent-BN interaction. BB can be used as a dispersion stabilizing agent. The solvent renders exfoliation when the polar molecules interact very strongly with the BN surface. BB have relatively high density and identical surface energy compared to BN which could result in its high peeling efficiency. DMF evaporates as a brown vapour when dried. The solvent consist of a mixed solution of Benzyl Benzoate (BB) and DMF and is used to exfoliate BN for the first time to the best of our knowledge. CTAB is a cationic surfactant which could increase the modulus of elasticity, electrical conductivity and tensile strength of a material. CTAB plays a major role in controlling nanoparticle size by selectively or more strongly binding to various emerging crystal facets [2]. The present work aims at bringing better exfoliation for BN with high yield.

2 MATERIALS AND METHODS

BN powder was purchased from HPLC (99% purity, AR grade) with a molecular weight of 24.82 g/mol and particle size of approximately 1µm. Benzyl Benzoate with a molecular weight of 212.25 g/mol supplied from HPLC was used in the present work. DMF used was supplied by Spectrochem Pvt Ltd, Mumbai. CTAB used was purchased from Sisco Research Laboratories with a molecular weight of 364.5 g/mol with AR grade (99% purity).

BN particles were exfoliated by liquid phase exfoliation method. The process was carried out by dispersion of pristine BN in a solution of BB and DMF. Two miscible solvents namely BB and DMF in equal proportion are stirred using a magnetic stirrer for 10 min. Pristine BN (B1) weighing 2 gm is added to the solvent mix and stirred well again for 5 min using the magnetic stirrer. The solution is then placed inside a probe sonicator for about an hour. The ultrasound provides high frequency pressure variations that lead to the formation of micro cavities within the solvent. The high shearing force produced as a result of the collapse of micro cavities renders the formation of exfoliated flakes. The solution is then centrifuged for 15 minutes at 3500 rpm. The resultant is then filtered and dried in an oven at 80°C for 2 days. The dried sample of BN (B2) is collected in a vial and preserved in a self-locked cover. The same procedure is repeated by adding CTAB to the mixed solvents containing B1 and (BN and CTAB in the ratio 1:1) the resulting dried sample is coded as B3. Another dried sample B4 after the same procedure is obtained by taking BN and CTAB in the ratio 1:1.5.

3 RESULTS AND DISCUSSIONS

XPRT-PRO X- ray diffractometer was used for investigation of the phase structure of the prepared BN samples by -. Figure 1(a) shows the XRD of pristine BN where the peaks corresponds to (002), (100), (101), (102), (004) planes of the hexagonal phase of BN (JCPDS card 34-0421). Diffraction patterns of the exfoliated samples are shown in Figure 1(b), 1(c), 1(d). The most intense peak were obtained for the 2θ values corresponding to 26.7° for B1. For sample B3 and B4, the CTAB modification on BN surface is prominent by the appearance of an additional peak which occurred at 21.6° [3]. Variation of 0.1° was obtained for 002 peak of sample B3 when compared to B1. The interlayer separation is higher for B3 with d spacing value of 3.32426 \AA for 26.81° . The interlayer separation for B3 is higher by an amount of 11% when compared to pristine BN. This increase in d spacing signifies that the sample B3 has been successfully exfoliated.

The Raman spectra of B1 shows a peak at 1366.53 cm^{-1} with high intensity. Based on the quality of exfoliation, a red shift or blue shift can be observed. A blue shift is attributed to the presence of monolayer whereas a red shift shows bilayer or more[4]. A peak was obtained for B3 at 1365.5 cm^{-1} which is in good agreement with the reported literature[5]. A red shift of 1.03 cm^{-1} was observed for B3 showing the presence of bilayers or more of BN. The peaks obtained for B2 and B4 also shows a red shift by 2.06 cm^{-1} and 3.11 cm^{-1} respectively. The intensity of the peaks of B3 and B4 has decreased on the addition of CTAB highlighting the modification done by CTAB on BN.

The characteristics of the prepared samples were further investigated using SEM and EDAX images are depicted in figures 3 and 4 respectively. The SEM images of B2, B3 and B4 show a disk like morphology. It can be concluded that the peeling of the bulk counterpart has taken place successfully. Both the thickness and lateral dimensions of the samples has decreased after exfoliation for B3 and B4. The average diameter of B3 was observed to be 95.7 nm . The energy dispersive X ray analyzer helps in elemental identification and provides quantitative information about the composition. The TGA curves for B1, B2, B3 and B4 are shown in figure 5 (a), (b), (c), (d). The TGA curve shows a modest mass loss on increasing temperature up to 800°C . However, it is prominent from fig.5(c) that the thermal stability of the sample B3 has improved. The onset decomposition temperature of B3 was observed to be 219.64°C . From the figure 4(a), a modest mass loss occurs up to 400°C was observed for B1 which might to due to the evaporation of volatile products present in the sample. However above 400°C , a very small increase of .31% in mass was observed which can be attributed to the oxidation of BN and subsequent production of boron tri oxide on the surface [6]. Considering B3, stability was observed till 219.64°C and abrupt decomposition was observed until 284.8°C , after which material remained stable. B4 was stable up to 203.42°C and proceeded to decompose until 293°C

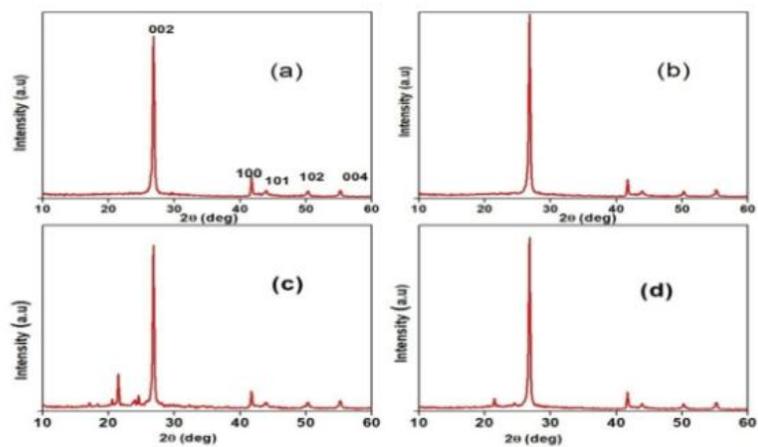


Figure 1. XRD of (a) pristine BN (B1), (b) exfoliated BN without CTAB (B2) (c) BN and CTAB in the ratio 1:1 (B3) (d) BN and CTAB in the ratio 1:1.5 (B4).

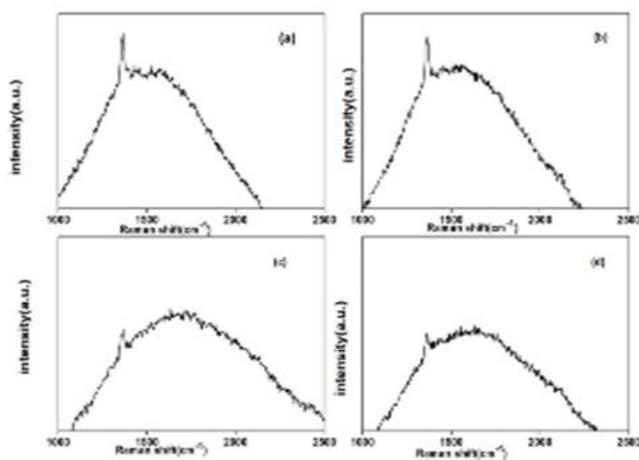


Figure 2. Raman spectrum of (a) B1 (b) B2 (c) B3 (d) B4.

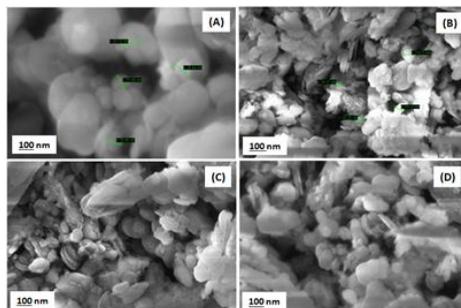


Figure 3. SEM images of (A) B1, (B) B2, (C) B3, (D) B4

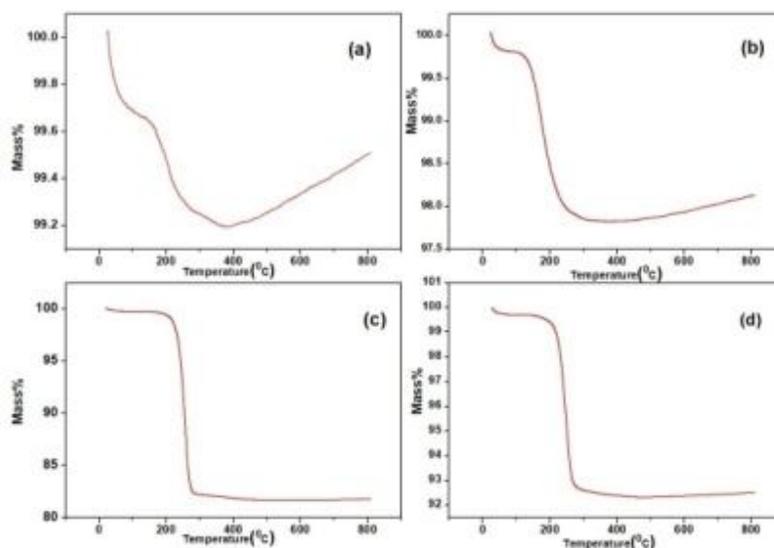


Figure 4. TGA of (a)B1, (b)B2, (c)B3, (d)B4.

SUMMARY

In this work, a novel and facile mixed solvent strategy along with a modifier was introduced for exfoliation of bulk BN powder. The prepared samples were characterized using XRD, Raman spectroscopy, SEM and TGA. XRD and Raman spectral analysis proved the presence of exfoliated nanosheets. A disc like morphology was obtained for the prepared samples by SEM analysis. BN and CTAB in the ratio of 1:1 proved better exfoliation. TGA presented the thermal analysis of the prepared samples. Surface modification using CTAB aided better exfoliation of BN with improved stability.

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