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Boron nitride nanomaterials with different morphologies: Synthesis, characterization and efficient application in dye adsorption

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Abstract

Novel boron nitride (BN) nanomaterials with unique and unprecedented properties such as semiconductor with constant band gap, high chemical stability, high thermal conductivity and excellent mechanical properties have been successfully fabricated in the present work in different morphologies as BN nanoparticles and BN nanosheets. Solid state high temperature chemical reactions were adopted for their engineering and various techniques like powder Fourier transform infrared spectroscopy, X-ray diffraction technique and high resolution transmission electron microscopy were employed to examine their morphology and other physicochemical properties. The FT-IR spectra revealed the presence of the B–N bond stretching and bending of B–N–B bond. The hexagonal structure of these BN nanomaterials was divulged from the XRD data, while their different morphology and size were depicted from the high resolution transmission electron microscopy. The nanoparticles are found to be spherical with average diameter of ~30 nm and the BN sheet is two dimensional with average thickness of ~0.90 nm. The lattice interplaner distance of 3.30 Å determined by high resolution transmission electron microscopy is in good agreement with that of calculated using XRD data. The high surface areas as calculated from the BET analysis are 120.68 $m^2\,g^{-1}$ and 50.02 $m^2\,g^{-1}$ for BN nanoparticles and BN nanosheets respectively. The present work also reports the adsorption behaviour of the synthesized BN nanomaterials towards the adsorption of two different dye molecules, namely, brilliant green and methyl orange. The adsorption conditions have been optimized by varying a number of experimental parameters such as initial dye concentration, adsorbent dosage, pH and time. The interactions of dye molecules with the adsorbate nanomaterials, nature of feasibility of adsorption process have been understood by performing calculations within the formalism of density functional theory at B3LYP/6-31G level of theory.

Keywords: Boron nitride nanomaterials; Dye adsorption; High resolution TEM; Density functional theory

1. Introduction

Boron nitride (BN) nanomaterials, isoelectronic and isostructural to carbon have attained a significant place in the recent world of nanoscience owing to their high thermal stability, conductivity and mechanical strength [1–3]. Their semiconducting nature with wide band gap (~5.5 eV) irrespective of structural parameters [4,5] and chemical inertness towards oxidation make them suitable for a plethora of applications [6,7]. Such unique attributes have dragged the major concentration of scientists in the recent years for the fabrication of BN nanomaterials in different morphologies such as nanotubes [8], nanoparticles [9], nanoribbons [10], nanosheets [11] and nanofibers [12]. Apart from their remarkable compatibility in electronic and mechanical devices, BN nanomaterials have been explored for their potential as adsorption surfaces with sure recyclability that is facilitated by their chemical inertness [13–15].

Different morphologies of BN nanomaterials have been tested as adsorbent for the removal of dyes that are the most widely used colouring agents in various industries such as paper, plastic, textile, food and cosmetics along the development of industries and human society. The concentration of

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dyes in the industrial effluent has a major contribution in the environmental pollution that causes direct destruction of flora and funna [16–18]. The economical and simplistic adsorption technology for waste water treatment [19] has gained superiority over the dye degradation process that is made difficult by highly stable and complex structure of dyes. A few BN nanomaterials with different morphologies have been used as adsorbent for the removal of dyes, solvents and oils. Lei et al. fabricated the porous BN nanosheets that showed great adsorption towards oils, solvents and dyes [20]. Xue et al. developed mesoporous hexagonal boron nitride fibres for the fast and efficient removal of methylene blue from the waste water [21]. Boron nitride nanocarpets have also been synthesized by Zhang et al. that exhibit quick adsorption rate for the adsorption of methylene blue [22]. Lian et al. have fabricated BN ultrathin fibrous nanonets and employed their excellent performance for water treatment by ultrafast adsorption of methylene blue dye [13].

Several theoretical investigations suggest the favourable and efficient adsorption of a large number of molecules including gases [14,23–25], aromatic compounds [15,26,27], drugs [28,29] and various metals [30,31] on the surface of BN nanomaterials. However, the experimental efforts to validate the wide applicability of BN nanomaterials are still lacking. The limited study reported in this respect is pertaining to efficient adsorption of H_2 gas over the surface of modified BN nano structures [32] and successful removal of Arsenic from water by its efficient adsorption on the surface of Fe_3O_4 nanoparticles coated boron nitride nanotubes [33].

The present study provides a comprehensive understanding of the efficiency of BN nanomaterials as advanced adsorbent material for effectual adsorption and removal of organic pollutants from waste water by experimental elucidation, further supported by theoretical investigations. The BN nanomaterials have been synthesized in two different morphologies i.e. BN nanoparticles and BN nanosheets using solid state reaction. The efficacy of the synthesized nanomateials towards the adsorption of brilliant green (BG) and methyl orange (MO) dyes have been explored in detail by taking into account the impact of various factors such as initial dye concentration, pH, adsorbent dosage and time. Up till now, no work has been carried out on the morphology based study of BN nanomaterials for the adsorption of cationic and anionic dyes with different experimental parameters along with this work also validated the theoretical suggestions with the experimental results. The experimental conclusion about rapid and efficient adsorption of dyes on the nanomaterial surface is backed up by density functional theory (DFT) based theoretical studies that provide a thorough understanding about feasibility and nature of adsorption.

2. Experimental

2.1. Chemicals

Boric acid (H_3BO_3, 99.5%) was obtained from Fisher Scientific. Urea ($CO(NH_2)_2$, 99%), melamine (99%), Methyl Orange and Brilliant Green were purchased from Central Drug House (CDH) and used without further purification. Water was deionized using an ultrafiltration system (Milli-Q, Milipore).

2.2. Fabrication of BN nanomaterials

Different morphologies of BN nanomaterials; BN nanoparticles and BN nanosheets were successfully synthesized by solid state thermal annealing methods using different reacting materials in Nitrogen gas atmosphere. The detail procedures were discussed below.

2.2.1. Synthesis of BN nanoparticles

To obtain the highly crystalline and pure BN nanoparticles, a commonly used solid state thermal annealing method was adopted for their fabrication [34]. Firstly the precursor was prepared by using boric acid and melamine as starting materials. Both the reacting materials were mixed well in pestle mortar in 1:1 M ratio and then sintered at 200 °C for 1 h and further for 2 h at 300 °C in nitrogen atmosphere. The obtained precursor was then subjected to pulverization and then loaded in alumina boat. Afterwards the alumina boat was heated in furnace at 1400 °C for 2 h in the presence of nitrogen gas atmosphere. The precursor was transformed into BN compounds with volatilization of H, O and C during annealing in the nano range. The final product was collected, washed with deionized water and then finally dried for characterization and use as adsorbent.

2.2.2. Synthesis of BN nanosheet

Boric acid and urea were used as starting materials for the synthesis of BN nanosheet [11]. To homogenize the reactants 1:12 M ratio of boric acid to urea were dissolved in 40 ml of deionized water and heated at 65 °C till the complete evaporation takes place. A homogeneous mixture of boric acid and urea obtained by this method was further heated at 900 °C for 5 h in the nitrogen atmosphere to fabricate the BN nanosheets. White coloured product was formed at the end of reaction that was extracted, washed with deionized water and then dried. The details of the reaction are explained by the following equations:

$$2B(OH)_3 \overset{\Delta}{\Longrightarrow} B_2O_3 + 3H_2O$$

$$NH_2CONH_2 \overset{\Delta}{\Longrightarrow} NH_3 + HNCO$$

$$B_2O_3 + 2NH_2 \overset{\Delta}{\Longrightarrow} 2BN + 3H_2O$$

On the basis of these reactions, the mechanism of the fabrication of sheet like morphology of BN has also been proposed. The production of ammonia gas in the second step of the reactions might form large bubbles of atomically thin hexagonal BN that got flattened at high temperature and resulted in the formation of two dimensional sheet like morphology of BN i.e. BN nanosheets. As suggested by Wang et al [35] "Chemical Blowing" method leads to the formation of BN and C_x-BN nanosheets.