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# Preparation of Boron Nitride and Polystyrene/Boron Nitride Composite Particles by Dehydrogenation in Ionic Liquids

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Boron nitride (BN) was prepared by the dehydrogenation of ammonia borane (AB) in an ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate, [Bmim][BF<sub>4</sub>]) at 300°C, which is lower than the temperature of the general preparation method of BN and below the decomposition temperature of polystyrene (PS). The reaction was performed at 120°C for 10 h under atmospheric pressure, and the product material was subsequently heated at 300°C for 24 h under reduced pressure in [Bmim][BF<sub>4</sub>]. The reaction rate and final conversion increased when [Bmim][BF<sub>4</sub>] was used as the medium as compared to those observed in the bulk system (in the absence of the solvent system). Moreover, PS/BN composite particles were successfully prepared by dehydrogenation in [Bmim][BF<sub>4</sub>] in the presence of cross-linked PS seed particles. Transmission electron microscopy images of ultrathin cross-of the composite particles confirmed the core–shell morphology of the particles with a PS core and a BN shell.

# Introduction

Ionic liquids, which are a class of salts that consist entirely of anions and cations and melt at approximately room temperature, have attracted considerable attraction recently because of their attractive properties such as nonvolatility, nonflammability, and high thermal stability. Numerous research groups have investigated ionic liquids as media in organic chemistry, electrochemistry, biochemistry applications, and polymer chemistry.<sup>1–8</sup> We have reported the preparations of polymer particles such as polystyrene (PS),<sup>9</sup> poly(acrylic acid) (PAA),<sup>10</sup> Nylon-6,<sup>11</sup> and PS/PAA composite particles<sup>12</sup> using ionic liquids as media.

The synthesis of inorganic materials such as silica, titania, and gold nanoparticles in ionic liquids has also been reported.<sup>13-22</sup> Kaper et al. reported the direct synthesis of highly crystalline titanium dioxide (rutile) nanoparticles and nanorods via sol–gel processes in an imidazolium-based ionic liquid at 80°C without high-temperature calcination.<sup>23</sup> It was reported that imidazolium-based ionic liquids form a liquid-crystal-like local structure derived from the interactions among the ionic liquid molecules, and that the sol–gel products grow along the local structure, which function as a template.

We previously reported the preparation of  $PS/Al(OH)_3$ composite particles with a PS core and a highly crystalline  $Al(OH)_3$  shell using a sol-gel reaction of aluminum isopropoxide in 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF<sub>4</sub>]) in the presence of PS seed particles (seededdispersion sol–gel process).<sup>24</sup> PS/Al<sub>2</sub>O<sub>3</sub> composite particles were subsequently prepared by heat-treating the obtained PS/Al(OH)<sub>3</sub> composite particles at 300°C, which is below the decomposition temperature of PS. We also successfully prepared PS/Mg(OH)<sub>2</sub> and PS/MgO core-shell composite particles in an ionic liquid,<sup>25</sup> where the shell formation mechanism was clarified from the viewpoint of the spreading coefficients calculated from interfacial tensions. The films and pellets prepared from such core–shell particles are expected to exhibit high thermal conductivity and be lightweight under the assumption that the highly thermally conductive metal-oxide shell forms continuous thermal-transport pathways with a low percolation threshold (Scheme 1).



**Scheme 1**. Schematic illustration of an organic/inorganic composite film having effective thermal transport pathways prepared by organic-core/inorganic shell composite particles.

Boron nitride (BN) exhibits high thermal conductivity (hexagonal phase: 60  $\text{Wm}^{-1}\text{K}^{-1}$ ; cubic phase: 1300  $\text{Wm}^{-1}\text{K}^{-1}$ ) and electrically insulating behavior; it is widely used as a filler for heat-release materials in electronic devices. In general, the preparation of BN requires high reaction temperatures (greater than 1500°C).<sup>26</sup> Recently, Zheng et al. synthesized turbostratic boron nitride in an ionic liquid (1-butyl-2,3dimethylimidazolium tetrafluoroborate) at relatively low temperatures. These results indicate that ionic liquids may be critical in preparing crystalline boron nitride.<sup>27</sup>

Ammonia borane (NH3BH3, AB) has attracted attention over the past three decades as a hydrogen-storage material for fuel cells and other energy devices because of its high hydrogen content (19.6 wt%) and hydrogen release potential.<sup>28</sup> AB is stable at room temperature; however, hydrogen gas is released approximately 100°C through dehydrogenation.<sup>29-31</sup> at Recently, Sneddon et al. reported that the hydrogen release rate of AB was enhanced and that the amount of hydrogen gas increased in the 1-butyl-3-methylimidazolium chloride ([Bmim]Cl)-solution system (2.2 mol H<sub>2</sub> per 1 mol AB) compared to those in the bulk system (0.9 mol H<sub>2</sub> per 1 mol AB) at 120°C.<sup>32</sup> If AB releases stoichiometric amounts of hydrogen gas (3 mol  $H_2$  per 1 mol AB, see Eq. (1)), the synthesis of BN should be possible at relatively low temperatures:

 $NH_3BH_3 \longrightarrow BN + 3H_2$  (1)

In this paper, we report the preparation of BN by the dehydrogenation of AB in ionic liquids and the effect of the reaction conditions on the reaction yield. This is the first report on the synthesis of BN utilizing dehydrogenation of AB in an "ionic liquid." Furthermore, the preparation of composite particles with a PS core and a BN shell is demonstrated using dehydrogenation in an ionic liquid in the presence of PS seed particles.

# Experimental

## Materials

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AB (97% purity, Sigma-Aldrich) was used as received. The ionic liquids used in this study, [Bmim]Cl (98% purity, Sigma-Aldrich), [Bmim][BF<sub>4</sub>] (97% purity, Sigma-Aldrich), 1-butyl-3methylimidazolium hexafluorophosphate ([Bmim][PF<sub>6</sub>], 96% Sigma-Aldrich), 1-butyl-3-methylimidazolium purity, bis(trifluoromethanesulfonyl)amide ([Bmim][TFSA], Nippon Synthetic Chemical Industry), and N,N-diethyl-N-methyl-N-(2methoxyethyl)ammonium tetrafluoroborate ( $[DEME][BF_4]$ , 98% purity, Kanto Chemical), were dried at 120°C for 3 h before use. Styrene was purified by distillation under reduced pressure in N2 atmosphere. Divinylbenzene (DVB) was washed with aqueous 1 M NaOH to remove the inhibitor and was subsequently dried with calcium hydride. Azobisisobutyronitrile (AIBN) was recrystallized in methanol

and dried in vacuo. Polyvinylpyrrolidone (PVP, numberaverage molecular weight: 360,000) was used as received. The water used in all experiments was obtained from an Elix UV (Millipore Co., Japan) purification system and exhibited a resistivity of  $18.2 \text{ M}\Omega$  cm.

#### Preparation of BN in ionic liquids by dehydrogenation of AB

AB (0.1 g) was dissolved in ionic liquid (2.0 g) and the solution was heated at various temperatures (80–150°C) in an oil bath under gentle stirring. In the case of further heat treatment, the sample was put into a glass tube and degassed using several vacuum/N<sub>2</sub> cycles, and subsequently, the vacuum-sealed glass tube (ca 15 mL) was heated at a higher temperature (300°C) using an oil bath. The precipitated product was washed with methanol by centrifugation and vacuum dried at room temperature. For comparison, the dehydrogenation of AB in the bulk system (melting point of AB: 104°C) was performed under the same conditions.

#### Preparation of cross-linked PS seed particles

PS seed particles were prepared by emulsifier-free emulsion polymerization in an aqueous medium, as previously reported.<sup>24</sup> Cross-linked PS particles were synthesized by the seeded copolymerization of styrene (0.125 g) and DVB (0.144 g) in the presence of PS seed particles (0.54 g) with AIBN (3.9 mg) as an initiator.<sup>33</sup> All ingredients were sealed in a glass tube under N<sub>2</sub> atmosphere, which was horizontally shaken at 120 cycles/min (2-cm strokes) in an ice bath at ~0°C for 24 h for the monomer absorption in PS seed particles; the tube was subsequently maintained at 70°C for 24 h for polymerization.

### Dehydrogenation of AB in ionic liquids in the presence of crosslinked PS seed particles

The medium of the cross-linked PS dispersion (containing 0.1 g of PS particles) was changed from water to methanol by centrifugation, and then PVP (10 mg) dissolved in [Bmim][BF<sub>4</sub>] (2.0 g) was added to the dispersion. Methanol was evaporated at 60°C to change the medium to [Bmim][BF<sub>4</sub>], and subsequently, AB (0.1 g) was dissolved in the dispersion. Dehydrogenation was performed under various conditions by gentle stirring. Further heat treatment (300°C) of the obtained sample was carried out using the vacuum-sealed glass tube in the same way as the PS seed-absence system. After the reaction, the product was washed with methanol by centrifugation and dried at room temperature under vacuum.

#### Characterization

The conversion of AB by dehydrogenation was determined from the volume of the released hydrogen gas, as measured by water displacement, using the following equation:

Conversion (%) = 
$$\frac{V_{H_2}/V_0}{3N_{AB}} \times 100$$

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where  $V_{\rm H_2}$  is the volume of the released hydrogen (cm<sup>3</sup>),  $V_0$  is the volume of the ideal gas under standard conditions (24.8  $\times$  $10^3$  cm<sup>3</sup>/mol at 298 K and 0.1 MPa), and N<sub>AB</sub> is the initial number of moles of AB. The products were analyzed by Fourier transform-infrared spectrometry (FT-IR, FT/IR-6200, JASCO, Japan) using the pressed KBr pellet technique and Xray diffraction (XRD, RINT-TTR, Rigaku, Tokyo, Japan) using the  $2\theta/\theta$  method at a scanning rate of  $4^{\circ}/\text{min}$ ; the XRD was equipped with a CuK $\alpha$  radiation ( $\lambda = 1.5418$  Å) source operated at 50 kV and 300 mA. Scanning electron microscopy (SEM, JSM-6510, JEOL, Japan) observations of the particles coated with platinum/palladium alloy were performed at 20 kV. To observe the interior morphology of the composite particles, the dried particles were embedded in epoxy, cured at room temperature overnight, and subsequently microtomed. The ultrathin ~100-nm cross-sections were observed by transmission electron microscopy (TEM, JEM-1230, JEOL, Japan) performed at 100 kV. X-ray photoelectron spectroscopy (XPS) data were obtained with a ULVAC-PHI, INC. PHI Xtool apparatus using AlKa (1486.6 eV) at 15 kV and 50 W. A pressure of  $\sim 1 \times 10^{-6}$  Pa was maintained in the measurement chamber. The dried samples were spread on an indium plate with a spatula. The BN content of the composite particles was calculated from the weight loss of the composite particles measured by thermogravimetry (TGA, EXSTAR TG/DTA6200, SII NanoTechnology, Japan) performed at a heating rate of 10°C/min from 30 to 500°C under N<sub>2</sub> atmosphere.

# **Results and Discussion**

# Dehydrogenation of AB in various ionic liquids in the absence of PS particles

Dehydrogenation of AB was performed in various ionic liquids at 100°C for 24 h to determine the optimum medium for the preparation of composite particles, i.e., a medium that dissolves AB but not the product. After mixing and vigorous stirring at room temperature, AB dissolved completely in [Bmim]Cl, [Bmim][BF<sub>4</sub>], and [DEME][BF<sub>4</sub>], but not in [Bmim][PF<sub>6</sub>] or [Bmim][TFSA]. After the reaction, the mixtures were heated at 100°C for 24 h and a white precipitate formed only in [Bmim][BF<sub>4</sub>]; in contrast, no precipitates were observed in [Bmim][Cl and [DEME][BF<sub>4</sub>]. On the basis of these results, [Bmim][BF<sub>4</sub>] was chosen as the reaction medium in subsequent experiments.

Figure 1 shows the conversion versus time plots for AB dehydrogenation in the bulk system and  $[Bmim][BF_4]$  system at various temperatures. All reactions proceeded smoothly without an induction period; however, the reaction rates and final conversions were obviously different. In the case of the bulk system at 120°C (filled circles), the reaction proceeded to 67% conversion in 10 h. However, in the case of the [Bmim][BF\_4] system (open symbols), the final conversion increased as the reaction temperature was increased and proceeded to 86% conversion at 120°C. Moreover, when the dehydrogenation reaction was carried out at 300°C, the

reaction proceeded to 88% conversion. Sneddon et al. reported that the dehydrogenation of AB was enhanced in [Bmim]Cl, where [Bmim]Cl was hypothesized to stabilize the intermediate diammoniate of diborane (a more reactive species). In this study, [Bmim][BF<sub>4</sub>] may have stabilized the intermediate in the same



**Figure 1**. Conversion versus time for the dehydrogenation of AB in the bulk system at 120°C (filled circles, •) and in the [Bmim][BF<sub>4</sub>] system at 80°C (open triangles,  $\triangle$ ), 100°C (open squares,  $\Box$ ), and 120°C (open circles,  $\circ$ ).

manner as [Bmim]Cl, and the dehydrogenation reactions were consequently enhanced.

To obtain dry samples for FTIR analyses, the obtained products (white precipitates) were centrifuged in methanol, which dissolves AB and  $[Bmim][BF_4]$  but not BN. However, the products were immediately dissolved when methanol was added, which suggested that a sufficient number of boron-nitrogen bonds did not form and that the obtained products could be oligomers of BN. To prepare BN with high molecular weight, dehydrogenation was performed at higher temperatures. However, when dehydrogenation was performed at temperatures greater than 150°C, hydrogen gas was released vigorously and bumping occurred (Figure 2c). To prevent the rapid release of hydrogen, the reaction was performed at 120°C for 10 h, and the reaction mixture was subsequently heated to 300°C for 24 h. After the stepwise reaction, the system became turbid without bumping and the obtained products did not dissolve in methanol. However, [Bmim][BF<sub>4</sub>] was colored owing to oxidation after the reaction at 300°C (Figure 2d) and the product was stained brown owing to [Bmim][BF<sub>4</sub>] (Figure 2d'). To avoid the oxidation



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of [Bmim][BF<sub>4</sub>], the reaction at 300°C was performed under reduced pressure using a vacuum-sealed glass tube after nitrogen purge. The vacuum facilitated the release of hydrogen gas and accelerated the

**Figure 2.** Visual appearances of AB dehydrogenation before (a) and after (b–e) being heated in [Bmim][BF<sub>4</sub>] under various conditions and the appearances of the obtained products after being washed with methanol (d' and e'). The reaction temperatures (°C), times (h), and pressures were (b) 120, 10, atmospheric pressure (0.1 MPa); (c) 150, 10, 0.1; (d, d') 120, 10, 0.1  $\rightarrow$  300, 24, 0.1; and (e, e') 120, 10, 0.1  $\rightarrow$  300, 24, in a vacuum-sealed glass tube, respectively.

dehydrogenation. After the reaction at 300°C in a sealed glass tube (**Figure 2e**), coloring [Bmim][BF<sub>4</sub>] was prevented (although the color become yellowish) and the product (white powder) was obtained after washing with methanol (**Figure 2e'**). The product yield, measured gravimetrically, was 33%.

**Figure 3** shows the FT-IR spectra of the products prepared by dehydrogenation under various conditions. In the case of the product prepared in the bulk system at 120°C and subsequently heated at 300°C in a vacuum-sealed glass tube (i.e., a two-step dehydrogenation reaction) (**Figure 3a**), the characteristic peaks of AB at 1064, 1163, 1380, and 2180–2770 cm<sup>-1</sup> disappeared, and a broad peak at 1350–1630 cm<sup>-1</sup> was observed. However, the broad peak at 2970–3600 cm<sup>-1</sup> assigned to B-O stretching remained, which indicates that AB combined with oxygen to generate boric acid during the heating process. Even after the calcination of the dry product at 800°C (**Figure 3b**), the broad peak at 2970–3640 cm<sup>-1</sup> remained.



**Figure 3**. FT-IR spectra of products prepared by the dehydrogenation of AB in the bulk system (a, b) and [Bmim][BF<sub>4</sub>] system (c) under various conditions. The reaction temperature (°C), time (h), and pressure were (a) 120, 10, atmospheric pressure  $\rightarrow$  300, 24, reduced pressure; (b) 120, 10, atmospheric pressure  $\rightarrow$  300, 24, reduced pressure  $\rightarrow$  800, 3, atmospheric pressure; and (c) 120, 10, atmospheric pressure  $\rightarrow$  300, 24, in a vacuum-sealed glass tube.

These results indicate that once the B–O bonds forms it does not decompose at high temperatures such as 800°C. However, in the case of the product obtained by the two-step ( $120^{\circ}C \rightarrow 300^{\circ}C$ ) dehydrogenation in [Bmim][BF<sub>4</sub>] (Figure 3c), the broad peaks at 2970–3640 cm<sup>-1</sup> almost disappeared and a more intense peak at 1275–1710 cm<sup>-1</sup> corresponding to B–N bonds was observed. These results suggest that BN could be successfully prepared using

[Bmim][BF<sub>4</sub>] as a medium at temperatures less than the decomposition temperature of PS.

Figure 4 shows the XRD spectra of the products prepared by the two-step dehydrogenation in the bulk and [Bmim][BF<sub>4</sub>] systems. The XRD pattern of the product in the bulk system contained characteristic sharp peaks at 25°, 26°, and 28°; however, these peaks were not assigned to AB (JCPDS File Card No. 13-0292, circle symbols) or to hexagonal BN (h-BN, JCPDS File Card No. 34-0421, triangle symbol). In contrast, the XRD pattern of the product obtained in [Bmim][BF<sub>4</sub>] contained a broad peak at 26°, which seems to be assigned to the (002) reflection of turbostratic BN (t-BN),  $\frac{34-37}{10}$  in which BN layers are stacked irregularly. Furthermore, after heat treatment of the obtained product at 1000°C for 3 h under N<sub>2</sub> flow, the peak of (002) (27°) slightly shifted and grew up more sharply, and a peak of 41° corresponding to (100) reflection appeared in the XRD pattern of products (Figure 4c), indicating formation of hexagonal BN(h-BN). This result strongly supports the fact that BN was successfully prepared by the dehydrogenation of AB in [Bmim][BF<sub>4</sub>] under mild conditions (~300°C), although the BN exhibited turbostratic structure.



**Figure 4.** XRD spectra of products prepared by the dehydrogenation of AB in the bulk system (a) and in a vacuum-sealed glass tube [Bmim][BF<sub>4</sub>] system (b) at 120°C, followed by subsequent heating at 300°C and products after heat treatment of (b) at 1000°C for 3 h (c).

### Dehydrogenation in the presence of PS seed particles

The dehydrogenation of AB in [Bmim][BF<sub>4</sub>] was performed in the presence of PS seed particles, which were prepared via the emulsifier-free emulsion polymerization of styrene in an aqueous medium. However, large PS aggregates were obtained after the dehydrogenation reaction because of the absence of a colloidal stabilizer and the glass-transition temperature of PS. To improve the colloidal stability of the seed particles, we used PVP as a colloidal stabilizer and cross-linked PS particles as seed particles. After the two-step dehydrogenation ( $120 \rightarrow$  $300^{\circ}$ C) in the presence of the cross-linked PS particles in a sealed tube, a stable, unaggregated emulsion was obtained, but most of the particles exhibited the same sizes as those of the cross-linked PS seed particles, and considerable agglomeration assumed to be generated inorganic compounds was observed Published on 17 January 2014. Downloaded by Aston University on 18/01/2014 10:16:12.

from SEM observation (no data). It was suggested that the rate of two-step dehydrogenation was so fast that inorganic compounds did not deposit on the surface of cross-linked PS seed particles homogeneously. To deposit the generated inorganic compounds on the surface of the seed particles, the step-wise heat treatment from 80°C to 300°C (i.e., a multistep dehydrogenation reaction: 80°C (10 h, atmospheric pressure (0.1 MPa))  $\rightarrow$  100°C (10 h, 0.1 MPa)  $\rightarrow$  120°C (1 h, 0.1 MPa)  $\rightarrow$  150°C (1 h, 0.1 MPa)  $\rightarrow$  120°C (1 h, 0.1 MPa)  $\rightarrow$  250°C (1 h, in a vacuum-sealed glass tube)  $\rightarrow$  250°C (1 h, in a vacuum-sealed glass tube)  $\rightarrow$  300°C (24 h, in a vacuum-sealed glass tube)) were carried out.



**Figure 5**. SEM photographs (a, b) of cross-linked PS seed particles (a) and the obtained particles prepared by the multi-step dehydrogenation reaction of AB in the [Bmim][BF<sub>4</sub>] system in the presence of cross-linked PS seed particles (b). TEM photographs (a', b') of RuO<sub>4</sub>-stained ultrathin cross-sections of cross-linked PS seed particles (a') and the obtained particles (b')

Figures 5a and 5b show SEM photographs of cross-linked PS seed particles and products (after washing with methanol) prepared by the multi-step dehydrogenation of AB in a sealed glass tube [Bmim][BF<sub>4</sub>] system and in the presence of cross-linked PS seed particles. Before dehydrogenation, the seed particles exhibited a smooth surface and their diameter was 410 nm with high monodispersity. After the multi-step dehydrogenation reaction, the particles maintained their particle shape with rough surfaces, which indicates that BN was adsorbed onto the PS seed particles.

**Figures 5a'** and **5b'** show TEM photographs of  $RuO_4$ stained ultrathin cross-sections of cross-linked PS seed particles and the obtained particles prepared by the multi-step dehydrogenation of AB in [Bmim][BF<sub>4</sub>] in the presence of cross-linked PS seed particles. The core–shell morphology was clearly observed in the TEM photographs, where the dark core and light shell regions represent PS and BN, respectively.

**Figure 6** shows the FT-IR spectrum of the particles obtained by the multi-step dehydrogenation of AB in  $[Bmim][BF_4]$  in the presence of the cross-linked PS seed

particles. Both the characteristic sharp peaks of PS at 697 and 754  $\text{cm}^{-1}$  and a broad peak of BN at 1280–1600  $\text{cm}^{-1}$  were clearly observed in the FT-IR spectrum, which indicates that PS did not decompose and that PS/BN composite particles could be obtained.

Moreover, the XPS data clearly show that the  $B_{1s}$  (189 eV) and  $N_{1s}$  peak (398 eV) due to BN were observed in the obtained composite particles (**Figure 7**), which indicates that BN was successfully prepared and adsorbed onto the surface of the PS seed particles.  $F_{1s}$  peak (685 eV) and  $O_{1s}$  (531 eV) were also observed because of the existence of remaining [Bmim][BF<sub>4</sub>]



and some oxide.

Figure 6. FT-IR spectrum of products prepared by the multi-step dehydrogenation of AB in the sealed tube [Bmim][BF4] system in the presence of cross-linked PS seed particles.

Moreover, the XPS data clearly show that the  $B_{1s}$  (189 eV) and  $N_{1s}$  peak (398 eV) due to BN were observed in the obtained composite particles (**Figure 7**), which indicates that BN was successfully prepared and adsorbed onto the surface of the PS seed particles.  $F_{1s}$  peak (685 eV) and  $O_{1s}$  (531 eV) were also observed because of the existence of remaining [Bmim][BF<sub>4</sub>] and some oxide.



Figure 7. X-ray photoelectron spectra of products prepared by the multistep dehydrogenation of AB in the sealed-tube [Bmim][BF<sub>4</sub>] system in the presence of cross-linked PS seed particles.

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Quantitative analysis of the composite particles was conducted by TGA under N<sub>2</sub> atmosphere. **Figure 8** shows the TGA curves of cross-linked PS seed particles, BN particles, and PS/BN composite particles prepared by the two-step dehydrogenation of AB in [Bmim][BF<sub>4</sub>] in the presence of the cross-linked PS seed particles. The cross-linked PS seed particles were completely decomposed at 500°C. However, BN and PS/BN composite particles partially remained after decomposition at this temperature, with residual weights of 62% and 18%, respectively. Given these values, the ratio of PS/BN (w/w) was calculated to be 71/29 (100/40). The theoretical weight ratio of PS/BN was 56/44, which we calculated on the basis of the initial amount of AB after the



Figure 8. TGA curves of cross-linked PS (solid line), products prepared by two-step dehydrogenation reactions in [Bmim][BF<sub>4</sub>] at 120°C, followed by heating at 300°C in the absence (BN, broken line) and products prepared by multi-step dehydrogenation of AB in the presence of cross-linked PS seed particles (PS/BN, one-dot chain line); samples were heated at a rate of 10°C/min under N<sub>2</sub> atmosphere.

dehydrogenation reaction was completed by assuming that all BN adhered to the surface of the seed particles. From these results, we determined the efficiency of the shell formation to be 52%.

#### Conclusions

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In this study, a low-temperature approach to BN synthesis by the dehydrogenation of AB in  $[Bmim][BF_4]$  was demonstrated.  $[Bmim][BF_4]$  enhanced the reaction rate and the final conversion of AB. The reaction temperature and pressure strongly affected the conversion of the dehydrogenation reaction and the final product yield. A stepwise reaction at 120°C and subsequent heating at 300°C were found to be efficient for the preparation of BN. Moreover, PS/BN composite particles were successfully prepared by the muti-step dehydrogenation of AB from 80°C to 300°C in  $[Bmim][BF_4]$  in the presence of cross-linked PS seed particles. TEM images of the ultrathin cross-sections of the composite particles clearly showed the particles' core–shell morphology. The applications of the composite particles as high-thermal-release materials will be reported in the future.

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#### Notes and references

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<sup>†</sup> Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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# **RSC Advances**

# **Table of Contents Entry**



A novel synthetic route for the preparation of boron nitride (BN) by dehydrogenation of ammonia borane using an ionic

liquid as a medium was investigated under mild conditions. Polystyrene (PS)-core/BN-shell composite particles were

successfully prepared by dehydrogenation in the presence of PS seed particles.