

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][BF₄]) 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][BF₄]. The reaction rate and final conversion increased when [Bmim][BF₄] 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][BF₄] in the presence of cross-linked PS seed particles. Transmission electron microscopy images of ultrathin cross-sections of the composite particles confirmed the core-shell morphology of the particles with a PS core and a BN shell.

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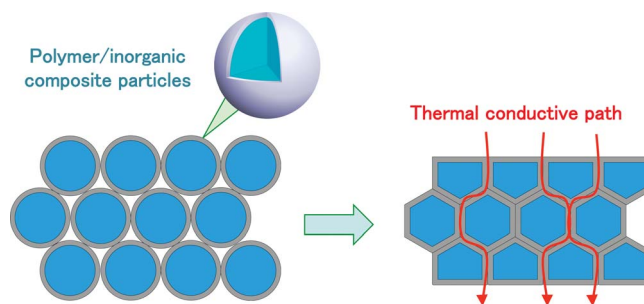
Introduction

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.^{1–8} We have reported the preparations of polymer particles such as polystyrene (PS),⁹ poly(acrylic acid) (PAA),¹⁰ Nylon-6,¹¹ and PS/PAA composite particles¹² using ionic liquids as media.

The synthesis of inorganic materials such as silica, titania, and gold nanoparticles in ionic liquids has also been reported.^{13–22} 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.²³ 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][BF₄]) in the presence of PS seed particles (seeded-dispersion sol-gel process).²⁴ PS/Al₂O₃ composite particles were subsequently prepared by heat-treating the obtained PS/Al(OH)₃ composite particles at 300 °C, which is below the decomposition temperature of PS. We also successfully prepared PS/Mg(OH)₂ and PS/MgO core-shell composite particles in an ionic liquid,²⁵ 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 inorganic shell forms continuous thermal-transport pathways with a low percolation threshold (Scheme 1).



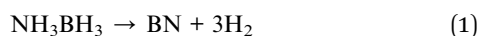
Scheme 1 Schematic illustration of an organic/inorganic composite film having effective thermal transport pathways prepared by organic core/inorganic shell composite particles.

^aGraduate School of Engineering, Kobe University, Rokko, Nada, Kobe 657-8501, Japan. E-mail: minamihi@kobe-u.ac.jp; Fax: +81 78 803 6197; Tel: +81 78 803 6197

^bMagnetic Material & Surface Modification Department, Metallic & Inorganic Material Engineering Division, Toyota Motor Corporation, Toyota-cho, Toyota, Aichi 471-8572, Japan

Boron nitride (BN) exhibits high thermal conductivity (hexagonal phase: $60 \text{ W m}^{-1} \text{ K}^{-1}$; cubic phase: $1300 \text{ W m}^{-1} \text{ K}^{-1}$) 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).²⁶ Recently, Zheng *et al.* synthesized turbostratic boron nitride in an ionic liquid (1-butyl-2,3-dimethylimidazolium tetrafluoroborate) at relatively low temperatures. This result indicates that ionic liquids may be critical in preparing crystalline boron nitride.²⁷

Ammonia borane (NH_3BH_3 , 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.²⁸ AB is stable at room temperature; however, hydrogen gas is released at approximately 100°C through dehydrogenation.^{29–31} 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_2 per 1 mol AB) compared to those in the bulk system (0.9 mol H_2 per 1 mol AB) at 120°C .³² If AB releases stoichiometric amounts of hydrogen gas (3 mol H_2 per 1 mol AB, see eqn (1)), the synthesis of BN should be possible at relatively low temperatures:



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

AB (97% purity, Sigma-Aldrich) was used as received. The ionic liquids used in this study, [Bmim]Cl (98% purity, Sigma-Aldrich), [Bmim][BF₄] (97% purity, Sigma-Aldrich), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆], 96% purity, Sigma-Aldrich), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([Bmim][TFSA], Nippon Synthetic Chemical Industry), and *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium tetrafluoroborate ([DEME][BF₄], 98% purity, Kanto Chemical), were dried at 120°C for 3 h before use. Styrene was purified by distillation under reduced pressure in N_2 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, number-average 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 $18.2 \text{ M}\Omega \text{ cm}$.

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_2 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.²⁴ 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.³³ All ingredients were sealed in a glass tube under N_2 atmosphere, which was horizontally shaken at 120 cycles per min (2 cm strokes) in an ice bath at $\sim 0^\circ\text{C}$ 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 an ionic liquid in the presence of cross-linked 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][BF₄] (2.0 g) was added to the dispersion. Methanol was evaporated at 60°C to change the medium to [Bmim][BF₄], 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:

$$\text{Conversion}(\%) = \frac{V_{\text{H}_2}/V_0}{3N_{\text{AB}}} \times 100$$

where V_{H_2} is the volume of the released hydrogen (cm^3), V_0 is the volume of the ideal gas under standard conditions ($24.8 \times 10^3 \text{ cm}^3 \text{ mol}^{-1}$ at 298 K and 0.1 MPa), and N_{AB} 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 X-ray diffraction (XRD, RINT-TTR, Rigaku, Tokyo, Japan) using the $2\theta/\theta$ method at a scanning rate of 4° min^{-1} ; the XRD was equipped with a

CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) 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 $\sim 100 \text{ nm}$ 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 X-tool apparatus using AlK α (1486.6 eV) at 15 kV and 50 W. A pressure of $\sim 1 \times 10^{-6} \text{ Pa}$ was maintained in the measurement chamber. The dried samples were spread on a carbon tape 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 $10 \text{ }^\circ\text{C min}^{-1}$ from 30 to $500 \text{ }^\circ\text{C}$ under N_2 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 $100 \text{ }^\circ\text{C}$ 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 $_4$], and [DEME][BF $_4$], but not in [Bmim][PF $_6$] or [Bmim][TfSA]. After the reaction, the mixtures were heated at $100 \text{ }^\circ\text{C}$ for 24 h and a white precipitate formed only in [Bmim][BF $_4$]; in contrast, no precipitates were observed in [Bmim]Cl and [DEME][BF $_4$]. On the basis of these results, [Bmim][BF $_4$] was chosen as the reaction medium in subsequent experiments.

Fig. 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 $120 \text{ }^\circ\text{C}$ (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 $120 \text{ }^\circ\text{C}$. Moreover, when the dehydrogenation reaction was carried out at $300 \text{ }^\circ\text{C}$, 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).³¹ In this study, [Bmim][BF $_4$] may have stabilized the intermediate in the same manner as [Bmim]Cl, and the dehydrogenation reactions were consequently enhanced.

To obtain dry samples for FT-IR analyses, the obtained products (white precipitates) were centrifuged in methanol, which dissolves AB and [Bmim][BF $_4$] but not BN. However, the

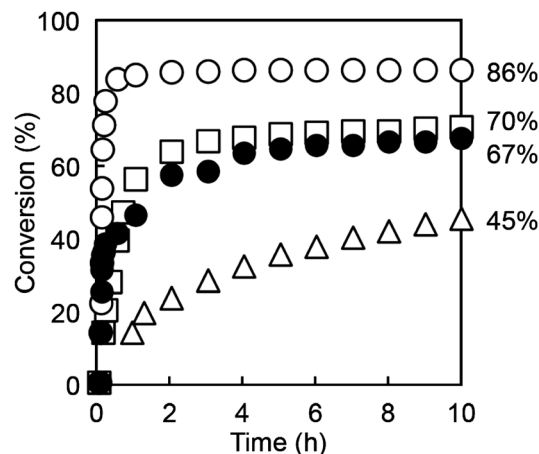


Fig. 1 Conversion *versus* time plots for the dehydrogenation of AB in the bulk system at $120 \text{ }^\circ\text{C}$ (filled circles, ●) and in the [Bmim][BF $_4$] system at $80 \text{ }^\circ\text{C}$ (open triangles, △), $100 \text{ }^\circ\text{C}$ (open squares, □), and $120 \text{ }^\circ\text{C}$ (open circles, ○).

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 $150 \text{ }^\circ\text{C}$, hydrogen gas was released vigorously and bumping occurred (Fig. 2c). To prevent the rapid release of hydrogen, the reaction was performed at $120 \text{ }^\circ\text{C}$ for 10 h, and the reaction mixture was subsequently heated at $300 \text{ }^\circ\text{C}$ 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 $_4$] was colored owing to oxidation after the reaction at $300 \text{ }^\circ\text{C}$ (Fig. 2d) and the product was stained brown owing to [Bmim][BF $_4$] (Fig. 2d'). To avoid the oxidation of [Bmim][BF $_4$], the reaction at $300 \text{ }^\circ\text{C}$ was performed under reduced pressure using a vacuum-sealed glass

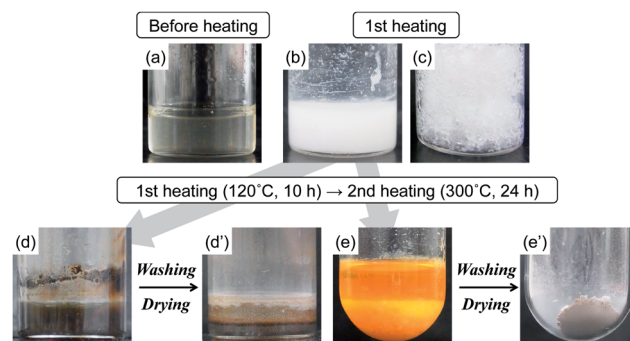


Fig. 2 Visual appearances of AB dehydrogenation before (a) and after (b–e) being heated in [Bmim][BF $_4$] under various conditions and the appearances of the obtained products after being washed with methanol (d' and e'). The reaction temperatures ($^\circ\text{C}$), times (h), and pressures were (b) 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.

tube after nitrogen purge. The vacuum facilitated the release of hydrogen gas and accelerated the dehydrogenation. After the reaction at 300 °C in a sealed glass tube (Fig. 2e), coloring [Bmim][BF₄] was prevented (although the color become yellowish) and the product (white powder) was obtained after washing with methanol (Fig. 2e'). The product yield, measured gravimetrically, was 33%.

Fig. 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) (Fig. 3a), the characteristic peaks of AB at 1064, 1163, 1380, and 2180–2770 cm⁻¹ disappeared, and a broad peak at 1350–1630 cm⁻¹ was observed. However, the broad peak at 2970–3600 cm⁻¹ 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 (Fig. 3b), the broad peak at 2970–3640 cm⁻¹ remained.

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 °C → 300 °C) dehydrogenation in [Bmim][BF₄] (Fig. 3c), the broad peaks at 2970–3640 cm⁻¹ almost disappeared and a more intense peak at 1275–1710 cm⁻¹ corresponding to B–N bonds was observed. These results suggest that BN could be successfully prepared using [Bmim][BF₄] as a medium at temperatures less than the decomposition temperature of PS.

Fig. 4 shows the XRD spectra of the products prepared by the two-step dehydrogenation in the bulk and [Bmim][BF₄] 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, filled circle symbols) or to hexagonal BN (h-BN, JCPDS File Card no. 34-0421, triangle symbol). In contrast, the XRD pattern of

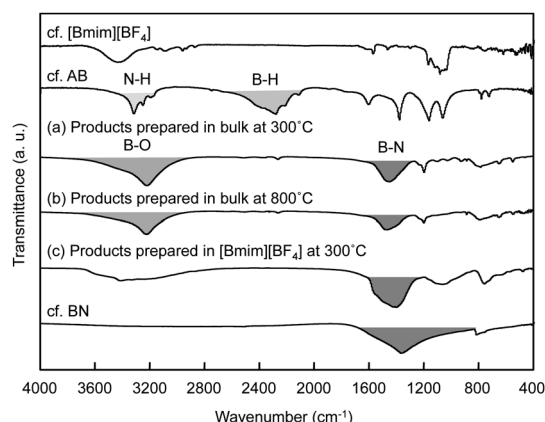


Fig. 3 FT-IR spectra of products prepared by the dehydrogenation of AB in the bulk system (a and b) and [Bmim][BF₄] system (c) under various conditions. The reaction temperature (°C), time (h), and pressure were (a) 120, 10, atmospheric pressure → 300, 24, reduced pressure; (b) 120, 10, atmospheric pressure → 300, 24, reduced pressure → 800, 3, atmospheric pressure; and (c) 120, 10, atmospheric pressure → 300, 24, in a vacuum-sealed glass tube.

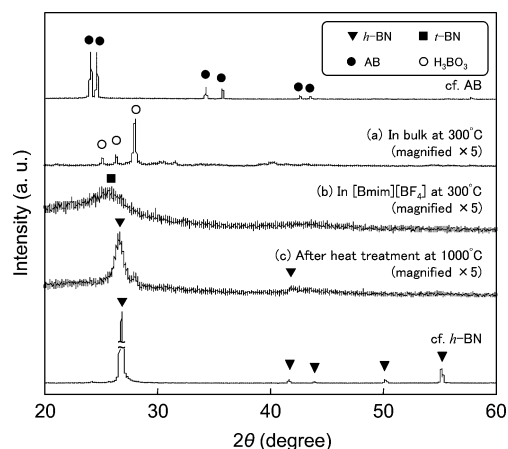


Fig. 4 XRD spectra of products prepared by the dehydrogenation of AB in the bulk system (a) and in a vacuum-sealed glass tube [Bmim][BF₄] system (b) at 120 °C, followed by subsequent heating at 300 °C and products after heat treatment of (b) at 1000 °C for 3 h (c).

the product obtained in [Bmim][BF₄] contained a broad peak at 26°, which seems to be assigned to the (002) reflection of turbostratic BN (t-BN),^{34–37} in which BN layers are stacked irregularly. Furthermore, after heat treatment of the obtained product at 1000 °C for 3 h under N₂ 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 (Fig. 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][BF₄] under mild conditions (~300 °C), although the BN exhibited turbostratic structure.

Dehydrogenation in the presence of cross-linked PS seed particles

The dehydrogenation of AB in [Bmim][BF₄] 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 → 300 °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 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 $^{\circ}\text{C}$ (10 h, 0.1 MPa) \rightarrow 120 $^{\circ}\text{C}$ (1 h, 0.1 MPa) \rightarrow 150 $^{\circ}\text{C}$ (1 h, 0.1 MPa) \rightarrow 180 $^{\circ}\text{C}$ (1 h, in a vacuum-sealed glass tube) \rightarrow 200 $^{\circ}\text{C}$ (1 h, in a vacuum-sealed glass tube) \rightarrow 250 $^{\circ}\text{C}$ (1 h, in a vacuum-sealed glass tube) \rightarrow 300 $^{\circ}\text{C}$ (24 h, in a vacuum-sealed glass tube) were carried out.

Fig. 5a and b 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][BF₄] 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.

Fig. 5a' and b' show TEM photographs of RuO₄-stained ultrathin cross-sections of cross-linked PS seed particles and the obtained particles prepared by the multi-step dehydrogenation of AB in [Bmim][BF₄] 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.

Fig. 6 shows the FT-IR spectrum of the particles obtained by the multi-step dehydrogenation of AB in [Bmim][BF₄] in the presence of the cross-linked PS seed particles. Both the characteristic sharp peaks of PS at 697 and 754 cm⁻¹ and a broad peak of BN at 1280–1600 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 (Fig. 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

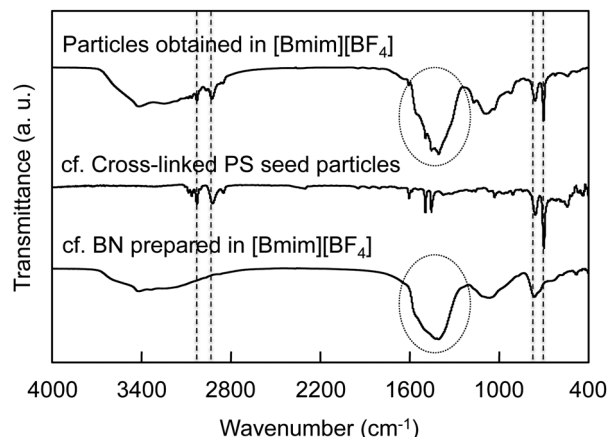


Fig. 6 FT-IR spectrum of products prepared by the multi-step dehydrogenation of AB in the sealed tube [Bmim][BF₄] system in the presence of cross-linked PS seed particles.

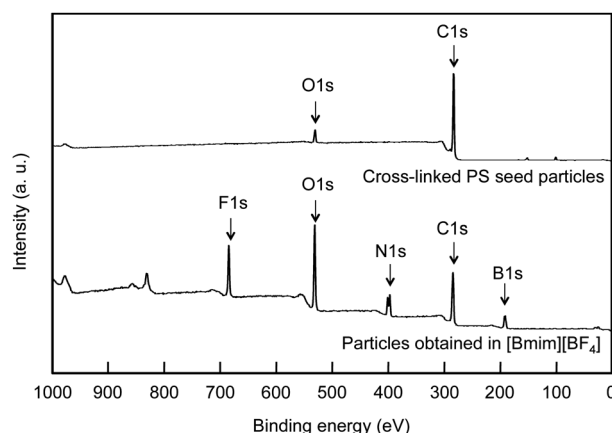


Fig. 7 X-ray photoelectron spectra of cross-linked PS seed particles and products prepared by the multi-step dehydrogenation of AB in the sealed-tube [Bmim][BF₄] system in the presence of cross-linked PS seed particles.

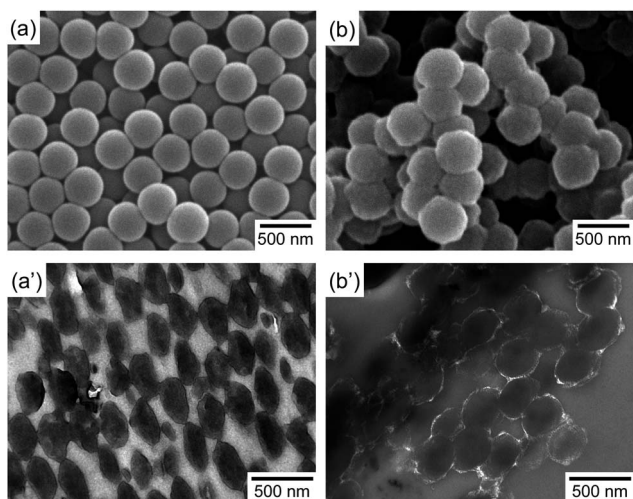


Fig. 5 SEM photographs (a and b) of cross-linked PS seed particles (a) and the obtained particles prepared by the multi-step dehydrogenation reaction of AB in the [Bmim][BF₄] system in the presence of cross-linked PS seed particles (b). TEM photographs (a' and b') of RuO₄-stained ultrathin cross-sections of cross-linked PS seed particles (a') and the obtained particles (b').

observed because of the existence of remaining [Bmim][BF₄] and some oxide.

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 (Fig. 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][BF₄] and some oxide.

Quantitative analysis of the composite particles was conducted by TGA under N₂ atmosphere. Fig. 8 shows the TGA curves of cross-linked PS seed particles, BN particles, and PS/BN composite particles prepared by the multi-step dehydrogenation of AB in [Bmim][BF₄] in the presence of the cross-linked PS seed particles. The cross-linked PS seed particles were completely decomposed at 500 $^{\circ}\text{C}$. However, BN and PS/BN composite particles partially remained after decomposition at this temperature, with residual weights of 62% and 18%,

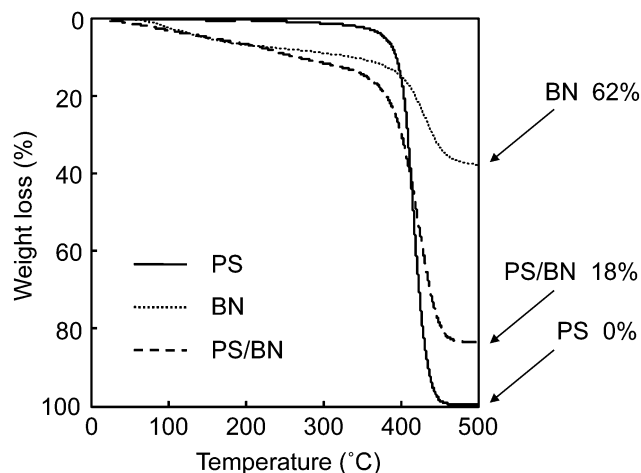


Fig. 8 TGA curves of cross-linked PS (solid line), products prepared by two-step dehydrogenation reactions in [Bmim][BF₄] at 120 °C, followed by heating at 300 °C in the absence of cross-linked PS seed particles (BN, broken line) and products prepared by multi-step dehydrogenation of AB in the presence of cross-linked PS seed particles (PS/BN, one-dot chain line); samples were heated at a rate of 10 °C min⁻¹ under N₂ atmosphere.

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 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

In this study, a low-temperature approach to BN synthesis by the dehydrogenation of AB in [Bmim][BF₄] was demonstrated. [Bmim][BF₄] 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 multi-step dehydrogenation of AB from 80 °C to 300 °C in [Bmim][BF₄] 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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