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# *In situ* molten phase-assisted self-healing for maintaining fiber morphology during conversion from melamine diborate to boron nitride†

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$C_3N_6H_6 \cdot 2H_3BO_3$  (M·2B) is a highly promising precursor of boron nitride (BN) fibers due to its eco-friendly and low-cost fabrication. However, it is still unclear why the fibers can maintain their morphology in spite of drastic weight loss (nearly 80 wt%) during M·2B-to-BN pyrolysis. Herein, an interesting cracking and self-healing behavior of the heated M·2B fibers was observed at initial pyrolysis. *In situ* formed molten boron oxide ( $B_2O_3$ ) was figured out to be the healing agent for the cracks and subsequently merged into the continuous matrix enclosing melamine/melem molecules, which subsequently acted as a nitrogen source. The  $B_2O_3$  matrix helped to keep the fiber morphology undamaged under the second weight-loss stage in the pyrolysis process. This strategy of taking advantage of the *in situ* formed molten phase for healing cracks offers detailed guidance to prepare defect-free M·2B-derived BN fibers and would be significant in defect repair for other ceramics.

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## Introduction

Due to the excellent comprehensive performances of thermal stability, chemical corrosion tolerance, oxidation resistance, neutron absorption, high thermal conductivity, electrical insulation and low dielectric constant,<sup>1–4</sup> hexagonal boron nitride (BN) holds great promise in various fields such as aerospace, high-temperature filtration, nuclear industry, and microelectronics. As typical BN materials, BN fibers similar to anisotropic BNNs enjoy wide attention owing to their unique properties provided by their high-aspect-ratio morphology.<sup>5,6</sup>

Up to now, numerous fabrication techniques have been developed for the high-efficiency production of BN fibers, which are mostly based on the spinning process that requires strict manipulations.<sup>7–11</sup> In addition, the pyrolysis of a  $C_3N_6H_6 \cdot 2H_3BO_3$  (M·2B) supra-molecule adduct is an alternative way and promising for large-scale production owing to the facile and eco-friendly fabrication of M·2B.<sup>12–14</sup>

Unfortunately, the ceramic yield of M·2B is much lower (~20 wt%) than that of other reported polymeric precursors of BN,<sup>15–18</sup> for example, 57 wt% yield of poly[2,4,6-tris(iso-

propylamino)borazine].<sup>17</sup> This implies that substantial release occurs during thermal conversion from M·2B to the final BN fibers. Moreover, M·2B is a supra-molecule constructed by low-strength hydrogen bonding<sup>19,20</sup> that might fail to self-support at a high temperature, resulting in structural collapse. These two disadvantages may cause serious defects in the final BN fibers. The fact, astonishingly, is that the M·2B-derived BN fibers display intact morphology basically inherited from initial M·2B.<sup>13,21</sup> It still remains unclear why the seemingly contradictory phenomenon occurs.

In this work, we observed unique self-healing behavior after morphological cracks were caused by huge weight loss. This self-healing behavior kept the fiber morphology intact, while its micro-structure was drastically broken and reconstructed during pyrolysis. The molten boron oxide ( $B_2O_3$ ) generated *in situ* from the  $H_3BO_3$  portion was proven to work for healing the cracks and repairing the fiber. Moreover, the boron oxide network could enclose melamine molecules and its condensate melem to prevent them from evaporation, which was crucial to keep the fibers intact as pyrolysis and nitridation proceeded in the subsequent process.

## Experimental section

### Synthesis of $C_3N_6H_6 \cdot 2H_3BO_3$

A mixture of  $C_3N_6H_6$  and  $H_3BO_3$  (analytical reagents, Sino-pharm Chemical Reagent Co., Ltd.) with a molar ratio of 1 : 2 was added into de-ionized water and dissolved at 85 °C in a water bath with vigorous stirring; the concentration of  $C_3N_6H_6 \cdot (H_3BO_3)$  was set as 0.08 mol L<sup>-1</sup> (0.16 mol L<sup>-1</sup>) to ensure

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complete dissolution. Then, the hot aqueous solution was naturally cooled down to precipitate the  $\text{C}_3\text{N}_6\text{H}_6 \cdot 2\text{H}_3\text{BO}_3$  ( $\text{M} \cdot 2\text{B}$ ) flocculent. Subsequently, the white flocculent was frozen and dried using a vacuum freeze-dryer (LGJ-FD, Beijing Songyuan Huaxing Technology Develop Co., Ltd, China) to get well-dispersed  $\text{M} \cdot 2\text{B}$  fibers.

### Thermal treatment of $\text{C}_3\text{N}_6\text{H}_6 \cdot 2\text{H}_3\text{BO}_3$

The thermal behavior of  $\text{M} \cdot 2\text{B}$  was analyzed using thermogravimetry and differential scanning calorimetry (TG-DSC, NETZSCH STA449F5, Germany); the heating rate was set as  $10^\circ\text{C min}^{-1}$ . Based on the results, the  $\text{M} \cdot 2\text{B}$  fibers were separately heated to  $125^\circ\text{C}$ ,  $150^\circ\text{C}$ ,  $200^\circ\text{C}$ ,  $400^\circ\text{C}$ ,  $550^\circ\text{C}$ ,  $650^\circ\text{C}$ , and  $1000^\circ\text{C}$  at the same temperature ramping rate and immediately cooled down. The thermal treatments were conducted in a quartz tubular furnace under a protective  $\text{N}_2$  flow. The obtained samples were designated as  $\text{M} \cdot 2\text{B}_{125}$ ,  $\text{M} \cdot 2\text{B}_{150}$ ,  $\text{M} \cdot 2\text{B}_{200}$ ,  $\text{M} \cdot 2\text{B}_{400}$ ,  $\text{M} \cdot 2\text{B}_{550}$ ,  $\text{M} \cdot 2\text{B}_{650}$ , and  $\text{M} \cdot 2\text{B}_{1000}$ . For comparison, melamine and boric acid underwent the same TG-DSC testing and were also heated at  $150^\circ\text{C}$ ,  $200^\circ\text{C}$ , and  $400^\circ\text{C}$ . To explore the effect of the self-healing process on the morphology of the final BN fibers, the  $\text{M} \cdot 2\text{B}$  fibers were also heated under a stage-variable  $\text{N}_2$  or  $\text{NH}_3$  atmosphere. For example, the  $\text{M} \cdot 2\text{B}$  fiber was heated to  $700^\circ\text{C}$  for 1 hour under  $\text{NH}_3$  and subsequently heated to  $1000^\circ\text{C}$  under switched  $\text{N}_2$ .

### Characterization and corrosion testing

The morphologies of the samples were observed by field-emission scanning electron microscopy (SEM, Hitachi S-4800, Japan), and the constituents were characterized through Fourier transform infrared spectroscopy (FT-IR, Frontier, PerkinElmer, USA), X-ray diffraction (XRD, Bruker AXS D8 Advance diffractometer, Germany), and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy in a  $\text{DMSO-d}_6$  solvent (400 MHz Agilent 400/54/ASP, USA). The molten transition point of monophasic  $\text{H}_3\text{BO}_3$  was measured using the melting point apparatus (WRS-2A, Shanghai INESA Physico-Optical Instrument Co., Ltd.).

The corrosion testing of the  $\text{M} \cdot 2\text{B}_T$  fiber ( $T = 150, 200, 400$ , and  $550^\circ\text{C}$ ) was conducted using ethanol (EA) and ethylene glycol (EG) as corrosive agents. Initially, two samples were separately immersed in EA and EG for 1 minute and then taken out for washing 3 times by de-ionized water *via* a vacuum filtration apparatus. After that, the treated samples were dried over-night in an oven at  $80^\circ\text{C}$  for observing morphology. Furthermore, the  $\text{M} \cdot 2\text{B}_T$  fibers (0.02 g) were dipped in 4 ml solvent (EA and EG) for 6 hours to estimate their solubility, which reflected the corrosion resistance of the fibers.

## Results and discussion

### Morphology transformation

Fig. 1a indicates the thermal behavior of  $\text{M} \cdot 2\text{B}$  using TG-DSC; the whole pyrolysis procedure can be divided into two obvious weight-loss stages. In the first stage, in the range of  $125\text{--}200^\circ\text{C}$ , there is a sharp endothermic peak at  $159.9^\circ\text{C}$  due to intense weight loss. During the second stage, the gravimetric curve

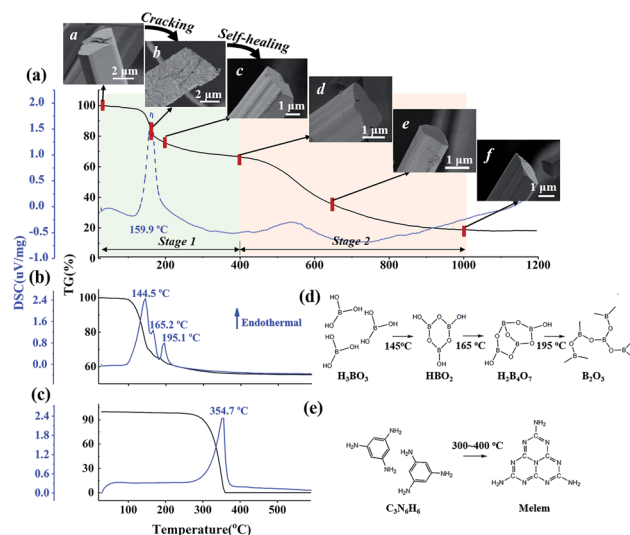


Fig. 1 TG-DSC curves of (a)  $\text{M} \cdot 2\text{B}$  supramolecular fibers, (b)  $\text{H}_3\text{BO}_3$  and (c)  $\text{C}_3\text{N}_6\text{H}_6$ . In (a), the first weight-loss stage is in the range of  $20\text{--}400^\circ\text{C}$ ; the second weight-loss stage is in the range of  $400\text{--}1000^\circ\text{C}$ , the inset SEM images demonstrate the morphological evolution of the  $\text{C}_3\text{N}_6\text{H}_6 \cdot 2\text{H}_3\text{BO}_3$  fibers during thermal treatment: a  $\text{M} \cdot 2\text{B}$ , b  $\text{M} \cdot 2\text{B}_{150}$ , c  $\text{M} \cdot 2\text{B}_{200}$ , d  $\text{M} \cdot 2\text{B}_{400}$ , e  $\text{M} \cdot 2\text{B}_{650}$ , f  $\text{M} \cdot 2\text{B}_{1000}$ . (d) Molecular transformation of  $\text{H}_3\text{BO}_3$  and (e)  $\text{C}_3\text{N}_6\text{H}_6$  in the heating process. In (d),  $\text{H}_3\text{BO}_3$  is converted to metaboric acid ( $\text{HBO}_2$ ) and further to tetraboric acid  $\text{H}_2\text{B}_4\text{O}_7$  and finally to a boron oxide structure. In (e),  $\text{C}_3\text{N}_6\text{H}_6$  condenses to melem at  $300\text{--}400^\circ\text{C}$ .<sup>22</sup>

slowly decreases from  $500$  to  $1000^\circ\text{C}$ , and a broad weak endothermic peak is located at  $535^\circ\text{C}$ . The insets show the morphology of the  $\text{M} \cdot 2\text{B}$  fiber and its thermal products after being heated separately at  $150^\circ\text{C}$ ,  $200^\circ\text{C}$ ,  $400^\circ\text{C}$ ,  $650^\circ\text{C}$ , and  $1000^\circ\text{C}$ ; they are designated as  $\text{M} \cdot 2\text{B}_{150}$ ,  $\text{M} \cdot 2\text{B}_{200}$ ,  $\text{M} \cdot 2\text{B}_{400}$ ,  $\text{M} \cdot 2\text{B}_{650}$ , and  $\text{M} \cdot 2\text{B}_{1000}$ , respectively. It was obvious that a drastic variation in the fiber's morphology occurred at the first stage; the fiber cracked when heated at  $150^\circ\text{C}$  and self-healed at  $200^\circ\text{C}$ . After this, the fiber got smoother at  $400^\circ\text{C}$  (inset (d) of Fig. 1a) and was intact in the whole second stage (from inset (d) to inset (f) of Fig. 1a). In the final stage, the  $\text{M} \cdot 2\text{B}_{1000}$  fiber displayed compact morphology. Thus, self-healing was proven to be the key to maintain the fiber's morphology in spite of the ultralow yield ( $\sim 20\text{ wt}\%$ ) of  $\text{M} \cdot 2\text{B}$ .

The fiber's cracking could undoubtedly be mainly attributed to the intense weight loss, revealing substantial decomposition at  $150^\circ\text{C}$ , but it was not clear why the self-healing behavior of  $\text{M} \cdot 2\text{B}_{200}$  occurred. To explore the reason, the structural transformation during cracking-healing was analyzed.

Considering that  $\text{M} \cdot 2\text{B}$  is an adduct of  $\text{H}_3\text{BO}_3$  and  $\text{C}_3\text{N}_6\text{H}_6$  connected *via* hydrogen bonding,<sup>20</sup> we studied the thermal behavior of the two components separately. Fig. 1b and c display the TG-DSC curves of  $\text{H}_3\text{BO}_3$  and  $\text{C}_3\text{N}_6\text{H}_6$ , respectively. It can be found that the same-region weight loss of boric acid occurs (Fig. 1b) as the first-stage weight loss of  $\text{M} \cdot 2\text{B}$ . Meanwhile,  $\text{C}_3\text{N}_6\text{H}_6$  remained stable at  $150\text{--}200^\circ\text{C}$ , as implied by the flat TG curve (Fig. 1c) and the XRD patterns of the heated products (Fig. S1†).



The weight loss of boric acid could be divided into three stages according to three sharp endothermic peaks, separately corresponding to the different stages of the dehydration of  $\text{H}_3\text{BO}_3$ , as shown in Fig. 1d. These reaction equations were proved by the XRD patterns of the heating products (Fig. S1a†). Thus, the first-stage weight loss of  $\text{M} \cdot 2\text{B}$  and the corresponding morphology evolution were basically attributed to the dehydration of  $\text{H}_3\text{BO}_3$  in  $\text{M} \cdot 2\text{B}$ . At the subsequent stage from 200 to 400 °C, there was no obvious weight loss against the sublimation and condensation of melamine (Fig. 1c and e), which would be discussed later. This stable stage ensured that the morphology of the  $\text{M} \cdot 2\text{B}_{400}$  fiber became more dense and smooth rather than broken.

Based on the analysis of the thermal transformation of the pure phases of  $\text{C}_3\text{N}_6\text{H}_6$  and  $\text{H}_3\text{BO}_3$ , the structural evolution of  $\text{M} \cdot 2\text{B}$  involving morphological cracking–healing was further studied using FT-IR spectroscopy and XRD. As shown in Fig. 2a, plenty of sharp peaks disappear after the conversion from  $\text{M} \cdot 2\text{B}$  to  $\text{M} \cdot 2\text{B}_{150}$ , especially in the fingerprint region (marked by the light green rectangle areas) of the hydrogen-bonded structure. The FTIR peaks at  $1186\text{ cm}^{-1}$  and  $786\text{ cm}^{-1}$  that respectively represents bending and twisting vibrations of B–OH, became feeble as to  $\text{M} \cdot 2\text{B}_{150}$ . This indicated the drastic removal of hydroxyl groups, which was in accordance with the dehydration of  $\text{H}_3\text{BO}_3$ . Meanwhile, the highly crystallized  $\text{M} \cdot 2\text{B}$  was converted into an unordered phase of  $\text{M} \cdot 2\text{B}_{150}$  characterized as double broad peaks (Fig. 2b).

$\text{M} \cdot 2\text{B}_{125}$  displays an intermediate structure, revealing the transformation process from  $\text{M} \cdot 2\text{B}$  to unordered  $\text{M} \cdot 2\text{B}_{150}$ , which was characterized as weaker peaks located mainly in the green fingerprint region in the IR spectrum and the co-existence of sharp and broad peaks in the XRD pattern. Therefore, the drastic removal of hydroxyl groups due to the dehydration of  $\text{H}_3\text{BO}_3$  resulted in the breakage of the  $\text{M} \cdot 2\text{B}$  crystal and thus

structural disordering. Morphology cracking could be attributed to the drastic structure transformation and also the huge release of the removed  $\text{H}_2\text{O}$ . As for the micro-structure of the cracked fiber, it should be noted that the sharp XRD peaks of  $\text{M} \cdot 2\text{B}_{125}$  correspond well with the  $(-110)$ ,  $(012)$ ,  $(111)$  and  $(102)$  crystal planes of melamine (ICSD PDF#39-1950) but not  $\text{M} \cdot 2\text{B}$  (Fig. 3a). This means that there occurred the assembly of melamine molecules to form crystals, while disordering occurred in the initial  $\text{M} \cdot 2\text{B}$  crystal, allowing for the fact that  $\text{C}_3\text{N}_6\text{H}_6$  was molecularly isolated by  $\text{H}_3\text{BO}_3$  in  $\text{M} \cdot 2\text{B}$ . Thus, the double broad peaks of  $\text{M} \cdot 2\text{B}_{150}$  were proved to result from the widening of the  $(-110)$  and  $(102)$  diffraction peaks and indicated the existence of melamine micro-crystals in the  $\text{M} \cdot 2\text{B}_{150}$  fiber.

From the cracked  $\text{M} \cdot 2\text{B}_{150}$  to the healed  $\text{M} \cdot 2\text{B}_{200}$ , there also occurred intense structural transformation. In addition to the IR peaks belonging to  $-\text{NH}_2$ , C–N,  $\text{BO}_3$ , triazine ring, and  $\text{B}_3\text{O}_3$ , the evolved peak of  $\text{BO}_4$  at  $1050\text{ cm}^{-1}$  indicates the formation of a  $\text{B}_2\text{O}_3$  network.<sup>23,26</sup> Two undefined peaks at  $1240\text{ cm}^{-1}$  and  $1302\text{ cm}^{-1}$  existing for  $\text{M} \cdot 2\text{B}_{200-400}$  may be related to the C–O–B structure formed between melamine and boron oxide,<sup>27</sup> which can keep melamine non-volatile in the range of 300–400 °C (Fig. 1a and c). The  $^{13}\text{C}$  NMR spectra of monophasic melamine,  $\text{M} \cdot 2\text{B}$ ,  $\text{M} \cdot 2\text{B}_{150}$  and  $\text{M} \cdot 2\text{B}_{200}$  (Fig. S2†) also proved the consistent structural evolution, which especially revealed a slight difference between  $\text{M} \cdot 2\text{B}_{150}$  and  $\text{M} \cdot 2\text{B}_{200}$ . The change may be caused by the newly formed carbonaceous structure.

Besides, the double broad XRD peaks of  $\text{M} \cdot 2\text{B}_{150}$  merged into an envelope peak of  $\text{M} \cdot 2\text{B}_{200-400}$ . Interestingly, a broad peak belonging to  $\text{g-B}_2\text{O}_3$  was located at  $23^\circ$  (Fig. S1a†) between the double broad peaks located at  $16.3^\circ$  and  $26.2^\circ$ . To study this in detail, we fitted the XRD peaks of  $\text{M} \cdot 2\text{B}_{150}$ ,  $\text{M} \cdot 2\text{B}_{200}$ , and  $\text{M} \cdot 2\text{B}_{400}$  using that of  $\text{g-B}_2\text{O}_3$  as a reference. As shown in Fig. 3b, the envelope peak for the healed  $\text{M} \cdot 2\text{B}_{200}$  fiber can be well fitted as the double peaks of  $\text{M} \cdot 2\text{B}_{150}$  and a broad peak of  $\text{g-B}_2\text{O}_3$ , and the envelope peak of smoothed  $\text{M} \cdot 2\text{B}_{400}$  becomes more

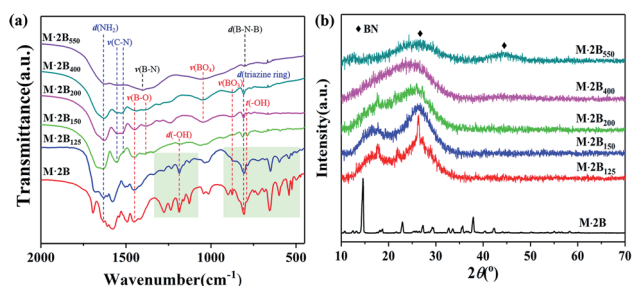


Fig. 2 (a) FT-IR spectra and (b) XRD patterns of the  $\text{M} \cdot 2\text{B}$  supramolecule and its heated products  $\text{M} \cdot 2\text{B}_{125}$ ,  $\text{M} \cdot 2\text{B}_{150}$ ,  $\text{M} \cdot 2\text{B}_{200}$ ,  $\text{M} \cdot 2\text{B}_{400}$ ,  $\text{M} \cdot 2\text{B}_{550}$ . The light green rectangle areas in (a) are the fingerprint region of the hydrogen-bonded adduct structure, and the absorption bands are labeled as follows:  $\nu(\text{NH}_2)$ :  $-\text{NH}_2$  bending,  $1620\text{ cm}^{-1}$ ;  $\nu(\text{C-N})$ : C–N stretching,  $1552\text{ cm}^{-1}$  and  $1525\text{ cm}^{-1}$ ;  $\nu(\text{B-O})$ :  $1450\text{ cm}^{-1}$  to B–O asymmetric stretching in  $\text{BO}_3$  and  $1380\text{ cm}^{-1}$  to B–O stretching in  $\text{B}_3\text{O}_3$  ring;  $\nu(\text{B-N})$ : B–N stretching at  $1400\text{ cm}^{-1}$ ;  $\nu(\text{OH})$ :  $-\text{OH}$  bending,  $1186\text{ cm}^{-1}$ ;  $\nu(\text{BO}_4)$ : B–O stretching in the  $\text{BO}_4$  unit,  $1050\text{ cm}^{-1}$ ;  $\nu(\text{BO}_3)$ : B–O symmetric stretching in the  $\text{BO}_3$  unit,  $873\text{ cm}^{-1}$ ;  $\nu(\text{triazine ring})$ : triazine ring bending at  $808\text{ cm}^{-1}$ ;  $\nu(\text{B-N-B})$ : out-of-plane bending of B–N–B at  $802\text{ cm}^{-1}$ ;  $\nu(\text{OH})$ : out-of-plane  $-\text{O-H}$  twisting at  $786\text{ cm}^{-1}$ .<sup>23–25</sup>

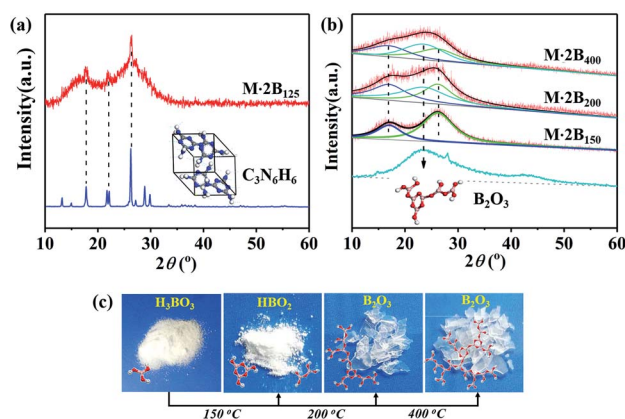


Fig. 3 (a) Analysis of the XRD pattern of  $\text{M} \cdot 2\text{B}_{125}$  in comparison with that of melamine. (b) Peak fitting of the XRD patterns of  $\text{M} \cdot 2\text{B}_{150}$ ,  $\text{M} \cdot 2\text{B}_{200}$ , and  $\text{M} \cdot 2\text{B}_{400}$  using  $\text{B}_2\text{O}_3$  as a reference. (c) Photographs of the original  $\text{H}_3\text{BO}_3$  and heat treatment products:  $\text{HBO}_2$  after 150 °C heating,  $\text{B}_2\text{O}_3$  after 200–400 °C heating, the insets are the corresponding molecular structures.



integrated owing to the more intense peak of  $g\text{-B}_2\text{O}_3$ , while the double peaks belonging to melamine decrease. Therefore, it was confirmed that a  $g\text{-B}_2\text{O}_3$  phase evolved in  $\text{M}\cdot 2\text{B}_{200-400}$ , which may be related to the self-healing of the fiber. Fig. 3c displays the photos of  $\text{H}_3\text{BO}_3$  and its heated products. Metaboric acid formed at  $150^\circ\text{C}$  was a white powder just like boric acid, but  $g\text{-B}_2\text{O}_3$  obtained at  $200\text{--}400^\circ\text{C}$  turned into a glass-like solid, which revealed that it was melted. The result of the melting point measurement of  $\text{H}_3\text{BO}_3$  also proved that a viscous phase evolved at  $206.2\text{--}207.8^\circ\text{C}$ . Allowing for the same boron–oxygen network in  $\text{M}\cdot 2\text{B}_{200-400}$  as in pure  $\text{B}_2\text{O}_3$ , we have reason to believe that the viscous  $\text{B}_2\text{O}_3$  formed *in situ* played a key role in healing the fiber's cracks. Besides, melamine and condensed melem displayed a powder state (Fig. S3†), indicating that the solid state remained during heating. This melamine/melem solid could prevent the excessive flow of viscous  $\text{B}_2\text{O}_3$  and helped avoid the fusion of fibers. In the final stage, the self-healed  $\text{M}\cdot 2\text{B}_{200-400}$  fiber was composed of  $\text{B}_2\text{O}_3$  glass and melamine/melem.

Moreover, to determine whether the B–O oligomer was uniformly distributed in  $\text{M}\cdot 2\text{B}_{150}$  and  $\text{B}_2\text{O}_3$  acted as a matrix in  $\text{M}\cdot 2\text{B}_{200-400}$ , the fibers underwent corrosion testing by EG (ethylene glycol) and EA (ethanol) considering that  $\text{B}_2\text{O}_3$  could be rapidly dissolved in EG while remaining stable in EA for a long period. The testing went on merely for 1 minute for avoiding complete dissolution, and the corroded fibers were separately designated as  $\text{M}\cdot 2\text{B}_{T\text{-EG}}$  and  $\text{M}\cdot 2\text{B}_{T\text{-EA}}$  ( $T = 150, 200, 400^\circ\text{C}$ ).

As shown in Fig. S5e and f,† all the  $\text{M}\cdot 2\text{B}_{T\text{-EG}}$  fibers collapse into pieces due to the severe corrosion in EG. These results disclosed that the B–O oligomer or  $\text{B}_2\text{O}_3$  was uniform throughout the whole fiber. After 6 hour corrosion, these fibers were completely dissolved, while the  $\text{M}\cdot 2\text{B}_{550}$  fiber remained undissolved due to the predominant BN phase (Fig. S4a†). In contrast, the samples in EA were partially dissolved or undissolved (Fig. S4b†). After being corroded for 1 minute in EA,  $\text{M}\cdot 2\text{B}_{T\text{-EA}}$  maintained the fiber's profile (Fig. S5b and S5c†) despite slight etching on the surface of  $\text{M}\cdot 2\text{B}_{150\text{-EA}}$ , which was composed of parallel short rods (Fig. S5a†) resulting from the decomposition of the intact  $\text{M}\cdot 2\text{B}$  fiber. The partial dissolution of the B–O oligomer at the interface between the rods disclosed this unique morphology.

The cracks in  $\text{M}\cdot 2\text{B}_{150}$  might be the gaps between the mismatched rod bundles. As for  $\text{M}\cdot 2\text{B}_{200\text{-EA}}$ , the ultrafine fibers generated on the basis of the original  $\text{M}\cdot 2\text{B}_{200}$  fiber (Fig. S5b†) might be attributed to the assembly of  $\text{C}_3\text{N}_6\text{H}_6$  and  $\text{H}_3\text{BO}_3$  (formed *via* the moisture absorption of superficial  $\text{B}_2\text{O}_3$ ) in an ethanol solution.  $\text{M}\cdot 2\text{B}_{400\text{-EA}}$  maintained the morphology for the initially smooth surface and the inactive melem. In summary, the different corrosion behaviors of the  $\text{M}\cdot 2\text{B}_T$  fibers in EA compared with that in EG confirmed that the B–O oligomer or  $\text{B}_2\text{O}_3$  was the dominant phase in affecting the fiber's morphology. In other words,  $\text{B}_2\text{O}_3$  acted as the matrix in the  $\text{M}\cdot 2\text{B}_{200-400}$  fiber in which melamine/melem was enclosed.

On the basis of the above-mentioned discussion, the structural conversion corresponding to “cracking and self-healing” morphology transformation was discussed in detail. The

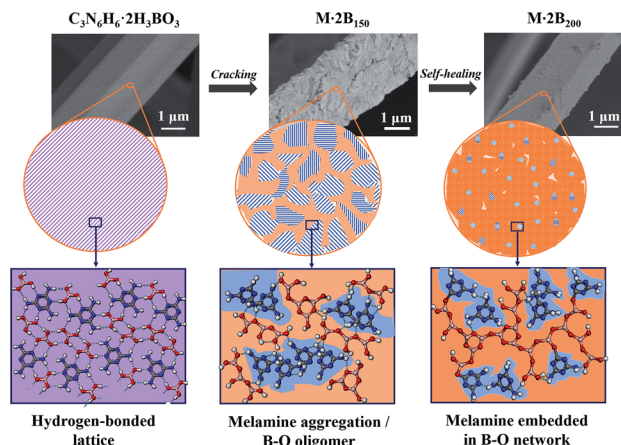


Fig. 4 Schematic illustration of microstructural evolution corresponding to the morphological transformation: cracking and self-healing.

schematic illustration in Fig. 4 shows structure evolution corresponding to the staged morphology. Initially,  $\text{M}\cdot 2\text{B}$  with intact fibrous morphology possessed a hydrogen-bonded lattice, in which  $\text{C}_3\text{N}_6\text{H}_6$  and  $\text{H}_3\text{BO}_3$  were arranged uniformly and orderly. After heating at  $150^\circ\text{C}$ ,  $\text{H}_3\text{BO}_3$  was dehydrated and formed a B–O oligomer, while the  $\text{C}_3\text{N}_6\text{H}_6$  molecules aggregated and assembled into tiny crystals. This resulted in the breakage of the ordered hydrogen-bonded structure and the intact fiber decomposed into short-rod bundles. However, the profile of the fiber was maintained integrated owing to the existence of the B–O oligomer at the interface of the rods. As a result, the cracked structure was derived from the mismatched gaps of the bundles. For  $\text{M}\cdot 2\text{B}_{200}$ , the extended  $\text{B}_2\text{O}_3$  network was formed as a result of further dehydration, while the  $\text{C}_3\text{N}_6\text{H}_6$  domain shrank and was isolated by the continuous  $\text{B}_2\text{O}_3$  matrix. Thus, the cracked structure of  $\text{M}\cdot 2\text{B}_{150}$  was healed by the *in situ* viscous matrix. Our results provide a self-healing strategy for inorganic materials, which is different from that for organic polymers involving reversible bonding.<sup>28,29</sup>

To explore the effect of the “self-healing” process on the morphology of the final BN fiber, we treated the  $\text{M}\cdot 2\text{B}$  fibers under different pyrolysis conditions with a stage-variable atmosphere. As shown in Fig. 5, there are three sets of contrasts. In Fig. 5a and b, the BN fiber obtained after treatment under an  $\text{NH}_3$  atmosphere is defective, while that obtained under  $\text{N}_2$  is smooth in spite of undergoing the same heating process at  $1000^\circ\text{C}$  for 1 hour. The difference in the fiber morphologies could be attributed to “self-healing” between  $200$  and  $400^\circ\text{C}$ . As is well-known, the complex reaction between  $\text{B}_2\text{O}_3$  and  $\text{NH}_3$  occurs at a temperature close to  $200^\circ\text{C}$ , forming a non-melting  $(\text{B}_2\text{O}_3)_n\cdot \text{NH}_3$  compound,<sup>30</sup> which prevents the cracked fiber from self-healing, while the molten  $\text{B}_2\text{O}_3$  phase formed under a nitrogen atmosphere assists in healing the cracks.

The same comparisons were performed at temperatures lower than  $1000^\circ\text{C}$ . As shown in Fig. 5c and d, the  $\text{M}\cdot 2\text{B}$  green fiber is separately heated under an  $\text{NH}_3$  atmosphere and



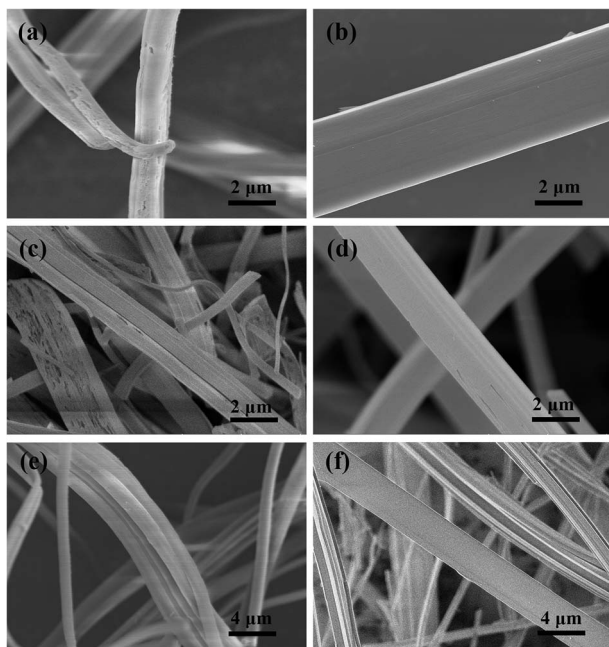


Fig. 5 (a) BN fibers obtained after heating at 1000 °C for 1 hour under  $\text{NH}_3$  atmosphere; (b) heating at 1000 °C for 1 hour under  $\text{N}_2$  atmosphere; (c) heating at 700 °C for 1 hour under  $\text{NH}_3$  and subsequent heating at 1000 °C under  $\text{N}_2$ ; (d) heating at 700 °C for 1 hour in vacuum and subsequent heating at 1000 °C under  $\text{N}_2$ ; (e) heating at 400 °C for 1 hour under  $\text{NH}_3$  and heating to 1000 °C under  $\text{N}_2$ ; (f) heating at 400 °C for 1 hour under  $\text{N}_2$  and subsequently at 700 °C for 1 hour under  $\text{NH}_3$ , and finally to 1000 °C under  $\text{N}_2$ .

vacuum at 700 °C. As shown in Fig. 5e and f, the M·2B green fiber is separately treated at 400 °C under the different combination of  $\text{NH}_3/\text{N}_2$  atmosphere. Both these comparisons indicated the same results as those obtained from Fig. 5a and b; the fibers pyrolyzed under  $\text{NH}_3$  were defective, while the fibers pyrolyzed under  $\text{N}_2$  or vacuum were smooth. In summary, the significance of self-healing assisted by the molten  $\text{B}_2\text{O}_3$  formed at 200 °C is crucial to obtain defect-free BN fibers. The result is of great significance to provide guidance to fabricate dense BN fibers when applying an active atmosphere such as  $\text{NH}_3$  for better nitridation and complete removal of carbon.

## Conclusions

In summary, the dehydration of  $\text{H}_3\text{BO}_3$  and evolution of  $\text{B}_2\text{O}_3$  were figured out to be responsible for the unique “cracking and self-healing” morphological transformation. The resulting fiber was composed of a  $\text{B}_2\text{O}_3$  matrix, in which melamine/melem was enclosed. This compound structure ensured stable morphology at the subsequent pyrolysis and nitridation stages and laid the foundation for the BN fiber. The self-healing mechanism assisted by the *in situ* molten phase can be adopted to guide the preparation of high-performance M·2B-derived BN fibers and can also be significant for other precursor-derived ceramic materials, especially those with low yields.

## Conflicts of interest

There are no conflicts to declare.

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