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# Metal-free Nitrogen- and Boron-Codoped mesoporous carbons for Primary Amides Synthesis from Primary Alcohols via Direct Oxidative Dehydrogenation

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ABSTRACT: Metal-free catalysts show superior sustainability and cost-effectiveness, as well as less susceptible to poisoning over metal and metal oxide catalysts. In this respect, we present the

synthesis and characterization of metal-free mesoporous nitrogen- and boron-codoped nanocarbon (meso-N,B/C), which exhibits good catalytic performance with conversion of 89% and selectivity of 83% towards amides synthesis from primary alcohols using NH4OAc as ammonia resource under oxygen atmosphere. The facile codoping synthetic strategy was executed by pyrolysis of nitrogen-enriched ligand 4,5-diazafluorene-9-one azine (DAA) and H<sub>3</sub>BO<sub>3</sub> as nitrogen and boron content modulator, respectively. Significantly, control experiments revealed that the reaction proceeded through direct oxidative dehydrogenation of hemiaminal after aldehyde-ammonia condensation, which was different remarkably from that in the previous literature. Density functional theory (DFT) calculations further demonstrate that the selective preference for benzamide largely benefits from the strong adsorption and enhanced activity of oxygen molecule via the interaction with B atom doped in the catalyst. The active sites in the meso-N,B/C catalyst are proposed to be B atom bonded with N within the graphitic carbon sheets. This founding opens up avenues for the development of modified carbon materials on metal-free catalysis.

KEYWORDS: N, B-codoped carbon, mesoporous carbon, primary amides, oxidative dehydrogenation, DFT calculations

#### **INTRODUCTION**

Since the past decade, there exists an increasing interest in the development of metal-free catalysts for organic synthesis due to their distinct advantages over metal-based catalysts, such as lower cost as well as higher reliability, biocompatibility and sustainability.<sup>1</sup> Metal-free materials behave completely differently from traditional metal/metal oxide materials in catalysis, which have revolutionized the field of catalysis.<sup>2</sup> Carbon materials as a typical nonmetallic

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heterogeneous catalysts, have shown promising application on Friedel–Crafts alkylation reactions,<sup>3</sup> reductive hydrogen atom transfer reactions,<sup>4</sup> and oxidation of amines<sup>5</sup> and arenes<sup>6</sup>. Heteroatom dopants (e.g., B, N, F, P or S) can effectively modulate the electrical properties and surface physicochemical features of carbons, resulting in enhanced activity of carbocatalysts or bringing about some new chemical functions.<sup>7</sup> Specifically, N-doped graphene have been recently found to catalyze selective oxidation of ethylbenzene<sup>8</sup> and epoxidation of trans-stilbene and styrene<sup>9</sup> owing to the more metal-like d band electronic structure of the ortho-carbon atom next to the doped N atom. Such heteroatom doping strategy could tune the electron features of carbon correlated to catalysis. However, reactions are limited to simple catalytic hydrogenations and oxidations currently. Targeting design over the electrical properties of carbocatalysts for other challenging synthetic organic reactions remains a challenge. Finding a practical, effective method to fabricate carbon nanostructures with controllable heteroatom doping may push the limits of metal-free carbocatalyst performance, thus stimulate progress in this area.

Amides and their derivatives represent commercially important class of compounds given their widespread applications as intermediates for the manufacture of biological as well as chemicals and polymer compounds.<sup>10</sup> In the drive towards green and sustainable chemistry, direct amide synthesis from readily available alcohol attracts significant interest in which reagents used are non-toxic and pollution-free.<sup>11</sup> Since Milstein *et al.* reported secondary amides synthesis from primary alcohols and amines with a PNN pincer-type Ru complex with evolution of H<sub>2</sub>,<sup>12</sup> many successive efforts have been made and most of them employed noble metals such as homogeneous Ru<sup>13</sup>, Rh<sup>14</sup> complexes, and heterogeneous Ag/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>15</sup> Besides, despite the excellent catalytic performance of the heterogeneous Au-based catalysts on amides synthesis from alcohols and amines under molecular oxygen with excessive indispensable base

additive,<sup>16,17</sup> it is hard to implement large-scale application because of exorbitant cost. And when it occurred to inorganic ammonia, applicability of the above-mentioned Au-based system is only limited to benzamide, and the yield is low (50% yield). Recently, a series of primary amides were successfully achieved by Ru(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> in a two-step strategy (Scheme 1):<sup>18</sup> 1) initially, it occurs oxidative dehydrogenation of the alcohol to the aldehyde. Condensation of the aldehyde with ammonia proceeds to form a hemiaminal intermediate, followed by dehydration to aldimine and undergoes immediately oxidative dehydrogenation to nitriles; 2) the nitriles further hydrolyzes into the final primary amides product with additional water. Non-noble-metal-based catalysts OMS-2<sup>19</sup> and MnO<sub>2</sub>/GO<sup>20</sup> have been currently developed for one-step primary amide synthesis from alcohol, which went through same dehydration-dehydrogenation-hydration sequence of the hemiaminal. Besides, nanoscale iron oxide catalyst was also occupied to catalyze aromatic aldehyde with ammonia to achieve primary amides.<sup>21</sup>

$$R \longrightarrow OH \xrightarrow{1) O_2}_{-H_2O} R \longrightarrow O \xrightarrow{NH_3} \left[ \begin{array}{c} NH_2 \\ R \longrightarrow OH \end{array} \right]$$

$$\int (-H_2O) \\ H_2O \\ R \longrightarrow NH_2 \xrightarrow{2) H_2O}_{-H_2O} R - CN \xrightarrow{O_2}_{-H_2O} R \xrightarrow{NH}$$

Scheme 1 General reaction pathway for amides synthesis from primary alcohols and ammonia

Despite the significant progress achieved by the above metal-based catalysts, metal-free catalytic procedure for primary amides still remains strongly desirable from both economical and ecological perspective, but very challenging. In this contribution, we design and synthesize N,B-codoped nanocarbons via pyrolysis of nitrogen-rich 4,5-diazafluorene-9-one azine (DAA) and H<sub>3</sub>BO<sub>3</sub>. Hard template method using silica colloid as template can equip the N,B-codoped

nanocarbons with high specific surface area for preparing an mesoporous codoping nanocarbons meso-N,B/C. The as-designed codoped carbocatalysts show high reactivity towards primary amides directly from primary alcohols using NH<sub>4</sub>OAc as ammonia resource under oxygen atmosphere. Unexpectedly, the metal-free primary amides synthesis system undergoes via a novel direct oxidative dehydrogenation strategy of the hemiaminal, not the general dehydration-dehydrogenation-hydration sequence reported in the previous literature.

#### **RESULTS AND DISCUSSION**

Different mass ratio of polypyridyl ligand DAA and H<sub>3</sub>BO<sub>3</sub> as nitrogen and boron resource, respectively, were mixed thoroughly at the molecular level before SiO<sub>2</sub> nanosphere template was involved. Subsequent pyrolysis at 800°C for 2 hours under N<sub>2</sub> atmosphere and NaOH etch produced the final meso-N,B/C-x (x = 3, 1.5, 0.5), where x denoted the different mass ratio of DAA and H<sub>3</sub>BO<sub>3</sub>. For comparison, undoped mesoporous carbon (meso-C) derived from sucrose and bulk N,B/C without any hard template assistant were also prepared. All these materials were tested for their catalytic activity for the benchmark oxidative amidation of benzyl alcohol (**1a**).

As showed in Table 1, the reaction hardly proceeded in the absence of catalyst (Table 1, entry 1). Precursors DAA and H<sub>3</sub>BO<sub>3</sub> were nearly inactive, suggesting that the active species should be formed during pyrolysis (Table 1, entry 2). As expected, undoped mesoporous carbon showed low activity (Table 1, entry 3), whereas the as-designed meso-N,B/C samples obtained by pyrolysis of DAA and H<sub>3</sub>BO<sub>3</sub>, could considerably prompt the transformation of **1a** under the same condition (Table 1, entries 4-6). Combined these results with X-ray photoemission spectroscopy (XPS) analysis (Table 2 and S1), it was discovered that when B concentration increased from 1.52 at% in the meso-N,B/C-3 sample to 2.36 at% in the meso-N,B/C-1.5 sample,

the selectivity of benzamide (2a) versus benzonitrile (3a) ( $S_{2a/3a}$ ) was enhanced from 7.3 to 9.2. It seemed that  $S_{2a/3a}$  correlated to the doping content of B in consideration of the nearly same N concentration in meso-N,B/C-*x* samples as showed in XPS

Table 1. Aerobic oxidative amidation of benzyl alcohol over different catalysts<sup>a</sup>

$ \begin{array}{c}                                     $						
entry	catalyst	conv.(%) <sup>b</sup>		sel.(%) <sup>t</sup>	)	
		_	2a	<b>3</b> a	2a:3a	
1	-	8	-	trace	-	
2	DAA+H <sub>3</sub> BO <sub>3</sub>	8	-	trace	-	
3	meso-C	26	42	10	4.2	
4	meso-N,B/C-3	81	80	11	7.3	
5	meso-N,B/C-1.5	89	83	9	9.2	
6	meso-N,B/C-0.5	76	84	9	9.3	
7	meso-N/C	77	63	18	3.5	
8	N,B/C	36	54	13	4.2	
<sup>a</sup> Reaction conditions: 1a (0.5 mmol), catalyst (50 mg), 2.5						

equiv. NH<sub>4</sub>OAc, 5 bar O<sub>2</sub>, 1 ml *t*-amyl alcohol, 130  $^{\circ}$ C, 18 h. <sup>*b*</sup>Conversion and selectivity were determined by GC, naphthalene as inner standard.

analysis. However, further multiplying  $H_3BO_3$  dosage only resulted in a slightly greater B concentration (2.67 at%) in meso-N,B/C-0.5 sample and, thus a similar  $S_{2a/3a}$  (9.3). The effect of surface area, pore volume and pore size on the final selectivity should be excluded according to the N<sub>2</sub> physical adsorption analysis results of meso-N,B/C-x samples (Table 2). Among them, the meso-N,B/C-1.5 performed the best, giving the highest conversion of **1a** (89%) and selectivity

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towards **2a** (83%, Table 1, entry 5). For comparison, meso-N/C catalyst derived solely from DAA was also tested,  $S_{2n/3n}$  dropped sharply to 3.5, suggesting that B dopant play a pivotal role in improving amide selectivity (Table 1, entry 7). Bulk N,B/C catalyst gave low conversion, which indicated that the high surface area and pore volume contribute to expose more active sites, and thus superior activity (Table 1, entry 8). This conventional concept is corroborated by that the specific surface area increased from 0 to 513 m<sup>2</sup>/g after the involvement of SiO<sub>2</sub> template (Table S2). Inaddition to catalyst optimization, the reaction conditions were also optimized (Table S3–S4, Figure S1): 50mg meso-N,B/C-1.5, 2.5 equiv of NH<sub>4</sub>OAc, 1 mL of *t*-amyl alcohol, reaction temper ature at 130 °C under 0.5 MPa O<sub>2</sub> for 18 h. Considering the relatively low conversion of meso-N,B/C-0.5, we used meso-N,B/C-1.5 as the best-in-class catalyst in all subsequent experiment. All these results indicate the key role of special electronic structure and thus physicochemical property of carbocatalyst in tuning the reaction chemoselectivity. Moreover, the meso-N,B/C-1.5 catalyst shows good stability after six reactions with a little activity decline (Table S5).

Table 2. Textural and physicochemical properties of meso-N,B/C-x

samples(meso-	SBET	S <sub>Micro</sub>	$S_{Meso}$	V <sub>Total</sub>	D <sub>pore</sub> <sup>a</sup>	$\operatorname{Content}(\%)^b$			
N,B/C)	$(m^2/g)$	$(m^{2}/g)$	$(m^{2}/g)$	(cc/g)	(nm)	В	С	Ν	0
-3	546	177	369	1.41	17.3	1.52	76.93	10.15	11.39
-1.5	513	149	365	1.80	11.9	2.36	77.06	10.11	10.47
-0.5	555	177	378	1.42	12.1	2.67	76.49	10.20	10.63

<sup>a</sup>Calculated using the BJH method.<sup>b</sup>Measured by XPS.





**Figure 1.** (a) SEM, (b,c) TEM images of meso-N,B/C-1.5, inlet: the selected-area electron diffraction (SAED) image. (d) Raman spectrum of meso-N,B/C-*x* 

SEM images for as-designed meso-N,B/C was displayed in Figure 1a. The material featured the sponge-like morphology resulting from silicon sphere template. The interlacing of pores were displayed in TEM images with a diameter of several to dozen nanometers (Figure 1b), which is in agreement with N<sub>2</sub> physical adsorption results (Figure S2). At higher resolution, it was observed that nanocarbon wall was of very high graphitic degree (Figure 1c). As showed in the Raman spectrum, I<sub>D</sub>/I<sub>G</sub> increased along with the increasing boron doping (1.06 and 3.19 for meso-N,B/C-3 and -1.5), which means higher defect density and disorder degree of nanocarbon material (Figure 1d). The energy-dispersive X-ray (EDX) spectrum clearly proved no metal

pollution (Figure S3). Energy-dispersive spectroscopy (EDS) mapping revealed that N and B were uniformly doped into the mesoporous carbon bulk (Figure S4). The uniform doping was due to the molecule-level mixture of DAA and H<sub>3</sub>BO<sub>3</sub> before thermal calcination.



Figure 2. (a) B1s, (b) C1s, (c) N1s, (d) O1s spectra of meso-N,B/C-1.5

To identify surface chemical state of B and N dopants, we performed XPS on the meso-N,B/C-*x* samples (Figure 2 and S5). The B 1s spectrum could be divided into three components

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(Figure 2a): the primary binding energy peak of 191.3 eV is assigned to B-N<sub>3</sub> structure with *h*-BN-like configuration.<sup>22</sup> A lower one at 190.5 eV implies a contribution from the B-C bonding configurations in C-B-N<sub>2</sub>,<sup>23</sup> which is due to C atoms have a lower electronegativity than N. Another comparable signal at 192.5 eV is characteristic for B-O bonding.<sup>22c</sup> Noteworthy, B-C<sub>3</sub> and C<sub>2</sub>-B-N should have a lower binding energy (about 187.4 and 188.9 eV, severally) than C-B-N<sub>2</sub>,<sup>23-24</sup> which has not been observed in all samples. Solid-state <sup>11</sup>B MAS NMR spectra have three observable peaks (Figure S6): the broad region at 20-25 ppm signifies a typical *h*-BN structure;<sup>25</sup> the sharp peak at 13.3 ppm can be attributed to B-O structure similar to that of bulk B<sub>2</sub>O<sub>3</sub>;<sup>26</sup> another sharp peak at around 0 ppm results from B-C structure,<sup>27</sup> which are consistent with the XPS results. The N 1s spectrum was composed of four peaks centered at 398.6, 399.8, 401.1 and 403.5 eV, corresponding to pyridinic N, pyrrolic N, graphitic N and pyridinic N-oxide (Figure 2c).<sup>28</sup> The main peak at 398.6 eV may include the signal at 398.0 eV from NB<sub>3</sub> trigonal units in *h*-BN.<sup>22b, 22d</sup> Combined with the experimental results in Table 1, it was proposed that B bonded with N (B-N<sub>3</sub> or C-B-N<sub>2</sub>) was major active sites targeting amides versus nitriles.

In addition, the main C 1s component at 284.7 eV is assigned to graphitic C=C species (Figure 2b), whereas three relatively smaller peaks centered at 285.3, 286.2 and 287.9 eV, corresponding to different C-N bonds (including B-C-N)<sup>24</sup>, C-O and O-C=O bonding, severally.<sup>29</sup> The C 1s spectrum revealed that there is scarcely any C-B<sub>3</sub> (283.6 eV) component.<sup>22a, 22b</sup> The employment of the inorganic template and the H<sub>3</sub>BO<sub>3</sub> precursor resulted unconsciously in a considerable amount of O implant. The O 1s spectrum were deconvoluted into three components with binding energy peaks centering at 533.4, 532.2, and 531.1 eV (Figure 2d). Peaks locating at 533.4 and 532.2 eV belonged to the C–OH and/or C–O–O–H groups and C=O groups, respectively. The peak at 531.1 eV corresponds to the absorbed oxygen-containing components (for example CO<sub>2</sub>,

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H<sub>2</sub>O et al.) According to the literature,<sup>29a, 30</sup> for the sp<sup>2</sup> carbon material of high surface area, universal strong gas adsorption enables them as catalysts by activating gas, especially polarizable  $O_2$ ,  $CO_2$  or NO and organic molecule for chemical transformation.

The FTIR spectra of all of meso-N,B/C-*x* samples with various contents of boron are shown in Figure 3. Two bands at 772 and 1398 cm<sup>-1</sup> are assigned to the characteristic in-plane stretching and out-of-plane bending vibrations of *h*-BN,<sup>22b, 31</sup> respectively, and increased gradually with increasing B content. In agreement with XPS, FTIR demonstrates that boron is involved in the structure of the as-obtained materials and is bonded to N to form B-N unit. In addition, the broad band at 3430 cm<sup>-1</sup> is related to N-H or O-H stretching vibrations or water molecules.<sup>32</sup> The stronger bands are assigned to C=N (1590 cm<sup>-1</sup>), and C-N (1254 cm<sup>-1</sup>).<sup>22b</sup> B-O bands (1200, 1350, 1450 cm<sup>-1</sup>) are overlapping with the carbon-nitrogen bands.



Figure 3. FTIR spectra of meso-N,B/C-x



Figure 4. Possible reaction pathway for primary amides synthesis from alcohols



### Scheme 2 Control experiments

In previous work,<sup>19-20</sup> it was widely believed that the hemiaminal undergo dehydrationdehydrogenation-hydration sequence to amides after aldehyde-ammonia condensation (Figure 4, Path B). To figure out whether our system experienced the hydration of nitriles or not, benzonitrile instead of benzyl alcohol was used as the substrate under standard condition. It was found that no benzamide was detected, even if water was added (Scheme 2).



**Figure 5.** (a) The structure of periodic BN-doped graphene model. (b) The adsorption configurations of hemiaminal(left) and  $O_2(right)$ . (c) The potential energy surface of path A and path B. The inset picture shows the corresponding structure of the intermediate, following after the dehydrogenation of hemiaminal. (d) Structures of transition states of path A and path B. The grey, blue, pink and red balls represent carbon, nitrogen, boron and oxygen atoms, respectively

Based on the results *vide supra*, it is rational to deduce that the present meso-N,B/C-catalyzed system possibly proceeds through the direct challenging oxidative dehydrogenation of hemiaminal (path A). It was indirectly attested that meso-N,B/C was capable to catalyze the dehydrogenation process by benzaldehyde and tetrahydrofuran reacted to the detectable corresponding amide (Scheme S1).

To rationalize scenario above, BN-doped graphene supercell were built for the density functional theory (DFT) calculations based on the XPS analysis and FTIR spectra (Figure 5a). The optimized adsorption configurations of the hemiaminal and oxygen molecule are shown in

Figure 5b and the corresponding adsorption energies are listed in Table 3. It can be found that hemiaminal adsorbs parallelly on surface, and benzene ring of hemiaminal is about 3.27 Å away from surface. Calculated adsorption energy is -1.16 eV, mainly due to  $\pi$ - $\pi$  interaction with respect to the BN-doped graphene. Hemiaminal adsorption in perpendicular configuration is about 0.45 eV weaker. On the other hand, calculated adsorption energy of oxygen molecule is -1.64 eV, stronger binding than hemiaminal. This means that oxygen molecule rather than hemiaminal will first populate the BN sites, and adsorbed oxygen molecule at BN sites reacts with the coming hemiaminal afterward. We note that binding strength of oxygen molecule towards the BN sites is much stronger than its binding toward the pristine graphene (-0.21 eV). For graphene doped with graphitic (-0.42 eV) and pyridinic nitrogen (-0.26 eV), though they bind oxygen molecules slightly stronger, subsequent dissociation barrier are as high as 1.70 eV and 2.14 eV (Figure S7). These results indicate that compared to the pristine graphene or graphene doped with graphitic and pyridinic nitrogen, the B-N sites in graphene is more efficiently to adsorb and active oxygen molecule.

 Table 3. Adsorption energetics of intermediates

Intermediates	$E_{\rm ads}/{\rm eV}$
hemiaminal	-1.16
O <sub>2</sub>	-1.64
ООН	-3.01
$H_2O$	-0.28
O (w.r.t. 1/2 O <sub>2</sub> )	-2.15
benzamide	-1.11
aldimine	-1.27

Potential energy surfaces of path A (oxidative dehydrogenation) and path B (direct dehydration) were calculated and shown in Figure 5c. The adsorption energies of involved intermediates  $E_{ads}$  are listed in Table 3. For path A, benzamide is produced via two oxidative dehydrogenation steps. The dehydrogenation of first hydrogen from -CH group to adsorbed oxygen molecule is slightly endothermic with a reaction energy of 0.07 eV and low activation energy of 0.82 eV. The corresponding transition state is given in Figure 5d TS1. Hemiaminal attacks absorbed oxygen molecule from top, and the hydrogen is located in the middle of carbon and oxygen atoms with a bond distance of 1.32 Å and 1.29 Å, respectively. The modest reaction barrier can be understood via the hydrogen transfer between C and O. For second dehydrogenation from -OH group to OOH\* to form benzamide and water, the corresponding process is nearly barrierless and highly exothermic with reaction energy of -3.27 eV. High exothermic could be rationalized by strong binding strength between oxygen atom left with the BN sites, whose dissociative adsorption energy with respect to oxygen molecule in gas phase is -2.15 eV (Table 3). As seen from Figure 5c, the overall barrier for two dehydrogenation steps in path A is only 0.82 eV with favorable exothermic reaction energy. In contrast, the barrier for the direct dehydration in path B over the BN site is 2.45 eV with thermal neutral reaction energy. Larger barrier comes mainly from the direct C-O bond breaking and H atom transformation without pronounced stabilization of the corresponding TS (Figure 5d TS2). Compared to path A, the calculated barrier for direct dehydration (path B) is considerably high, a fact of that makes path B kinetically unfavorable. Moreover, as indicated above, the BN sites will be populated mainly by oxygen due to its stronger binding than hemiaminal. In other word, there are actually no sites available for direct dehydration of hemiaminal over the BN sites, a fact of that further inhibits path B.

In order to study the scope of the metal-free meso-N,B/C-catalyzed amidation, various kinds of structurally diverse benzylic alcohols were tested and the desired amides were obtained in moderate to high yields as shown in Table 4. Methylbenzyl alcohol gave toluamides (2b–2c) in moderate yields. In the case of methyl substituted derivatives, the electronic effect resulting from different location of -CH<sub>3</sub> at benzene ring was not significant; benzylic alcohols with electron-donating -OCH<sub>3</sub> group as well as electron-withdrawing

Table 4. meso-N,B/C-catalyzed aerobic oxidative amidation of alcohols to primary amides

Entry	Substrate	Product	Yield(%)
1	он 1а	NH <sub>2</sub> 2a	74
2	он 1b	о NH <sub>2</sub> 2b	55
3	он	NH <sub>2</sub> 2c	64
4	MeO OH 1d	Meo NH <sub>2</sub>	72
5	F OH	F NH <sub>2</sub> 2e	61
6	CI OH	CI NH <sub>2</sub> 2f	67
7	Br OH	Br NH <sub>2</sub> Br 2g	73
8	F <sub>3</sub> C OH	F <sub>3</sub> C NH <sub>2</sub> NH <sub>2</sub>	50



Reaction conditions: alcohols (0.5 mmol), catalyst (50 mg), NH<sub>4</sub>OAc (96mg, 2.5 equiv.), 5 bar  $O_2$ , 1 ml *t*-amyl alcohol, 130 °C, 18 h. Yields were determined by GC and confirmed by GC-MS.

halogen-substitutents can also give about 70% yields of the corresponding primary amides (2d–2g), and it went smoothly without dehalogenation. For strong electron-withdrawing groups,  $-CF_3$  and  $-NO_2$ , it also achieved moderate yield of the corresponding primary amides (2h–2i). Furthermore, pyridine and thiophene derivatives could transform to the corresponding amides (2j–2k) in 77% and 54% yields, respectively. Regrettably, it suffered from breakage during the transformation of cinnamyl alcohol, resulting in benzamide was formed as a main product. No adipoamide (2m) was obtained cause the inactivity of aliphatic alcohols.

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CONCLUSION

In summary, a novel nitrogen- and boron-codoped mesoporous carbon of high surface area were successfully prepared through pyrolysis of nitrogen-containing precursors DAA and H<sub>3</sub>BO<sub>3</sub> by hard-template approach. When being used as a metal-free catalyst in the aerobic oxidative amidation of primary alcohols with NH4OAc as ammonia resource under oxygen atmosphere, the optimal meso-N,B/C-1.5 showed the best catalytic performance with 89% conversion of benzyl alcohol and 83% selectivity for the desired product benzonitrile. Thorough investigations on the surface chemical and physical properties of the material revealed that such a good performance of mesoporous carbon catalysts is ascribed to homogeneous distribution of active B-N units as well as mesoporous structure and high surface area. DFT calculations further identified the strong interaction of O<sub>2</sub> molecule with boron atom in B-N unit, which further reinforced the activation ability of molecular oxygen. Heteroatoms codoping strategy makes the reaction proceed in the direct challenging oxidative dehydrogenation path of hemiaminal, not the general dehydration-dehydrogenation-hydration process. Such an unprecedented example will provide a guide for the development of metal-free catalysts and expansion towards challenging synthetic organic reactions is underway.

#### EXPERIMENTAL SECTION

**Preparation of catalysts.** DAA was prepared according to the literature (details in the Supporting Information). The typical meso-N,B/C-*x* catalysts were prepared as follows: DAA and H<sub>3</sub>BO<sub>3</sub> (270mg:90mg, x=3; 270mg:180mg, x=1.5; 270mg:540mg, x=0.5) were dissolved in successio into 40 mL DMF at 130 °C under vigorous stirring. After dissolution, 1200 mg Ludox HS-40 was added into the mixture under vigorous stirring. After evaporation of solvent, the obtained DAA/H<sub>3</sub>BO<sub>3</sub>/SiO<sub>2</sub> composites were directly pyrolyzed under N<sub>2</sub> at a heating ramp rate of 5 °C/min to 800 °C and the temperature was held for 2 h. Samples resulting from different

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mass ratio are denoted as meso-N,B/C-*x* catalysts (x= the mass ratio of DAA and H<sub>3</sub>BO<sub>3</sub>), and finally were obtained after removal of templates by 0.5 M NaOH etching for 5 h at 100 °C. meso-N/C and N,B/C were prepared in the similar process except no addition of H<sub>3</sub>BO<sub>3</sub> and Ludox HS-40, respectively. meso-C catalyst was derived from sucrose. 1g sucrose was added into 40 mL H<sub>2</sub>O under vigorous stirring. Then 1200 mg Ludox HS-40 was added into the mixture and then the whole reaction mixture was stirred at 60 °C for 5-6 hours. After evaporation of H<sub>2</sub>O at 100 °C, the obtained composites proceeded the above pyrolyzation treatment and NaOH-etching process to obtained as-designed meso-C catalyst.

General procedure for the synthesis of primary amides and catalyst recycling. In a typical amidation, 50 mg meso-N,B/C-x, 0.5 mmol benzyl alcohol, 96.4mg NH<sub>4</sub>OA<sub>C</sub> (2.5 equiv with respect to benzyl alcohol, and 1 mL *t*-amyl alcohol were placed in a vial fitted with a magnetic stir bar, septum, cap and needle. The vial was attached inside an autoclave and the reaction was carried out at 130 °C in O<sub>2</sub> (5 atm). Subsequently, the autoclave was stirred at the required time. After the completion of the reaction, the vial were removed from the autoclave. Naphthalene as standard was added and the reaction product was diluted with tetrahydrofuran followed by centrifugation and then analyzed by GC and GC mass spectrometry (GC-MS). The meso-N,B/C catalyst was separated by filtration, washed with methanol, and then calclined at 800 °C in N<sub>2</sub> prior to its use in the reuse experiment.

Catalyst characterization. Nitrogen sorption isotherms were determined at -196 °C using a QuadraSorb SI4 Station. Piror to the measurement, the samples were degassed in vacuum at 300 °C for 3 h, and the BrunauerEmmett-Teller (BET) surface areas of the samples were calculated using adsorption data. X-ray photoelectron spectroscopy (XPS) measurement was performed with an ESCALAB 250Xi imaging photoelectron spectrometer (Thermo Fisher

Scientific, USA) using a monochromatic Al K $\alpha$  X-ray (hv =1846.6 eV). Energy calibration was carried out using the C 1s peak of adventitious C at 284.8 eV. Transmission electron microscope (TEM) characterization was conducted on JEM-2100 microscope. Scanning electron microscope (SEM) images were conducted on a JSM-7800F microscope operating at an acceleration voltage of 20 kV.

**Computational Details.** A  $p(3\times5)$  monolayer of graphene slab, where a BN3 unit substitutes 4 carbon atoms, was used to model the corresponding adsorption and reaction. All spin polarized DFT calculations were performed with Vienna ab initio simulation pack-age (VASP).<sup>33</sup> In order to capture the Van der Waal interactions between molecules and the substrate, non-local functional optB86b-vdW was used.<sup>34</sup> Kohn-Sham orbitals were extended in a plane wave basis with a cutoff energy of 400 eV.

The substrate and adsorption molecules were fully relaxed during the calculation. A vacuum level of 20 Å was sufficient to avoid interactions between periodic slabs. The convergence energy and force were set to  $1 \times 10^{-4}$  eV and 0.02 eV/Å, respectively. Transition states (TSs) were determined by climbing-image nudged elastic band (CI-NEB) methods<sup>35</sup> and confirmed by frequency analysis.

The adsorption energy  $E_{ads}$  and activation energy of transition state  $E_{act}$  were calculated as:

 $E_{ads} = E_{ads/sub} - E_{mol} - E_{sub}$ (1)

 $E_{act} = (E_{act/sub} + E_{sub}) - (E_{ads1/sub} + E_{ads2/sub}) \quad (2)$ 

 The  $E_{ads/sub}$ ,  $E_{mol}$ ,  $E_{sub}$ ,  $E_{act/sub}$ ,  $E_{ads1/sub}$  and  $E_{ads2/sub}$  are the total energy of the adsorbed molecule, molecule in gas phase, the pure slab, the transition state, adsorbed molecules which are the reactants to form the transition state, respectively.

ASSOCIATED CONTENT

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# **Author Contributions**

Sensen Shang and Pei-Pei Chen contributed equally.

# Notes

The authors declare no competing financial interest.

# Supporting Information.

The following files are available free of charge.

Synthesis of DAA, optimization of reaction conditons, N2 adsorption analysis, XPS, EDX,

elemental maps, <sup>11</sup>B NMR, control experiments

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