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## **Green Chemistry**

### PAPER

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# Co embedded within biomass-derived mesoporous Ndoped carbon as an acid-resistant and chemoselective catalyst for transfer hydrodeoxygenation of biomass with formic acid<sup>†</sup>

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N-doped Co@C catalyst (Co@NC) is synthesized by one-pot carbonization of biomass-derived glucose and harmless melamine with CoCl<sub>2</sub> as catalyst, where C and N resources could be transformed into highly graphitic N-doped carbon, while the coordinated Co<sup>2+</sup> ions are reduced to uniform Co nanoparticles (NPs), which are embedded in N-doped graphitic structures. Under base-free conditions with formic acid (FA) as hydrogen-donor, the optimized Co@NC-700 (pyrolyzed at 700 °C) shows a highly efficient H<sub>2</sub> generation from FA and the best activity for vanillin hydrodeoxygenation (HDO) with FA. For example, Co@NC-700 exhibits 15.4 times higher activity in comparison to uncovered Co on AC (Co/AC), and affords >95% vanillin conversion with 2-methoxy-4-methylphenol (MMP) as sole product at 180 °C for 4 h. Compared with molecular hydrogen, Co@NC-700 gives a much higher activity and MMP selectivity for vanillin HDO with FA. The Co@NC-700 demonstrates enhanced acid-resistance in acid medium and adsorption for vanillin, and is recyclable and versatile for hydrogenating various unsaturated compounds. The superior performance of Co@NC-700 could be ascribed to N-derived defective sites on Co@NC, which could play multiple roles as the base additives for FA dehydrogenation and as metal-like active center for vanillin HDO.

#### Introduction

The use of renewable biomass to replace the limited fossil fuels has been recognized as a potential solution for the sustainable production of liquid fuels and valuable chemicals.<sup>1</sup> For instance, sustainable fuels obtained by the hydrodeoxygenation (HDO) of phenolic bio-oils derived from pyrolysis of lignin or cellulose offer good prospects for industrial applications.<sup>2</sup> Most of the methods reported in the literature require the use of a stoichiometric amount of sensitive reagents or dangerous hydrogen gas under high pressure.<sup>3,4</sup> Catalytic transfer hydrogenation (CTH) has become the center of attraction because the hydrogen donors,<sup>5,6</sup> such as alcohols and organic acids, are readily available, inexpensive, easy to handle, and do not require elaborate experimental setups, such as high pressure reactors. However, the use of various alcohols can lead to side reactions (esterification or condensation with the

intermediate products) and reduce the selectivity of desired products, and the separation of dehydrogenized byproducts makes CTH process complicated.<sup>7-9</sup>

Formic acid (FA), a byproduct from the acidic hydrolysis of biomass,<sup>10</sup> has attracted a great deal of attention as a suitable liquid for hydrogen production and as an energy source for hydrogenation reactions. Hydrogen stored in FA can be released *via* a catalytic dehydrogenation reaction (HCOOH $\rightarrow$ H<sub>2</sub>+CO<sub>2</sub>). However, the basic process is accompanied by undesired dehydration pathway (HCOOH $\rightarrow$ H<sub>2</sub>O+CO), which would reduce the stability of catalyst due to the intrinsically weak CO tolerance of metal.<sup>11</sup> Many homogeneous and heterogeneous catalytic systems have shown efficiency for H<sub>2</sub> evolution by FA decomposition.<sup>12-14</sup> However, in order to achieve a high efficiency, CTH with FA is always carried out over noble metals (such as Au, Ru, Pd) with the help of excess bases (NaOH, triethylamine).<sup>15-18</sup> As for non-noble metals, these catalysts



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Scheme 1 Earth-abundant Co catalyzed CTH of biomass with FA under basefree condition.

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Scheme 2 Schematic illustration of synthesis of Co@NC-x catalyst.

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require high temperature, long reaction time, high catalytic loading, and a tedious procedure, and are easily deactivated in the present of FA due to bad tolerance to acidic environment and CO impurities.<sup>7, 19-22</sup> So far, there are still few reports on the use of a versatile catalytic system that enables selective HDO of biomass with FA with an excellent switch in selectivity just by adjusting the reaction conditions. Therefore, the rational design of acid- and COtolerated catalysts based on earth-abundant metals for CTH of biomass with FA is challenging and attractive (Scheme 1).

Nitrogen-doped carbon has been proven to be a fascinating catalytic material.<sup>23</sup> Doping with electron-rich nitrogen modifies the surface structure of carbons, endows enhanced  $\pi$ -binding ability and improved basicity,<sup>24</sup> which enables the applications of carbon with improved performance in catalysis. In traditional CTH process, FA-triethylamine system is frequently used for improving dehydrogenation of FA.<sup>15-17</sup> Here, similar chemical environment of nitrogen in triethylamine and nitrogen-doped carbon may make Ndoped carbon as 'heterogeneous N-type species' for N-mediated FA dehydrogenation, affording some attractive characters (high stability, recyclability, etc.). As expected, carbon nitrides have been reported as efficient supports for Pd-involved CTH process.<sup>12, 25</sup> The role of N-doping in modifing the electron density of the supported metals (Mott-Schottky effect) and the catalytic activity has been recently highlighted.<sup>12</sup> It is reported that the CN's electronic state is very sensitive to the materials contacted, which induces CN as metal-like active site for hydrogen activation.<sup>26</sup> For example, novel N-doped graphene encapsulating metal NP catalysts, including Co, Fe, Ni, Mo multi-metallic catalysts have been developed for hydrogenation under high  $H_2$  pressure.<sup>27-35</sup> The inner metal core and N species on the carbon shell can significantly decrease the dissociation energies of  $H_2$ ,<sup>29, 34</sup> proving the ability of carbon shell in the hybrids to H<sub>2</sub> activation.

Based on above considerations, mesoporous N-doped carbon encapsulating Co catalysts (Co@NC) are prepared through one-pot carbonization of biomass-derived glucose, melamine and CoCl<sub>2</sub> (Scheme 2). The unique structure of Co@NC plays multiple roles for CTH of biomass with FA, including 1) N-doped carbon shell strictly controls the aggregation of NPs, 2) the strong interaction between Co core and N-doped carbon shell influences the electronic structure that induces CN as metal-like active site for dehydrogenation of FA and hydrogenation of substrate, 3) N-doped carbon shell physically isolates Co from the acid environment and protects metal from poisoning or leaching. This catalyst exhibits high yield and excellent chemoselectivity (typically 100%) for HDO of vanillin to MMP using FA as reductant. The whole reaction system does not generate byproducts or harmful products. Moreover, the Co@NC catalyst exhibits superior recyclability and excellent stability after being reused at least five times. This work may promote the investigation of low-cost Co-based catalysts for highly chemoselective HDO of biomass in the chemical industry.

#### **Results and discussion**

Characterizations of nanostructured Co@NC materials



Fig. 1 SEM images of (a) Co@NC-500, (b) Co@NC-600, (c) Co@NC-700 and (d) Co@NC-800.

The surface morphology of Co@NC-x is imaged by SEM. As shown in Fig. 1, Co@NC-x samples show significantly different morphologies under different pyrolysis temperature. Compared with Co@NC-500 and Co@NC-600, Co@NC-700 exhibits clear sponge-like structure. Further increasing temperature to 800 °C, however, leads to Co@NC-800 with slight agglomeration and pore shrink.





The N<sub>2</sub> adsorption/desorption isotherm (Fig. 2 and Fig. S1) shows that Co@NC-x derived from higher pyrolysis temperature exhibits a typical Type IV one with an apparent hysteresis loop in the  $p/p_0$  range of 0.4–1.0, indicating the presence of a large number of mesopores in Co@NC-x, as confirmed by the corresponding pore distribution curve (Fig. S1). Meanwhile, high pyrolysis temperature leads to large pore volume but narrow mean pore size (Table S1). For example, the surface area and average pore size of Co@NC-700 are calculated to be 380.9 m<sup>2</sup> g<sup>-1</sup> and 4.3 nm, respectively. This result is also consistent with the reported experimental regularity that chlorates can be used as porogen in the preparation of porous carbon materials with high surface area.<sup>36</sup>

XRD patterns (Fig. 3) show that C(002) diffraction peak is gradually strengthened with increasing pyrolysis temperature, indicating the increased graphitization of carbon skeleton.<sup>37</sup> The

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metallic Co diffraction peak is strengthened only at higher pyrolysis temperature (> 700 °C). Raman spectra in Fig. 4 show that both D and G peaks sharpen evidently. Comparatively, Co@NC-700 gives relatively high value of  $I_D/I_G$  (1.35, Table S2), indicating that the crystalline carbon tends to be disordered.<sup>38</sup> Another peak detected at ~670  $\text{cm}^{-1}$  can be assigned to the Raman-active mode of Co-O/Co-N, in which Co@NC-700 and Co@NC-600 show stronger peak, implying a higher crystallinity of Co-O/Co-N species.<sup>39</sup> Further increasing pyrolysis temperature to 800 °C weakens the intensity of the peak again, indicating that CoO<sub>x</sub> and Co-N form firstly, followed by reacting with carbon elements released from precursor to generate Co<sup>0</sup> during the carbonization.<sup>21</sup>



Fig. 3 XRD patterns of (a) Co@C-700, (b) Co@N-700, (c) Co@NC-500, (d) Co@NC-600, (e) Co@NC-700 and (f) Co@NC-800.

![](_page_3_Figure_8.jpeg)

Fig. 4 The Raman spectra of (a) Co@NC-500, (b) Co@NC-600, (c) Co@NC-700 and (d) Co@NC-800.

FT-IR spectra (Fig. S2) show that the bands at ~3400, 1580 and 1210 cm<sup>-1</sup> weaken obviously with increasing the temperature, implying the emission of polar species (such as N or O) under heat treatment. The N1s spectra of Co@NC-x (Fig. 5) can be separated into pyridinic nitrogen (N-1), pyrrolic nitrogen (N-2), graphitic nitrogen (N-3), and pyridine oxide-N (N-4) at 398.5, 400.1, 401.1, and 403.3 eV, respectively. Apart from obvious decrease of N content (from 10.0 to 2.7 %, Table S2), Co@NC-x undergoes significant rearrangement of N species compared to that of Co@NC-500 (Table S3).<sup>40</sup> It is found that the N-1 and N-2 atoms account for >85% of the content in OMNC-500 and OMNC-

600, but decrease sharply to 64.8% in OMNC-700 and 57.75% in OMNC-800. Noticeably, with the increase of temperature from 500 to 800 °C, the proportion of graphitic nitrogen shows an increase from 0 to 42.24%, indicating that graphitic nitrogen tends to generate induced by transition metal under high temperatures. Meanwhile, the Co 2p spectra of Co@NC-x (Fig. 6) show obvious negative-shift as increasing the pyrolysis temperature from 500 to 800°C, implying that the Co-O/Co-N species in Co@NC-x are reduced in situ to metallic Co during thermal decomposition (Table S3). For example, Co@NC-500 possesses nearly 12.37% Co<sup>0</sup>, and this value increases to 19.94 and 26.02 % for Co@NC-700 and Co@NC-800, respectively. It was reported that if the reduction potential of metal ions were -0.27 volts or higher (such as Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>), they would be reduced to metal NPs by the direct pyrolysis in inert atmosphere.<sup>21</sup>

![](_page_3_Figure_12.jpeg)

Fig. 5 The N1s spectra of (a) Co@NC-500, (b) Co@NC-600, (c) Co@NC-700 and (d) Co@NC-800.

![](_page_3_Figure_14.jpeg)

![](_page_3_Figure_15.jpeg)

The detailed morphology of the Co@NC-x catalyst is disclosed by TEM (Figs. 7, S4 and S5). It can be seen that the particle size of NPs is in the range of 5-60 nm, and higher pyrolysis temperature affords wide particle size distribution as well as large mean particle size (Fig. S4). It is found that the average particle size in Co@NC-500, Co@NC-600, Co@NC-700 and Co@NC-800 is 15.3, 16.1, 24.4 and 31.4 nm, respectively. It can be observed that, after being etched with HCl, rich cavities appear in Co@NC-700 (Fig. 7a and b), and the particle sizes of Co have

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Fig. 7 TEM images (a-e), (f) STEM and (g) line scanning EDS elemental analysis of Co@NC-700.

a wide size distribution with a fraction of 10-40 nm particles. HRTEM (Fig. 7b-e) shows that the Co NPs are encapsulated by graphene layers and the well-defined core/shell structured Co@NC NPs form in mesoporous carbon framework. Fig. 7c highlights a typical metallic Co nanoparticle with crystal lattices of 0.215 nm, assigned to the (111) interplanar spacing of metallic Co, in which the Co NPs are encapsulated by well-ordered graphitic layers with a typical distance value of graphite (0.341 nm). Line scanning elemental analysis of Co@NC (Fig. 7f and g) has also confirmed that Co is well encapsulated in N-doped graphene shell in Co@NC-700. The formation of graphitic structure could efficiently facilitate the electron transfer, and prevent the leaching of acidity or the poisoning of Co NPs, thereby improving the catalytic activity.

# Catalytic property of Co@NC for transfer HDO of vanillin with FA $% \mathcal{F}_{\mathcal{F}}$

The prepared catalysts are studied for selective HDO of vanillin to MMP with FA as hydrogen source (Table 1). Blank test shows that no vanillin is transformed when no catalyst is used (entry 1). In a preliminary catalyst screening, the catalytic performance of catalysts based on iron, cobalt, nickel and copper pyrolysed with N-doped carbon is investigated at 180 °C in water. Among the different metals used (entries 2-5), Fe@NC-700, Ni@NC-700 and Cu@NC-700 give conversions of 9.7, 37.2 and 3.7 %, with all 100 % MMP selectivity. In contrast, the excellent conversion reaches up to 95.7 % over Co@NC-700 catalyst.

Next, the optimization of the pyrolysis temperature is carried out (entries 3, 6-8). The results show that the temperature significantly affects the activity of Co@NC-x catalyst and Co@NC obtained at 700  $^{\circ}$ C affords the best activity and 100 % MMP selectivity. However, other catalysts do not afford the desired catalytic effect. This is probably because the active sites Co@NC has almost not been formed when pyrolysed at 500  $^{\circ}$ C.<sup>37</sup> While annealing at the temperature higher than 800  $^{\circ}$ C, the CoOx or CoNx NPs tend to aggregate and to be further reduced to Co NPs. The Co-based

<b>ble 1</b> Transfer HDO of vanillin with FA over different catalysts. <sup>a</sup>								
	Entry	Catalysts	Conversion / %	MMP selectivity / %				
	1	-	1.1	-				
	2	Fe@NC-700	9.7	100				
	3	Co@NC-700	95.7	100				
	4	Ni@NC-700	37.2	100				
	5	Cu@NC-700	3.7	100				
	6	Co@NC-500	9.3	100				
	7	Co@NC-600	71.1	100				
	8	Co@NC-800	88.9	100				
	9	Co@N-700	67.2	98.8				
	10	Co@C-700	33.4	92.0				

 $^{o}$  Reaction conditions: vanillin (0.5 mmol), catalyst (7.9 mol% metal), FA (200 mg), H\_2O (10 mL), 0.5 MPa N\_2, 180  $^{\circ}$ C, 4 h.

![](_page_4_Figure_12.jpeg)

Fig. 8 Transfer HDO of vanillin under different temperatures. Reaction conditions: vanillin (0.5 mmol), FA (200 mg), catalyst (7.9 mol% Co),  $H_2O$  (10 mL), 0.5 MPa  $N_2$ , and 2h. Published on 26 October 2017. Downloaded by Tufts University on 27/10/2017 14:00:38

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catalyst prepared without melamine (Co@C) shows relatively low vanillin conversion (33.4 %) and MMP selectivity, while melaminederived Co@N affords significantly increased catalytic activity (67.2 %), which might be ascribed to the basicity derived from Ndoping of carbon skeleton (Fig. S6). In comparison with Co@NC-700, the relatively low activity of Co@N-700 could be ascribed to high metal loading (Fig. S7) and generation of large-sized NPs (Fig. S8). Furthermore, the reaction temperature effect on the activity of Co@NC-700 and Co/AC derived from common impregnation is studied (Fig. 8). The hydrogenation rate of vanillin catalyzed by Co/AC increases slowly, and only 6.2 % of conversion is achieved at 180 °C; however, the conversion over Co@NC-700 increases sharply from 10.7 to 95.7% as increasing temperature from 120 to 180 °C, which is 15.4 times that of Co/AC. Catalyst loading has a large impact on catalytic activity (Table S4), and decreasing catalyst usage leads to obvious decrease of vanillin conversion.

The effect of FA amount on catalytic activity is also studied (Table 2). It can be found that almost no conversion of vanillin occurs when no FA is used. Once FA is added gradually from 0 to 200 mg, the pH value of reaction system decreases sharply from ~7 to 1.2, for which a highly acidic environment is formed to aggravate the etching, leaching and inactivation of Co NPs. It has to be noted that Co/AC catalyst prepared by impregnation possesses nice Co dispersion (~15 nm, Fig. S10) but exhibits a poor catalytic activity. For example, as the FA amount increases from 0 to 100 mg, the vanillin conversion over Co/AC is low and increases slowly from 0.5

Table 2 Effect of FA amount on transfer HDO of vanillin over Co@NC-700 and Co/AC.

	FA/ y mg	рН	Co@NC-700		Co/AC	
Entry			Conversion / %	MMP selectivity / %	Conversion /%	MMP selectivity /%
1	0	~7.0	2.1	-	0.5	-
2	25	1.79	11.2	100	4.7	58.3
3	50	1.56	24.5	100	8.1	100
4	100	1.41	36.4	100	9.6	100
5	200	1.21	95.7	100	6.2	100

 $^{a}$  Reaction conditions: vanillin (0.5 mmol), catalyst (7.9 mol% Co),  $H_{2}O$  (10 mL), 0.5 MPa  $N_{2},$  180  $^{o}C,$  4 h.

![](_page_5_Figure_8.jpeg)

Reaction conditions: vanillin (0.5mmol), Co@NC-700 (7.9 mol% Co),  $H_2O$  (10 mL), 0.5 MPa  $N_2$  or  $H_2$ , 180 °C.

to 9.6 %. Further increasing the FA amount to 200 mg, however, leads to an obvious decrease of conversion to 6.2 %. In comparison, Co@NC-700 possesses good activities in the whole acid range. Increased FA amount causes significant increase of conversion. Even at a pH value of 1.2 (200 mg FA), the catalyst still shows fairly good catalytic performance for transfer HDO of vanillin. Considering the metal leaching might occur, both the filtrate of Co@NC-700 and Co/AC after reaction is checked by UV-vis spectra (Fig. S11). It is found that nearly no absorption peak can be observed from the filtrate of Co@NC-700, while the filtrate of Co/AC gives significant signal at 518 nm, indicating that obvious Co leaching occurs in water medium under acidic environment in the presence of FA. XRD pattern of the spent Co/AC (Fig. S12) shows that the Co or Co<sub>3</sub>O<sub>4</sub> reflections sharply weaken. ICP-AES analysis of the filtrate of Co@NC-700 further confirms that the Co content in the solution is below the detection limit, while 77.1% Co leaches into water for Co/AC during the reaction. These observations appear to be manifest that the CN shell plays a positive role in our system. On one hand, the novel CN shell physically isolates Co from the acidic environment and protects it from corrosion or poisoning. On the other hand, the intimate interaction between CN and inner Co induces CN to be activated by Co for CTH of vanillin with FA.

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Fig. 9 shows the dependencies of vanillin conversion and MMP selectivity in the HDO of vanillin with FA and molecular hydrogen over Co@NC-700. Using FA as hydrogen donor, vanillin is transformed gradually to MMP with a relatively constant rate and nearly converted fully to MMP as the sole product. In contrast, using molecular hydrogen as hydrogen donor, the hydrogenation rate seems to slow down after 2 h and only 34.8 % conversion and 84.8 % MMP selectivity can be achieved at 4 h. The transformation proceeds efficiently without any decrease in the performance in comparison with the small-scale transformation in Fig. S13, and MMP is produced in 100% selectivity and 92.7 % yield. This result indicates a different hydrogenation route in comparison to the earlier observation using molecular hydrogen as the hydrogen source, in which HMP was firstly generated and then hydrogenated into MMP under high concentration of HMP.<sup>41</sup> It could be concluded that FA plays an important role in the HDO of vanillin to MMP as the sole product via the interaction with vanillin or intermediates that suppresses the generation of HMP (Scheme 3).<sup>42</sup>

To further demonstrate the versatility of Co@NC-700, transfer hydrogenation of different unsaturated hydrocarbons is investigated in Table 3. As a common biomass-derived product, selective hydrogenation of benzaldehyde is carried out. It can be found that 98.6 % conversion is obtained at 180  $^{\circ}$ C in 4 h with 100 % benzyl alcohol selectivity (entry 2). In the case of phenylpropyl

![](_page_5_Figure_13.jpeg)

 $\mbox{Scheme 3}$  Possible reaction mechanism of transfer HDO of vanillin over Co@NC.

Entry	Substrato	Broduct	Conversion	Selectivity /
Liitiy	Substrate	FIDUUCL	/%	%
1	СНО	CH <sub>3</sub> OH	95.7	100
2	СНО	CH <sub>2</sub> OH	98.6	100
3	СНО	CH <sub>2</sub> OH	97.1	100
4	СНО	CH <sub>2</sub> OH	91.0	100
5			91.4	92.7
6 <sup>b</sup>	Н3СОССНО	H <sub>3</sub> CO <sup>CH</sup> 3	98.9	100
7 <sup>b</sup>	носно	HO CH3	99.5	93.0

Table 3 Transfer DHO or hydrogenation of unsaturated hydrocarbons over Co@NC-700.

<sup>a</sup> Reaction conditions: Substrate (0.5mmol), Co@NC-700 (7.9 mol% Co), FA (200 mg), H<sub>2</sub>O (10 mL), 0.5 MPa N<sub>2</sub>, 180 °C, 4h.
<sup>b</sup> 200 °C

aldehyde (entry 3), the reaction gives 97.1 % of conversion and 100 % of alcohol selectivity. Other  $\alpha$ ,  $\beta$ -unsaturated aldehyde, such as cinnamyl aldehyde (entry 4), affords the corresponding hydrocinnamyl alcohol with 91 % conversion without other side products. Next, a more challenging hydrogenation of quinoline toward 1,2,3,4-tetrahydroquinoline (THQ), due to the competitive hydrogenation of benzene ring, is demonstrated in entry 5. The result shows that Co@NC-700 affords 91.4 % quinoline conversion with THQ as the sole product in water, which exhibits obvious advantage over those noble metals using molecular hydrogen as reductant. Other substituted benzaldehydes (entries 6-7), such as hydroxyl benzaldehyde, methoxy benzaldehyde, afford the corresponding deoxy-products in relatively good yields.

In order to explore the mechanism of transfer HDO of vanillin over Co@NC-x, the dehydrogenation of FA is investigated. Fig. 10 shows that Co@NC-500 sample is less active for FA dehydrogenation (21.1 %). While higher pyrolysis temperature

![](_page_6_Figure_9.jpeg)

Fig. 10 FA dehydrogenation test over Co@NC-x.

Reaction conditions: FA (200 mg), catalyst (0.91 mol% Co vs. FA),  $H_2O$  (2 mL), 1 bar  $N_2,\,140\ ^oC,\,2$  h.

![](_page_6_Figure_12.jpeg)

boosts high catalytic activity, in which Co@NC-700 affords a full FA conversion at 140  $^{\circ}$ C for 2 h. In can be found the order of FA dehydrogenation is similar to the hydrogenation activity, indicating that the FA dehydrogenation could be the crucial step in the transfer HDO of vanillin over Co@NC-x catalysts.

The rich surface N dopants can serve as defect sites for increasing the hydrophilicity of carbons and wettability of the substrate on carbons.<sup>43</sup> It is reported that the more hydrophilic the catalyst, the more active it is for the HDO of vanillin in water. The adsorption test (Fig. S14 and 11) shows that the adsorption capacity of vanillin over Co@NC-x increases in the order of Co@NC-500< Co@NC-600< Co@NC-700 <Co@NC-800, and the adsorption capacity on Co@NC-700 and Co@NC-800 can reach > 40 mg/g. This result indicates a favourable interaction between vanillin and Co@NC-700 that leads to an increased vanillin concentration and accelerated reaction rate on surface of Co@NC-700.<sup>21</sup>

Considering the acidic environment due to the presence of FA, the recycle of catalyst is an important issue for the development of sustainable chemicals. Co@NC-700 can be easily recovered and reused five times without significant loss of efficiency (Fig. 12). The

![](_page_6_Figure_16.jpeg)

 $\label{eq:Fig. 12} \begin{array}{l} \mbox{Re-uses of Co@NC-700 for transfer HDO of vanillin.} \\ \mbox{Reaction conditions: vanillin (0.5 mmol), FA (200 mg), catalyst (7.9 mol% Co),} \\ \mbox{H}_2O (10 mL), 0.5 MPa N_2, 180 \ ^{\circ}C, 3h. \end{array}$ 

![](_page_7_Figure_4.jpeg)

XRD pattern (Fig. 13) of Co@NC-700 reused 5 times shows that only diffraction peaks of Co<sup>0</sup> are recorded and the crystalline state of Co NPs do not change significantly, which indicates the retention of the catalytic activity after being recycled. No Co metal is detected in the reaction solvent after completion of the reaction, showing much higher stability than that of Co/AC. This confirms the fact that CN shell holds the cobalt metal very tightly, thus prohibiting metal from leaching, and facilitating efficient catalyst recycling.

#### Conclusion

We have demonstrated an efficient method to synthesize a lowcost and eco-friendly Co@NC catalyst that can utilize FA, a cheap and readily available hydrogen donor, for highly efficient CTH of vanillin without adding any base additives. The catalysts are prepared by an accurate annealing procedure of the mixture of glucose, melamine and CoCl<sub>2</sub>. The Co NPs are uniformly encapsulated in porous N-doped carbon structure, which exhibits dramatically enhanced acid-resistance in present of FA and high catalytic activity as well as specific selectivity for transfer HDO of vanillin with MMP as sole product. Control experiments suggest that N-derived basic sites on Co@NC, which could play crucial roles as the base additives for FA dehydrogenation and N-doped carbon shell is tuned by embedded Co as metal-like active center for vanillin HDO. Moreover, this catalyst is stable and active for transfer hydrogenation of various unsaturated compounds. This study offers a simple way to prepare N-doped carbons from biomass as 'heterogeneous N-type ligands' for the non-noble metal-mediated transfer hydrogenation of biomass.

#### Experimental

#### Materials

The chemicals used included glucose (AR, Sigma-Aldrich), cobalt chloride (AR, Sinopharm), melamine (AR, Sinopharm). All other chemicals were of analytical purity if not otherwise noted.

#### **Catalysts preparation**

In a typical experiment, glucose, melamine and cobalt chloride were added to deionized water under stirring ((mass ratio of glucose/melamine/cobalt chloride=1:1:1)) (Scheme 2). The solution was then evaporated in air at 80  $^{\circ}$ C for removing the water. The powder was transferred into a crucible, heated to a given

temperature at a heating rate of 5 °C/min under a flow of nitrogen and kept for 4 h. The sample was treated in HCl (5 wt.%) at RT for 24 h to remove soluble cobalt species. The acid treated solid sample was recovered by filtration and washed with DI water until free of Cl<sup>-</sup>. Finally, the sample was dried and denoted as Co@NC-x, where x corresponds to the treatment temperature. For the synthesis of Co@C-x or Co@N-x, no melamine or no glucose was added. Replacing cobalt chloride with nickel chloride, ferric chloride or copper chloride synthesized Ni@NC-x, Fe@NC-x or Cu@NC-x, respectively.

#### Characterizations

Powder X-ray diffraction (XRD) was performed on a Bruker D8A25 diffractometer with CuK $\alpha$  radiation ( $\lambda$ =1.54184 Å) operating at 30 kV and 25 mA. Fourier transform infrared (FTIR) spectra were on an OPUS Fourier Transform Infrared analyzed Spectrophotometer in the range of 400-4000 cm<sup>-1</sup>. Raman spectra were collected at room temperature from 100 to 4000 cm<sup>-1</sup> with 514.5-nm argon ion laser (Rhenishaw Instruments, England). N<sub>2</sub> adsorption was carried out at -196 °C using an auto-adsorption analyzer (Micromeritics, TriStar II). Scanning electron images (SEM) were collected on JEOL (JSM6700F)) at an accelerating voltage of 15 kV. Transmission electron microscope (TEM) images were obtained using an accelerating voltage of 200 kV on a JEOL-135 2010F Transmission Electron Microscope. Thermal gravimetric analysis (TGA) was carried out with a Perkin Elmer thermoanalyzer under nitrogen atmosphere. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer PHI ESCA system.

#### Vanillin adsorption

50 mg of Co@NC was added into a 5 mL of vanillin aqueous solution with an initial concentration of 500 ppm and stirred at 30 °C. At a given interval, 0.1 mL of the suspension was diluted with water. The supernatant was then obtained by centrifugation and analyzed by a Shimadzu UV-visible UV-2550 spectrometer. The amount of adsorbed vanillin was calculated according to the equation: the amount of adsorbed vanillin  $=\frac{(c_o-c_r)\times V_o}{m_c}$ . Here  $C_0$  is the initial concentration of vanillin,  $C_r$  is the residual vanillin concentration after adsorption,  $V_0$  is the volume of aqueous solution, and  $m_c$  is the mass of sample.

#### **Catalytic reactions**

The hydrogenation reactions were performed in a 50 mL stainless autoclave with a Teflon liner. In a typical run, a certain amount of catalyst, 200 mg FA and 0.5 mmol vanillin were dispersed in 10 mL DI water. The autoclave was then sealed, purged and pressurized with N<sub>2</sub> to 0.5 MPa, and heated to 180 °C under magnetic stirring (1000 rpm). After the completion of reaction, the autoclave was quickly cooled down within cold water. The organic compounds was extracted by ethyl acetate, the catalyst was recovered from aqueous phase by centrifugation and then washed several times with ethanol for next use. The products and substrate were analyzed by gas chromatograph (Shimadzu 2010) with a 30 m capillary column (Rtx<sup>®</sup>-1) using a flame ionization detector (FID). Interpolated calibration was employed for product quantification using standard solutions of substrate and product. All the products were confirmed by GC-MS (Agilent 6890).

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