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# Facile Synthesis of Highly Efficient Co/Cu@NC Catalyst for Basefree Oxidation of Alcohols to Esters

Jiusheng Jiang, Xiang Li, Shengyu Du, Langchen Shi, Pingping Jiang, Pingbo Zhang, Yuming Dong, Yan Leng\*

The direct oxidation of alcohols to esters is an environmentally benign and cost-effective organic synthetic strategy, but it is still a great challenge to explore an economic, highly active, and long-term stable catalyst for efficient transformation of alcohols to esters under milder conditions. Herein, we developed cobalt and copper nanoparticles-co-decorated nitrogendoped carbon catalysts (CoCu@NC<sub>n</sub>) through two steps of ball milling and calcination. It was found that CoCu@NC<sub>n</sub> could catalyze the oxidation of alcohols to esters effectively in the absence of basic additives. The catalytic activity was much higher than those of monometallic Co@NC2 and Cu@NC2 samples, and the catalyst can be conveniently recovered and quite steadily reused. Through a series of control experiments and characterizations, it is concluded that the remarkable catalytic performance of CoCu@NC2 was associated with the synergistic effect between two metal components, the enhanced basic active sites and active surface area.

## Introduction

Esters are a class of most important compounds in organic transformations and have been wildly used in the field of fine chemicals, natural products, pharmaceuticals, and polymers.<sup>1-3</sup> Traditionally, esters are prepared by the Fischer esterification reaction of carboxylic acids or activated acid derivatives with alcohols, or transesterification reactions.<sup>4-8</sup> However, strong acidic or basic reaction conditions in those processes always result in large amounts of undesired byproducts and limit the reaction scope. With the developments in metal-catalyzed oxidation reactions,9-11 the direct oxidation of alcohols to esters (also known as oxidative esterification) has been recognized as an environmentally benign and cost-effective alternative to traditional ester synthesis.<sup>12-16</sup> For this purpose, various metal catalysts (e.g., Pd, Au, Pt) have been identified, but most of the known catalysts for such reactions are based on previous metals and mostly in homogeneous systems.<sup>17-19</sup> Moreover, a base additive was required in these cases, which is economically and environmentally unfavorable. Therefore, the development of inexpensive, non-noble metal, and easily recyclable heterogeneous catalysts for the oxidation of alcohols to esters becomes an attractive subject in sustainable chemical conversion process.

Transition metal nanoparticles (NPs), especially Co, Cu, Ni, Fe NPs, encapsulated in carbon materials (M@C) are becoming favorable catalytic materials.<sup>20-23</sup> Because of the nanoscale features as well as tunable properties such as compositions, porosity, surface area, and accessible active sites, M@C have shown great potential applications in heterogeneous catalysis. <sup>24-26</sup> In particular, Co NPs-based M@C (Co@C) are found to be useful and reusable catalysts for the oxidation of alcohols to esters.<sup>27-29</sup> In recent years, several strategies for turning the catalytic performance have been established. It is reported that doping carbon with heteroatoms could alter the physical properties of M@NC (acid-base property, electronic density, etc) and facilitate strong interaction with metal species, which might boost their final catalytic activities. For example, Co@NC catalysts activated by N-doping or S-doping have displayed improved catalytic activity toward the oxidative esterification of alcohols.<sup>30-33</sup> Very recently, the incorporating deliberately the second metal into M@C ( $M_1M_2@NC$ ) has been shown to be advantageous for enhanced catalytic performance particularly in electro-catalysis due to the modified electrical conductivity and oxidation status of bi-metal elements.34-38 Despite the versatile applications of bimetallic  $M_1M_2@NC$  in many OER, HER, and ORR processes, surprisingly, their use as catalysts for oxidative esterification has been seldom reported.

Herein, Co and Cu NPs-co-decorated N-doped carbon (CoCu@NC<sub>n</sub>) catalysts were prepared by a facile and effective mechanical mixing and calcination method using chitosan (CTS) and melamine as carbon and nitrogen sources, respectively. The synthesized CoCu@NCn were applied for direct oxidation of alcohols to esters under atmospheric conditions without the assistance of any base additives, presenting good to excellent catalytic activity and selectivity. Investigations on the correlation between CoCu@NCn structure and catalytic activity demonstrated that the

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synergistic effect between Co and Cu NPs, together with abundant basic sites arising from N-doping may be responsible for its good catalytic performance.

# Experimental

### Materials

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Chitosan was purchased from Macklin. Melamine, CoCl<sub>2</sub>.6H<sub>2</sub>O, and CuCl<sub>2</sub>.2H<sub>2</sub>O were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All the chemicals used in the experiment without further purification.

### Synthesis of CoCu@NCn

In a typical procedure, chitosan (0.5 g), melamine (0-1.0 g), and metal salts (0.17 g), (the molar ratio of Co/Cu was 1:1) were added into a 4.5 × 5.5 cm (diameter × height) screwcapped stainless steel reactor along with six stainless steel ball bearings. The reactor was ball milled for 30 min in a highspeed vibrating ball miller (AC 220V, 50 HZ). The obtained precursor mixture was carbonized at 800 °C for 2 h with 5 °C/min heating rate in N<sub>2</sub> atmosphere to give the final catalyst CoCu@NC<sub>n</sub>. When the chitosan/melamine quality ratio were adjusted to 0.5/0, 0.5/0.25, 0.5/0.5, 0.5/1.0 during the ball milling, the obtained samples were denoted as CoCu@NC<sub>0</sub>, CoCu@NC<sub>1</sub>, CoCu@NC<sub>2</sub>, and CoCu@NC<sub>3</sub>, respectively.

### Characterization

The nitrogen sorption isotherms and pore size distribution curves were measured at the temperature of liquid nitrogen (77 K) using a BELSORP-MINI analyzer. The metal content was measured using a Jarrell-Ash 1100 ICP-AES spectrometer. X-ray photoelectron spectroscopy (XPS) was conducted on a PHI 5000 Versa Probe X-ray photoelectron spectrometer equipped with Al Karadiation (1486.6 eV). XRD patterns were collected on a Bruker D8 Advance powder diffractometer using a Nifiltered Cu/Ka. TGA was performed using an STA 409 instrument from 50 to 800 °C in air at a heating rate of 10 °C/min. Raman experiments were performed using a PerkinElmer-Raman Station 400 F spectrometer equipped with a liquid  $N_2$  cooled charge-coupled device detector and a confocal microscope. A 350 mW near infrared 785 nm laser was used for analysis under ambient conditions. The basicity of samples was determined through temperature-programmed desorption of CO2-TPD by a Micromeritics BelCata II equipment. The sample was pre-treated in He flow at 150 °C for 3 h and cooled to room temperature. After being saturated with  $CO_2$ , the sample was purged with He for 1h at room temperature to sweep the physical molecule. Then TPD signals were recorded by performing CO<sub>2</sub> desorption from 50 to 900 °C at the rate of 10 °C/min. The morphology was studied by field emission scanning electron microscopy (FESEM; Hitachi S-4800, accelerated voltage: 5 kV). Scanning electron microscopy (SEM) images were acquired on a SUPERSCAN SSX-550 electron microscope. Transmission electron microscopy (TEM) images were recorded with a JEOL JEM-2100 electron microscope operated at 200 kV. The Co and Cu contents in CoCu@NC<sub>2</sub> were measured using a Jarrell-Ash 1100 ICP-AES spectrometer.

### **Catalytic tests**

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The oxidative esterification of benzyl alcohol was carried out in a 15 mL vial sealed with rubber plug. Typically, BenzyNaneokol (0.5 mmol), CH<sub>3</sub>OH (5 mL), and catalyst CoCu@NC<sub>n</sub> (40 mg) were added into the reactor, followed by heating to 60°C with continuous stirring over oil bath. The vial was degassed and purged with pure oxygen for 10 min, and a balloon filled with O<sub>2</sub> was inserted with a needle. After the reaction, the solid catalyst was collected by centrifugation. The liquid was identified by GC-MS equipped with a FID detector and a capillary column (SE-54 60 m × 0.32 mm × 0.25 mm). The recovered catalyst was washed with 0.1 M NaOH and pure CH<sub>3</sub>OH, respectively, dried at 60°C, retreated in N<sub>2</sub> atmosphere at 500 °C for 2 h, and then reused in the next run.

## **Results and discussion**

As a kind of cheap and easily obtained renewable biomass, CTS was chosen as a carbon source and melamine as a nitrogen source to ball mill with metal salts (CoCl<sub>2</sub> and CuCl<sub>2</sub>) for 30 min to form a mixture containing CTS, melamine,  $Co^{2+}$ , and  $Cu^{2+}$ . The obtained precursor mixture was then carbonized at 800°C in N<sub>2</sub> atmosphere to afford the catalysts CoCu@NC<sub>2</sub>. During this process, the Co<sup>2+</sup> and Cu<sup>2+</sup> ions were reduced to Co and Cu NPs while the surrounding organic ligands were polymerized to NC, resulting in Co and Cu NPs embedded in NC matrix. TG analysis shows that the stability of CoCu@NC<sub>2</sub> is high up to 300°C in air (Figure S1). The Co and Cu contents in CoCu@NC<sub>2</sub> are approximately 9.0 wt% and 9.1 wt%, respectively, as determined by ICP analysis. For the sake of comparison, a control catalyst (CoCu@NC<sub>0</sub>) was prepared without adding melamine, and monometallic Co@NC<sub>2</sub> and Cu@NC<sub>2</sub> samples were also prepared by carbonization of monometallic precursors.

The XRD diffraction pattern of CoCu@NC<sub>2</sub> exhibit a group of peaks at 44.1°, 51.2° and 75.8° corresponding to face-centered cubic Co (PDF # 15-0806) and peaks at 43.3°, 50.5°, and 74.0° corresponding to face-centered cubic Cu (PDF # 04-0836) (Figure 1A), confirming the formation of Co and Cu NPs-codecorated NC. The N-free sample CoCu@NC<sub>0</sub> also reveals the formation of cubic Co and Cu. The relative strong peak intensity was probably due to larger crystallite size of metal NPs in CoCu@NC<sub>0</sub> compared with CoCu@NC<sub>2</sub>. The existence of NC was revealed by Raman spectrum, which shows obvious D and G bands located at 1318 and 1574 cm<sup>-1</sup> (Figure S2). The porous structure of CoCu@NC<sub>2</sub> was evaluated by  $N_2$  sorption





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Fig. 2 (A, B, C) TEM images, (D) Diagram of  $CoCu@NC_2$  and (E) EDS maps of C, O, N, Co, and Cu for  $CoCu@NC_2$ 

measurement at 77 K (Figure 1B). CoCu@NC<sub>2</sub> exhibited typical IV isotherm with H3-type hysteresis loops between the pressure  $P/P_0 = \sim 0.5$ -1.0, indicating the presence of mesopores. The specific surface area was estimated to be 576 m<sup>2</sup>/g with an average pore size of 3.0 nm and pore volume of 0.306 m<sup>3</sup>/g.

The TEM image of CoCu@NC<sub>2</sub> exhibits a markedly crumpled sheets structure with irregular menses and visible pores (Figure 2A). The HRTEM images demonstrate that metal NPs have been successfully embedded in NC framework (Figure 2B). The interplanar spacing were calculated to be 2.05 and 2.11 °A, corresponding to the (111) and (111) planes of metal Co and Cu, respectively, which reveals good crystallinity (Figure 2C). The Co and Cu NPs have been found to be in close contact in some selected-area, this may facilitate the synergistic effect for high-efficient catalysis, as has been discussed hereinafter. The EDS elemental mapping images confirm that C, N, Co, and Cu were uniformly distributed in CoCu@NC<sub>2</sub> (Figure 2E). The above characterization results verified that the Co and Cu NPs have been successfully embedded in porous NC, and the resulting catalyst CoCu@NC2 possesses a reticular structure as shown in Figure 2D.

To further elucidate the detail chemical composition of CoCu@NC<sub>2</sub> as compared to that of monometallic Co@NC<sub>2</sub>, XPS measurements were performed (Figure S3). The Co 2p XPS spectrum for Co@NC<sub>2</sub> can be deconvoluted into four doublets, where the peaks at 779.2 and 794.5 eV can be assigned to metal Co<sup>0</sup>, the peaks at 781.3 and 796.2 eV correspond to Co<sup>3+</sup> originating from  $CoO_x$  or  $CoC_xN_y$ , and the peaks at 783.2 and 798.1 eV are assigned to  $Co^{2+}$  originating from  $Co-N_x$  species (Figure 3A). The formation of  $Co-N_x$  can be attributed to the abundant N-doping. In the Co 2p XPS spectrum of CoCu@NC<sub>2</sub>, the peak intensity for  $Co^{3+}$  and  $Co^{2+}$  increased significantly after the introduction of Cu. In addition, there is a shift in the peaks of Co3+ and Co2+ towards higher binding energy for CuCo@NC<sub>2</sub> as compared to that for Co@NC<sub>2</sub>, indicating a strong electron interaction between Cu and Co species. The Cu 2P spectrum of CuCo@NC2 only show the peaks (932.6 and 952.5 eV) assigned to the Cu metal without observing the peaks assigned to Cux+ (Figure 3B). This is mainly because of that the copper was reduced easier during the pyrolysis than the Co tended to exist in the form of Cu<sup>0,39</sup> The N 1s XPS spectra of Co@NC<sub>2</sub> and CuCo@NC<sub>2</sub> can be deconvoluted into graphitic-N (401.3 eV), pyrrolic-N (400.2 eV), M-N (398.9 eV)



Figure 3. (A) Co 2p, (B) Cu 2p, (C) N 1s, (D) C 1s XPS spectra of Co@NC<sub>2</sub> and CoCu@NC<sub>2</sub>

and pyridinic-N (398.2 eV) (Figure 3C). The presence of the peak at 398.9 eV further indicates the generation of Co-N<sub>x</sub>. It has been reported that more likely the metal species next to pyridinic N are important active sites for many catalytic processes.<sup>40,41</sup> The M-N and pyridinic-N content in CuCo@NC<sub>2</sub> is much higher than that of Co@NC<sub>2</sub>, confirming a high doping ratio of N, which would help enhance the metal catalytic activity. The peak situated at 285.9 eV in the C 1s XPS spectrum further proves the formation of C-N bond (Figure 3D).

Table 1 lists the catalytic performance of  $CoCu@NC_n$  for the oxidation of benzyl alcohol to ester with 1 bar  $O_2$  balloon under base-free conditions, together with comparisons with various control catalysts. The reaction could not proceed in the absence of either catalyst or  $O_2$ , or with metal-free NC as the catalyst (entry 1). It indicates that metal active centers are required to overcome the kinetic barrier to promote the benzyl alcohol conversion. CoCu@NC<sub>2</sub> offered the highest

 Table 1
 Oxidative esterification of benzyl alcohol over the synthesized catalysts.

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CH <sub>3</sub> CH <sub>3</sub> OH - CH <sub>3</sub> OH - CH <sub>3</sub> C				
Entry	Catalyst	Time (h)	Con. (%)	Sel. (%)
1	NC <sub>2</sub>	12	-	-
2	CoCu@NC <sub>2</sub>	12	100	100
3	CoCu <sub>0.5</sub> @NC <sub>2</sub>	12	78	89
4	Co@NC <sub>2</sub>	12	50	77
5	Cu@NC₂	12	5	
6	Co@NC <sub>2</sub> + Cu@NC <sub>2</sub>	12	42	65
7	CoCu@NC <sub>0</sub>	12	53	73
8	Co@NC <sub>0</sub>	12	8	12
9	CoCu@NC <sub>1</sub>	2	54	74
10	CoCu@NC <sub>2</sub>	2	67	83
11	CoCUMNC	2	11	71

Reaction conditions: 0.5 mmol benzyl alcohol, 5 mL CH<sub>3</sub>OH, 40 mg catalysis, 60 °C, O<sub>2</sub> ball. Catalyst mmol/benzyl alcohol mmol = 0.11/0.50. The main byproduct is benzaldehyde. The conversion and selectivity were determined by GC.





As has been reported, the N-doped carbon could act as built-in and "strengthened" Lewis base to accelerate the deprotonation process.<sup>47-49</sup> Therefore, we used CO<sub>2</sub>-TPD analysis to determine the basic properties of CuCo@NCn samples (Figure 4). The N-free sample CuCo@NC<sub>0</sub> has weak peaks in the CO<sub>2</sub>-desorption temperature range of 250-600 °C. Generally, CO<sub>2</sub>-TPD shows a positive relationship between the amount of basic sites and the area of peaks. The peak intensity increased obviously after the N-doping in CuCo@NC<sub>1</sub>, revealing that the basic sites were mainly ascribed to the Ndoping. CuCo@NC<sub>2</sub> possessed the strongest and maximum peak area, directly confirms the formation of abundant basic sites. As a result, CuCo@NC2 not only enable the oxidative esterification of alcohol to proceed in a base additive-free reaction system, but also exhibit a high activity and selectivity.

To investigate the general applicability of CoCu@NC<sub>2</sub> for oxidative esterification of alcohols to esters, the substrate scope was surveyed (Table 2). Both electron-donating (Br, Cl, NO<sub>2</sub>) and -with drawing (OCH<sub>3</sub> and CH<sub>3</sub>) group substituted benzyl alcohols were smoothly converted into the corresponding methyl esters in high conversions (> 90%) and selectivity at 60°C under the base-free conditions (1a-5a of table 2). The ortho-substituted benzyl alcohol and benzenedimethanol were relative tolerated, but the conversions and selectivity can be optimized by longer reaction time to 24 h (6a-7a of table 2). Even heterocyclic alcohols (cinnamyl alcohol and furfuryl alcohol) could be oxidized over CoCu@NC<sub>2</sub> to their corresponding esters with good conversion and high selectivity with a longer reaction

Conditions: 0.5 mmol substrates (0.1 mmol for 10b-12b), 5 mL CH<sub>3</sub>OH, 40

2a (60°C, 12h)

1a (60°C, 12h) C: 99.5% S: 99.6% C: 91.4% S: 99.5%

4a (60°C, 12h) C: 98.5% S: 98.9%



5a (60°C, 12h) C: 95.8% S: 84.9%



Table 2 CoCu@NC2-catalyzed oxidative esterifidation10f1/arroDsaldobolis2D

3a (60°C, 12h)

C: 99.0% S: 73.6%

6a (60°C, 12/24h)

C: 65.8%/92.4%

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CuCo@NC<sub>2</sub>

catalytic activity in a solid-liquid heterogeneous catalysis system (entry 2). GC spectra for this reaction performed at different reaction time indicate a complete transformation of benzyl alcohol to methyl benzoate with excellent selectivity of 100% (Figure S4). In contrast, the monometallic Co@NC<sub>2</sub> exhibited a low conversion of 50% and selectivity of 77% (entry 4). Moreover, only a trace amount benzyl alcohol was oxidized to benzaldehyde over Cu@NC<sub>2</sub> (entry 5). The above results indicate that the incorporation of Cu into Co@NC<sub>2</sub> (nCo:nCu = 1:1) could significantly promote the aerobic oxidative esterification of benzyl alcohol. Change the Cu content in CoCu@NC<sub>2</sub> resulted in lower conversion and selectivity (CoCu<sub>0.5</sub>@NC<sub>2</sub>, entry 3) probably due to the weakened synergetic effect between Co and Cu.42,43 Interestingly, Cu@NC<sub>2</sub> as an additive for the reaction with Co@NC<sub>2</sub> was less effective, indicating that the decoration of Co and Cu NPs into a single NC support was important to enhance the catalytic activity (entry 6). Similar kind of high catalytic activity of bimetallic catalysts was also observed in many electrochemical reactions and organic transformations.44-46

To check the role of N-doping on the catalytic performance of CoCu@NC<sub>2</sub> in the oxidative esterification, the reaction was carried out over a N-free control sample CoCu@NC<sub>0</sub>. However, a relative low conversion of 53% and selectivity of 73% was obtained (entry 7), which is much lower than that of CoCu@NC<sub>2</sub>. This implies that the N-doping also play an essential role in improving the overall activity of CoCu@NC<sub>2</sub>. Notably, another monometallic N-free sample Co@NC<sub>0</sub> was far less active than that of N-containing sample Co@NC<sub>2</sub>, presenting only 8% conversion and 12% selectivity (entry 8), further confirming the catalytically promotional role of N dopant for base-free oxidative esterification. By tuning the melamine content during the CoCu@NCn synthesis, the catalytic activity and selectivity can be adjusted. According to the initial activity in 2 h (entries 9-11), CoCu@NC1 offered 54% conversion with 74% selectivity. CoCu@NC<sub>2</sub> exhibited the best performance, giving 67% conversion and 83% selectivity. The further increase of melamine content for CoCu@NC<sub>3</sub> synthesis resulted in partial transformation of Co and Cu NPs into metal oxides as suggested by XRD patterns (Figure S5), and thus do not make a further increase in catalytic activity.

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time of 48 h (8a–9a of table 2). Finally, CoCu@NC<sub>2</sub> was applied to catalyze the aerobic esterification of benzyl alcohol with other aliphatic alcohols, including ethanol, propanol and butanol, the benzyl alcohol showed good to high conversions with considerable selectivity under the base-free condition (10a–12a of table 2). However, owing to the steric effect of fatty carbon chain, the long-chain alcohols have poor conversions and selectivity relative to methyl alcohol. These examples demonstrate that CoCu@NC<sub>2</sub> is a promising catalyst for oxidative esterification of a variety alcohols to esters. Obviously, the catalytic activity and selectivity of CoCu@NC<sub>2</sub> are superior to those obtained in base-containing systems (Table S1, entries 1-5). It is also higher or comparable to those of previously reported heterogeneous catalysts for oxidative esterification in base-free systems (Table S1, entries 6-10).

For the durability test, the catalyst CoCu@NC<sub>2</sub> was centrifuged, washed, and thermal treated at 500 °C, then reused in the next run. The catalyst showed a stable recyclability, the conversion was still up to 87% with selectivity maintained at 98% after five runs (Figure S6). The XRD pattern for the recovered catalyst was similar to that of the fresh one (Figure S7), and the ICP-AES analysis of the recycled catalyst showed negligible leaching of either Co or Cu, indicating a heterogeneous nature of CoCu@NC<sub>2</sub>.

### Conclusions

In conclusion, we have developed Co and Cu co-embedded Ndoped carbon catalysts (CoCu@NC<sub>n</sub>) based on a facile one-step carbonization strategy. With both Co and Cu nanoparticles embedded in a single NC support, synergetic active sites produced in the catalyst CoCu@NC<sub>2</sub>, and therefore caused a significant increase in catalytic activity and selectivity for aerobic oxidative esterification of alcohols to esters. N-doping was also demonstrated to be essential to form highly active catalysts with abundant basic sites that endow the oxidative esterification proceeded under base-free conditions. The CoCu@NC<sub>2</sub> exhibited remarkable catalytic performance under mild conditions for a wide variety of substrates and can be reusable for 5 times. The present strategy may be suitable for the exploration of more metal-based catalysts with enhanced activity and durability that can be applied in various catalytic processes.

### **Conflicts of interest**

There are no conflicts to declare

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View Article Online Facile Synthesis of Highly Efficient Co/Cu@NC Catalyst for Base-free Oxidation9/DONJ00172D of Alcohols to Esters

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Co/Cu nanoparticles co-decorated N-doped carbon exhibits excellent activity and stability

for base-free oxidation of alcohols to esters.