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Dual-immobilized copper catalyst: carbon	Leave this area blank for abstract info.
nitride-supported copper nanoparticles	
catalyzed oxidation of propargylic alcohols	
Wei Lv, Jing Tian, Yan Wang, Xiaoshu Zhu* and Xiaoquan Ya	o*
ОН	
Cu NPs-CN (10 mol%)	
R <sub>2</sub> TBHP, DCM, 40 °C	
recyclable catalyst	2



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# Dual-immobilized copper catalyst: carbon nitride-supported copper nanoparticles catalyzed oxidation of propargylic alcohols

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#### ARTICLE INFO

ABSTRACT

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*Keywords:* Copper nanoparticles Carbon nitride Immobilized ligand Catalytic oxidation Copper nanoparticles were supported and modified by carbon nitride, which was utilized as support and might work as a kind of immobilized *N*-donor ligand. The modified nanoparticle catalyst was evaluated with the oxidation of propargylic alcohols and showed highly catalytic efficiency as well as significant ligand or support effect in the reaction. The dual-immobilized nanoparticle catalyst could be recycled for 3 times at least without obvious decrease in catalytic activities.

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Recently, much attention has been attracted to the use of nanoparticles as catalysts in organic reactions.<sup>1</sup> Because of their easy preparation and relative stabilities in air, the nanoparticles of coinage metals, such as copper, silver and gold, were widely reported, and there are many excellent examples on their applications as catalysts in organic reactions.<sup>2</sup> In comparison with most of examples using surfactant-free nanoparticles as catalysts, there are few examples reported about the ligand effect on coinage metal nanoparticle-catalyzed reactions. Recently, several ligand-promoted or ligand & support-promoted, coinage nanoparticle-catalyzed reactions were reported by our groups and the others,<sup>3</sup> in which the utilization of ligands proved to be the key role to the reaction. However, in these examples, the ligands were introduced separately into the reaction mixture, which resulted in many difficulties to recover and reuse the ligands with the solid nanoparticle catalyst together. To resolve the problem, using immobilized ligand or functionalized support instead might be a possibility of choices.

Mesoporous carbon nitride is a novel superior material and has been wildly used as electrode materials because of its porous structure and amine-containing molecules.<sup>4</sup> On the other hand, its use for organic catalysis reports has not been concentrated ever.<sup>5</sup>. <sup>6</sup> Recently, Vinu and co-workers reported the synthesis of mesoporous carbon nitride and demonstrated that the Au nanoparticles embedded in mesoporous carbon nitride were a highly efficient and recyclable catalyst in a three-component coupling reaction of benzaldehyde, piperidine, and phenylacetylene to synthesize propargylamine.<sup>6a</sup> However, it

should be noted that the carbon nitride actually acted as a catalyst support only in the reaction, and there was no ligand/supporteffect observed.<sup>7</sup> Otherwise, Antonietti and his co-workers also reported a Pd nanoparticles supported on a mesoporous graphitic carbon nitride, Pd@mpg-C<sub>3</sub>N<sub>4</sub>, which was shown to be highly active and promoted the selective formation of cyclohexanone from the hydrogenation of phenol under atmospheric pressure of hydrogen in aqueous media,<sup>6b</sup> but no ligand/support effect was mentioned either.<sup>8</sup> Considering the sp3- and sp2- hybridized nitrogen-containing structure,<sup>4</sup> we suspected that carbon nitride might be used as a novel immobilized ligand or functionalized support, to achieve a greener approach to the ligand-promoted, metal nanoparticles-catalyzed reaction. As our first attempt, carbon nitride-supported copper nanoparticle catalyst (CuNPs-CN) was synthesized successfully following the reported method. The average size of copper nanoparticles is ca.20-30 nm based on the TEM image. 9, 10

Previously, a highly efficient, copper nanoparticles catalyzed oxidation of propargylic alcohols to ynones was reported with TBHP or air as oxidant by our group. <sup>3d</sup> With bipyridine as ligand, the reaction was accelerated significantly and gave good to excellent yields to a variety of propargylic alcohols. The nanoparticals could be recovered conveniently by centrifugation from the reaction mixture, but it is hard to be reused effectively without additional fresh ligand supplied. Thus, this reaction was selected as prototype to examine the catalytic activity and recyclability of the dual-immobilized copper catalyst.

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<b>Hadie II</b> Copper numopulation of <b>Hi</b> .	Table 1.	Copper	nano	particles	-catalyzed	d oxidation	of 1k. <sup>a</sup>
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		Cata Oxid	lyst (10 mol%) ant (10 eq.)			
Fritze	1k		Colored a	2k	Time (b)	X: 11 (01 )b
Entry	Catalyst	Oxidant	Solvent	Temperature (C)	Time (n)	
1	CuNPs	TBHP (10equiv)	DCM	40	6	93
2	CuNPs/bipyridine	TBHP (10equiv)	DCM	40	2	95
3	CuNPs-CN	TBHP (10equiv)	DCM	40	2	>99
4	CN	TBHP (10equiv)	DCM	40	24	ND <sup>c</sup>
5	CuNPs-AC	TBHP (10equiv)	DCM	40	24	83
6	CuNPs-CN	TBHP (5equiv)	DCM	40	24	99
7	CuNPs	TBHP (2equiv)	DCM	rt	6 <sup>d</sup>	46 <sup>e</sup>
8	CuNPs-CN	TBHP (2equiv)	DCM	rt	6 <sup>d</sup>	82 <sup>f</sup>
9	CuNPs-CN	TBHP (10equiv)	Toluene	80	2	93
10	CuNPs-CN	H <sub>2</sub> O <sub>2</sub> (10equiv)	DCM	40	24	46
11	CuNPs-CN	$H_2O_2(10equiv)$	Toluene	80	24	51
12	CuNPs-CN	H <sub>2</sub> O <sub>2</sub> (10equiv)	t-BuOH	80	24	55
13	CuNPs-CN	$O_2$	DCM	40	24	trace
14	CuNPs-CN	O <sub>2</sub>	THF	60	24	trace
15	CuNPs-CN	$O_2$	Toluene	80	24	50
16	CuNPs-CN	$O_2$	Dioxane	80	24	trace

<sup>a</sup> Reaction condition: 1k (0.1mmol), copper catalyst (10 mol%), TBHP (70% in water, 10 equiv.), dichloromethane (DCM, 1.5 mL).

<sup>b</sup> Isolated yields.

° Not detected.

<sup>d</sup> The reaction was interrupted at 6h.

<sup>e</sup> ca.50% of starting material was recovered.

<sup>f</sup> ca. 14% of starting material was recovered.

In the present work, utilizing the nitrogen-containing carbon material, carbon nitride, as functionalized support or immobilized ligand, a novel, ligand and metal dual-immobilized copper nanoparticle catalyst were prepared and evaluated with the oxidation of propargylic alcohol. Significant ligand/supporteffect was observed in the reaction as well as good to excellent yields were achieved. Furthermore, the dual-immobilized nanoparticle catalyst could be recycled for 3 times at least without obvious decrease in catalytic activities and no additional fresh ligands were required. To best of our knowledge, it is also the first report on the ligand/support-effect of carbon nitride in catalytic organic reactions.

The oxidation of 1-(naphthalene-1-yl)-3-phenyl prop-2-yn-1ol (**1k**) was selected as the prototype to start our investigation and screen for the optimized reaction conditions. With 10 mol% of copper nanoparticles as catalyst, 10 equiv. of TBHP as oxidant in DCM solution at 40 °C, we compared the catalytic characters of the carbon nitride-supported copper nanoparticles (CuNPs-CN)<sup>10</sup> with pure copper nanoparticals (CuNPs), CuNPs & bipyridine ligand and active carbon supported CuNPs (CuNPs-AC).<sup>11</sup>

It can be seen from Table 1, with CuNPs as catalyst, the desired product, 1-(naphthalen-2-yl)-3-phenylprop-2-yn-1-one (**2k**), was afforded successfully with 93% yield after 6 hours reaction (Table 1, entry 1). An obvious ligand effect was observed when 10 mol% bipyridine was added to the reaction mixture, and the reaction time was shorten from 6 hours to 2 hours with slightly increase in yield (entry 2). When CuNPs-CN was utilized as catalyst, a >99% of yield was achieved in 2 hours

(entry 3). These results above suggested that the carbon nitride might show some effect similar to the free bpy ligand in current reaction. Further more, in case the carbon nitride could catalyze the oxidation along, a blanket reaction was also carried out (entry 4). It is obviously that the copper nanoparticals should be the real catalyst in the supported metal catalyst.

To further understand the ligand/support effect of the nitrogen-containing carbon support material, a control experiment was also carried out with CuNPs-AC as catalyst, but the result was even worse than that of CuNPs (entries 1 and 3 *vs.* entry 5). It is obviously that the nitrogen-containing structure of carbon nitride improves the catalytic activity of CuNps similar to an *N*-donor ligand.

With the decrease of TBHP from 10 to 5 equivalents, 24h was required to entire the reaction (entry 6). In order to study the ligand/support effect of carbon nitride detailedly, we also decreased TBHP to 2 equiv. of **1k**, and carried the reactions at room temperature with CuNPs and CuNPs-CN as catalysts, respectively. It can be seen from entries 7 and 8, that under the milder condition, CuNPs-CN catalyst gave almost double yield than that of CuNPs during the same reaction time. This result provided another possible evidence that the carbon nitride support did improve the catalytic activity of CuNps under present conditions.

Toluene was also used as the solvent instead of DCM. The reaction was carried out at  $80^{\circ}$ C and **2k** was afforded with 93% of yield (entry 9). On the other hand, other oxidants were also scanned. H<sub>2</sub>O<sub>2</sub> gave moderate yields from 46%-55% (Table 1, entries 10-12). When oxygen was utilized as oxidant, only 50%

of 2k was obtaind in toluene solution at 80 °C after 24 hours reaction. (entries 13-16).

With the optimized reaction conditions in hand, we studied substrate scope of the reaction. <sup>12</sup> Typical results are listed in Table 2. It can be seen that the substrates derived from aromatic aldehydes and alkynes, no matter it is electron-rich or electron – deficient, gave the corresponding products in good to excellent yields (Table 2, entries 1-17). It was worthy to note that the substrates derived from aliphatic aldehydes and alkynes also gave excellent yields (entries13–15). Even with compound **1r** as substrate which was derived from salicyldehyde and usually sensitive to oxidation conditions, 60% of product was also achieved (entry 18). However, with 3-phenylprop-2-yn-1-ol (**1s**) as the starting material, a complicated reaction mixture was obtained and only 35% of **2s** was given even at room temperature (entry 19).

 Table 2. Carbon nitride supported copper nanoparticles

 catalyzed oxidation of propargylic alcohols<sup>a</sup>

<u>\_\_\_</u>

		Ps-CN (10 mol%) <u>3HP (10eq.)</u> R <sub>1</sub> CM 40°C R1		
Entry	1 R <sub>2</sub> Substrates	Products 2	Time (h)	Yield (%) <sup>b</sup>
1			2	>99
2			2	96
3			2	97
4	OMe OH OMe 1d		2	99
5	Br Je		6	86
6	Br If	Br 2r	8	95
7	CH Ig		8	81
8		Class Class	8	85
9			8	90
10			2	>99
11			2	>99
12		21	8	89
13	MeO Im	Meo 2m n-CaHb	2	97
14	n-GHH	n-C <sub>P</sub> H <sub>15</sub>	8	92



<sup>a</sup> Reaction condition: propargylic alcohol (0.1 mmol), CuNPs-CN (10 mol%), TBHP (70% in water, 10 equiv.), dichloromethane (DCM, 1.5 mL), 40 °C.

<sup>b</sup> Isolated yields.

<sup>c</sup> The reaction was carried out at room temperature.

In order to understand the nature of the CuNPs-CN catalyst further more, we also selected **1a**, **1m** and **1n** to detected more conditions, and the results were summarized in Table 3.

**Table 3.** Copper nanoparticles-catalyzed oxidation of **1a**, **1m** and **1n**.<sup>a</sup>

Entry	Sub.	Conditions	result <sup>b</sup>
1	1a	10 mol% CuNPs, 2 equiv. of TBHP, rt	6h, 94%
2	1a	10 mol% CuNPs, 10 equiv. of TBHP, 40 °C,	6h, 70%°
3	1a	10 mol% CuNPs-CN, 2 equiv. of TBHP, rt	$84\%^{d}$
4	1a	10 mol % CuNPs-CN, 10 equiv. of TBHP, 40 $^{\rm o}{\rm C}$	2h, 99%
5	1m	10 mol % CuNPs, 2 equiv. of TBHP, rt	38% <sup>c,d</sup>
6	1m	10 mol % CuNPs, 10equiv. of TBHP, 40 °C,	8h, 56% °
7	1m	10 mol % CuNPs-CN, 2 equiv. of TBHP, rt	$65\%^{d}$
8	1m	10 mol % CuNPs-CN, 10 equiv. of TBHP, 40 $^{\rm o}{\rm C}$	2h, 97%
9	1n	10 mol % CuNPs, 2 equiv. of TBHP, rt	$10\%^{d}$
10	1n	10% CuNPs, 10equiv. of TBHP, 40 °C,	$15\%^{c,d}$
11	1n	10 mol % CuNPs-CN, 2 equiv. of TBHP, rt	59% <sup>d</sup>
12	1n	10 mol % CuNPs-CN, 10 equiv. of TBHP, 40 °C	8h, 92%

<sup>a</sup> Reaction condition: propargylic alcohol (0.1 mmol), Cu catalyst (10 mol%), TBHP (70% in water, 10 equiv.), dichloromethane (DCM, 1.5 mL).

<sup>b</sup> Isolated yields.

<sup>c</sup> A complicated reaction mixture was obtained.

<sup>d</sup> The total conversion could not be reached even after overnight reaction.

As shown in Table 3, for substrate **1a**, the CuNPs seems show a little better catalytic activity than CuNPs-CN at room temperature (entry 1 vs entry 3). However, much worse result was obtained by using CuNPs as catalyst at 40 °C with 10 equiv of TBHP, and a complicated reaction mixture was obtained (entry 2 vs entry 4). On the other hand, when less reactive substrate **1m** and **1n** were examined, CuNPs-CN showed much better catalytic activity than CuNPs no matter at room temperature or 40 °C (entries 5-6 vs entries 7-8, entries 9-10 vs entries 11-12). These results above might indicate that the most suitable activation temperature for CuNPs-CN catalyst was 40 °C, and also provided evidence that the carbon nitride materials do modify the catalytic characters of CuNPs.

As a metal and ligand dual-immobilized catalyst, our original intention is to look for a novel strategy to recycle the catalyst and ligand together in the ligand-promoted, nanoparticle-catalyzed

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reactions to achieve a greener approach. Thus, we recovered the supported catalyst conveniently by centrifugation from the reaction mixture, and reused it directly with fresh solvent and substrate to examine the recyclability of the catalyst.<sup>13</sup> It can be seen from Table 3 that the catalyst could be reused for 3 times at least without appreciable loss in its catalytic activities (Table 4).<sup>14</sup> This result above showed the excellent potential for the recyclability of the dual-immobilized catalyst.

Table 4. The experiments of catalyst recycle.<sup>a</sup>



Run	Yield/%
1	>99
2	97
3	94
4	92

<sup>a</sup> Reaction condition: 1j (0.1 mmol), CuNPs-CN (10 mol%), DCM (1.5 mL), stirred at 40 °C for 2h.

#### <sup>b</sup> Isolated yields.

In conclusion, with carbon nitride as a functionalized support instead of bpy ligand, a novel ligand and metal dual-immobilized copper nanoparticle catalyst were prepared and evaluated with the oxidation of propargyl alcohol. Significant ligand/support effect was observed in the reaction as well as good to excellent yields were achieved. The carbon nitride-supported nanoparticle catalyst could be effectively recovered and reused for 3 times without obvious decrease in catalytic activities. The detailed mechanism, the effect of particle size, hole size and nitrogen content of carbon nitride as well as the scope of the reaction are currently under further investigation.

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- 10. Carbon nitride supported copper nanoparticles: Under nitrogen atmosphere, in a 250 mL three round-bottom flask equipped with a stir bar, 20 mL absolute alcohol was mixed with 40 mL aqueous solution of Cu(OAc)<sub>2</sub> (1 mmol), polyvinylpyrrolidone (PVP, average MW: 40,000, 200 mg) and carbon nitride (0.32 g) preheated to 40 °C. Then, 80 mL of aqueous solution containing sodium borohydride (NaBH4, 4 mmol) and potassium hydroxide (KOH, 4 mmol), was added dropwise into the solution over a period of 30 minutes, and black precipitates were observed in the mixture. The mixture was kept to stir vigorously for 2 h at 40 °C. Then, the particles were separated from the solution by high-speed centrifugation at 6500 ppm for 2 min. The precipitates were washed by distilled water, absolute alcohol and diethyl ether for 3 times, respectively. The final product was dried in vacuum at 80 °C overnight and stored under nitrogen atmosphere.
- 11. The detailed characterization of carbon nitride and its supported copper nanoparticles were described in supporting information. The TEM image of active carbon supported CuNPs was also provided in supporting information.
- 12. Typical procedure for carbon nitride supported copper nanoparticles catalyzed oxidation of propargylic alcohols (Entry 1, Table 2): 1-(Naphthalene-1-yl)-3-phenylprop-2-yn-1-ol (1k) (0.1 mmol), CuNPs-CN (10 mol%), TBHP (10 eq.) and DCM (1mL) were added into a 10-mL sealed tube in air. The mixture was stirred at 40 °C for 2 hours. Then, the reaction mixture was purified by flash column chromatography on silica gel (hexanes/EtOAc 15:1). Compound 2k was obtained in a >99 % of yield
- 13. Typical procedure for recycling of the catalyst: The oxidation of 1k (0.1 mmol scale) was carried out under the optimized reaction conditions for 2 hours. When the reaction was stopped, the solid catalysts were separated through the centrifugal method

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from the reaction mixture. The collected catalyst was washed with diethyl ether and dried under vacuum at room temperature. Then, fresh substrate 1k (0.1 mmol), TBHP (10 equiv.) and DCM (1.5 mL) was added to run the next reaction for another 2 hours.

14. As a control experiment, the bpy-Cu NPs catalyst was also reused with 1k as the substrate for one more time: without additional bpy ligand, 84% of yield was obtained after 14 h reaction; with fresh bpy ligand, the reaction finished in 8 h, and gave 91% of 2k.

#### **Supplementary Material**

Supplementary data associated with this article can be found in the online version.