

Cu₂O Nanocube-Catalyzed Cross-Coupling of Aryl Halides with Phenols via Ullmann Coupling

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Thermal and air-stable uniform Cu₂O nanocubes were employed in the development of a gram-scale, one-pot polyol synthesis. Herein is reported an efficient cross-coupling reaction of aryl halides and phenols with a catalytic amount

(0.1 mol-%) of Cu₂O nanocubes as recyclable catalyst and Cs₂CO₃ as the base in THF at 150 °C.

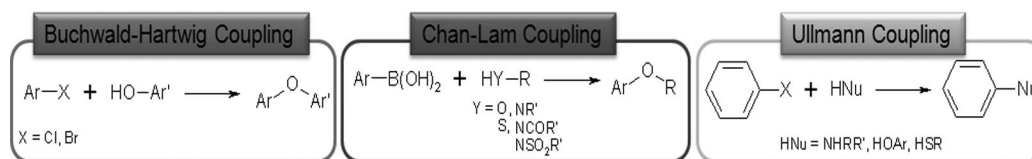
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Introduction

Formation of aryl ethers and oxygen heterocycles are one of the most important reactions in modern organic synthesis, as such bonds are found in pharmaceutical, agrochemical, material products, and commercial dyes. Furthermore, polyaromatics possess unique physical characteristics that make possible their use as organic conductors or semiconductors. As a result, approaches to synthesizing carbon–oxygen bonds have been investigated for over a century, and the last decade has witnessed over 3,000 papers reporting new routes to carbon–oxygen bond formation. A promising transformation used to construct aryl ethers and oxygen heterocycles involves the intramolecular Cu- or Pd-catalyzed C–O bond formation between aryl halides and alcohols.^[1]

In Scheme 1, three reactions are shown as examples. First, the direct Pd-catalyzed C–N and C–O bond formation between aryl halides or trifluoromethanesulfonates and amines (1° and 2° aliphatic or aromatic amines; imides,

amides, sulfonamides, sulfoximines) or between aryl halides or triflates and alcohols (aliphatic alcohols and phenols), in the presence of a stoichiometric amount of base is known as the *Buchwald–Hartwig cross-coupling*.^[2] Second, the arylation of compounds containing N–H and O–H bonds at room temperature with phenylboronic acids is promoted in the presence of cupric acetate and a tertiary amine, the reaction being called *Chan–Lam coupling*.^[3] Substrates include phenols, amines, anilines, amides, imides, ureas, carbamates, and sulfonamides. Thirdly, F. Ullmann observed in 1904 that the reaction of aryl halides with phenols to give diaryl ethers was significantly improved in the presence of copper powder. This copper-mediated synthesis of diaryl ethers is known as the *Ullmann condensation* (Ullmann biaryl ether synthesis). In 1906, I. Goldberg disclosed the copper-mediated formation of an aryl amine by reaction of an aryl halide with an amide in the presence of K₂CO₃/CuI (Goldberg reaction/Goldberg modified Ullmann condensation.) During the first 70 years of the 20th century, copper was nearly the only metal used for aryl–aryl bond formation, initially



Scheme 1.

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as copper metal in the reductive symmetrical coupling of aryl halides to yield the corresponding aromatic compound, as well as in the coupling of aryl halides with N-containing reactants, phenols, and related nucleophilic agents.^[4] In addition, carbon–oxygen bond formation through coupling between various *o*-silylaryl triflates and phenols with use of CsF has been reported.^[5]

In general, metal nanoparticle catalysts offer higher surface areas, and their chemical and physical characteristics differ from bulk metals.^[6] Transition-metal nanoparticles have become a very important class of catalysts, particularly those used for hydrogenation, oxidation, coupling reactions, and some photocatalytic reactions.^[7] Especially cuprous oxide (Cu_2O) offers important applications in *p*-type metal oxide semiconductors with promising applications in solar energy conversion, hydrogen production, superconductivity, negative electrode materials, and metal nanoparticle catalysts with higher catalytic activity.^[8] In this regard, the authors envisaged the application of readily available and inexpensive copper oxide nanoparticles as catalysts. This inspired focus upon the various aspects of catalysis with Cu_2O nanocubes for the formation of carbon–oxygen bonds. These copper-based catalysts are also attractive both from the economic and industrial points of view, as compared to palladium.

Results and Discussion

Typically, the synthesis of Cu_2O nanoparticles is carried out by a one-pot polyol process in the presence of poly(vinyl pyrrolidone) (PVP) as a surfactant and 1,5-pentane-diol (PD) as both reductant and solvent.^[9] The precursor solution, copper(II) acetylacetonate dissolved in PD, was injected in a single pot of a hot PVP solution in PD at 240 °C, and the reaction mixture was allowed to age for 15 min. During the reaction, the initial dark-green solution gradually changed to green and yellow, indicating the formation of Cu_2O nanocubes. The resulting particles were then dispersed in ethanol.

The scanning electron microscopy (SEM) image in Figure 1a and the transmission electron microscopy (TEM) image in Figure 1b show the monodisperse cubic Cu_2O nanoparticles (45.1 ± 3.1 nm). The X-ray diffraction (XRD) spectrum in Figure 1c shows typical reflection patterns of cuprite (JCPDS No. 77-0199).

As shown in Table 1, the reaction conditions were optimized by using phenol and iodobenzene. First, 5.0 mol-% Cu_2O nanocubes in DMF were refluxed for 1 h, and diphenyl ether was obtained in 75% yield. When the reaction time was increased to 4 h, 93% conversion was achieved. After that, in order to exploit the thermal stability of the Cu_2O catalyst, the reaction temperature was increased. Placing the reaction in a closed system at 150 °C by using a pressure tube and running the reaction for 1 h resulted in a 41% conversion. When the reaction time was increased to 4 h, 93% conversion was obtained under the same reaction conditions. In general, it was found that increasing the reaction temperature was an effective means of increasing the conversion. The effects of reducing the quantity of catalyst to 1.0 mol-% and changing the solvent to DMF, CH_3CN , or THF were also investigated. Ultimately, THF was chosen as the solvent. With 1.0 mol-% catalyst, a 100% conversion was achieved after a reaction time of 3 h. In the reaction with high catalyst concentration, there was no big difference

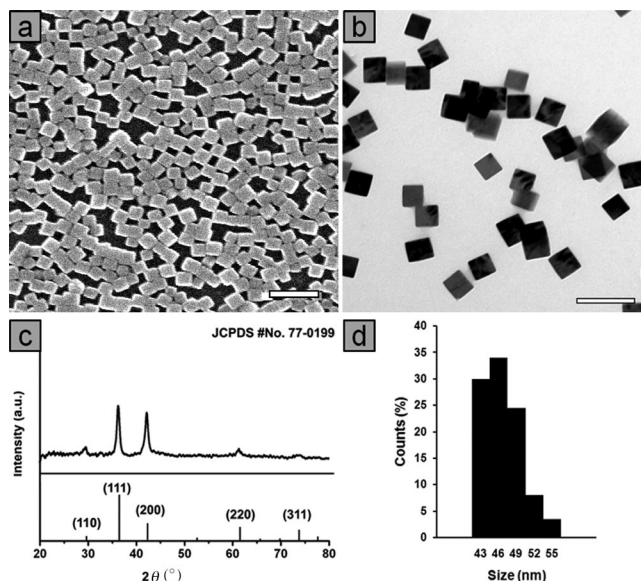


Figure 1. (a) SEM image, (b) TEM image, (c) XRD pattern, and (d) size distribution diagram of the Cu_2O nanocubes. The scale bars represent (a) 200 nm and (b) 100 nm.

in conversion between the reflux system and closed system, but the difference was big in the reaction with low catalyst concentration. The reaction temperature was also increased to 150 °C through use of a stainless steel reactor (see the Supporting Information), and the quantity of the catalyst could be significantly reduced to 0.1 mol-% to give a 100% conversion. In addition, the base was changed to Na_2CO_3 and K_2CO_3 , and the conversion was reduced to 71 and

Table 1. Optimization of reaction catalyzed by Cu_2O nanocubes.

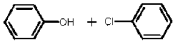
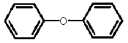
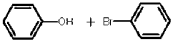
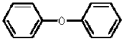
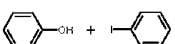
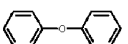
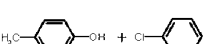
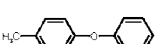

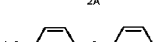




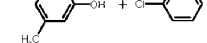
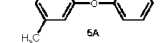
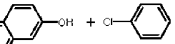
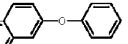
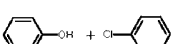
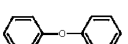

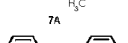
Entry	Catalyst conc. (mol-%)	Temp. (°C)	Time (h)	Base	Solvent	Conv. (%) ^[a]
1	blank	150	3	Cs_2CO_3	THF	N.D.
2	0.1 mol-%	reflux	3	Cs_2CO_3	THF	63
3	0.1 mol-%	150	1	Cs_2CO_3	THF	71 ^[c]
4	0.1 mol-%	150	2	Cs_2CO_3	THF	91 ^[c]
5	0.1 mol-%	150	3	K_2CO_3	THF	60 ^[c]
6	0.1 mol-%	150	3	Na_2CO_3	THF	71 ^[c]
7	0.1 mol-%	150	3	Cs_2CO_3	THF	100 ^[c]
8	0.1 mol-%	150	3	Cs_2CO_3	DMF	100 ^[c]
9	1 mol-%	100	1	Cs_2CO_3	THF	31 ^[b]
10	1 mol-%	100	3	Cs_2CO_3	DMF	97 ^[b]
11	1 mol-%	100	3	Cs_2CO_3	THF	100 ^[b]
12	1 mol-%	100	3	Cs_2CO_3	CH_3CN	100 ^[b]
13	5 mol-%	reflux	1	Cs_2CO_3	DMF	75
14	5 mol-%	reflux	4	Cs_2CO_3	DMF	95
15	5 mol-%	150	1	Cs_2CO_3	DMF	41 ^[b]
16	5 mol-%	150	4	Cs_2CO_3	DMF	93 ^[b]

[a] Determined by ^1H NMR spectroscopy. Yields are based on the amount of iodobenzene used. [b] Pressure tube used (0.38 M). [c] Stainless steel reactor used (1.21 M).

60%, respectively. Depending on the reaction time, the conversion also changed (91% for 2 h and 71% for 1 h). Finally, the optimum reaction conditions were acquired: cross-coupling of iodobenzene (1.6 mL, 0.014 mol) with selected phenols (1.3 g, 0.014 mol) with Cu₂O nanocubes (2.0 mg, 0.1 mol-%) in THF (10 mL) to afford the diphenyl ether. In addition, under these optimized reaction conditions, no reaction occurred in the absence of catalyst.

A wide variety of substrates with C–I, C–Br, and C–Cl bonds, as well as nucleophiles, have been examined. Relative reactivities of halogen-substituted substrates towards halophilic attack by a carbanion were also investigated. The following order of relative reactivities towards halophilic attack was ascertained: R–I, R–Br or R–Cl, with a bond reactivity order of: C–I > C–Br > C–Cl (entries 1–3, Table 2).

Table 2. Reaction of aryl halides with substituted phenols using Cu₂O nanocubes as catalyst.^[a]

Entry	Substrate	Product	Yield (%) ^[b]
1		 1A	76 (61)
2		 1A	94 (82)
3		 1A	100 (91)
4		 2A	100 (86)
5		 3A	100 (63)
6		 4A	100 (72)
7		 5A	91 (74)
8		 6A	58 (57)
9		 7A	98 (100)
10		 5A	100 (98)
11		 2A	51 (29)

[a] Reaction conditions: 0.1 mol-% Cu₂O nanocubes and 2 equiv. Cs₂CO₃ used, THF (1.21 M), 150 °C, 3 h. [b] Determined by ¹H NMR spectroscopy. Yields are based on the amount of substituted aryl halides used. Yields in parentheses are isolated yields after column chromatography on silica.

The reaction of substrates with electron-donating and electron-withdrawing groups on the phenol ring resulted in high yields of the cross-coupling products of aryl halides. In the case of methyl and methoxy substituents, the conversion yield was 100%. Furthermore, the reaction of substrates with NO₂ was examined and was found to have high conversion yields (100%). Naphthols are also possible reac-

tants, but yields decrease. Interestingly, 2-naphthol showed a similar trend. In order to examine the influence of substituents, ArI, 2-iodophenol, 3-iodophenol, and 4-iodophenol were selected for an experiment. As a result, 2-iodophenol showed 14% conversion, 3-iodophenol, 100%, and 4-iodophenol, 51% conversion.

As shown in Figure 2 (and Supporting Information), the structure of the Cu₂O nanocubes remained unchanged after the reaction, showing catalyst recyclability. In actuality, after the reaction, the Cu₂O nanocubes were separated through centrifugation and used in the cross-coupling of aryl halides with phenols at least three times without loss of catalytic activity (Table 3). However, for more recycling, the quantity of the catalyst collected decreased (the quantity of the first use was 2.0 mg), thus yields suffered. In order to compensate for this, work in this lab is currently focused on immobilizing Cu₂O nanocubes on support material like charcoal for use as an improved heterogeneous catalyst.

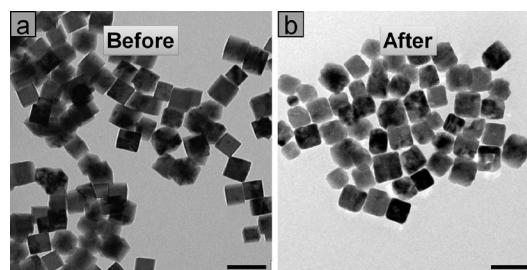


Figure 2. TEM images of Cu₂O nanocubes, (a) before and (b) after use. The scale bars represent 100 nm.

Table 3. Recycling of Cu₂O nanocubes.^[a]

Entry	Catalyst conc. (mol-%)	Conv. (%) ^[b]
1	0.1 mol-% nanocubes	100
2	Recovered form # 1	100
3	Recovered form # 2	98
4	Recovered form # 3	100

[a] Reaction conditions: 0.1 mol-% Cu₂O nanocubes and 2 equiv. Cs₂CO₃ used, THF, 150 °C, 3 h. [b] Determined by ¹H NMR spectroscopy. Yields are based on the amount of iodobenzene used.

Conclusions

In summary, uniform Cu₂O nanocubes have been synthesized on a gram scale. The best catalytic results were obtained by application of Ullmann coupling with well-designed, uniform, Cu₂O nanocubes, whereby a novel, uncomplicated, and economical method for the cross-coupling of aryl halides with phenols was developed. The process is simple and allows the formation of a diverse range of diaryl ethers in excellent yields. Overall, this methodology offers the competitive advantages of recyclability of the catalyst without further purification and loss of catalytic activity, low catalyst loading, wide-ranging substrate applicability, and high yields in short reaction times.

Experimental Section

Preparation of Cu₂O Nanocubes: PVP (Aldrich, Mw 55,000; 5.3 g) dissolved in PD (Aldrich, 96%; 45 mL) was heated to 240 °C under an inert atmosphere. Then, Cu(acac)₂ (STREM, 98%; 4.0 mmol) dissolved in PD (15 mL) was injected into the hot PVP solution at 240 °C, and the mixture was stirred for 15 min at the same temperature. The colloidal dispersion was cooled to room temperature, and the product was separated by adding acetone (150 mL) and centrifuging at 8000 rpm for 20 min. The precipitates were washed with ethanol several times and re-dispersed in ethanol (50 mL).

Catalytic Reactions: To a 25 mL stainless steel reactor were added Cu₂O nanocubes (2 mg, 0.1 mol-%), iodobenzene (1.6 mL, 0.014 mol), phenol (1.3 g, 0.014 mol), Cs₂CO₃ (9.1 g, 0.028 mol), and THF (10 mL). The reaction mixture was stirred at 150 °C in air. After three hours, the reaction mixture was poured into saturated aqueous NaHCO₃ solution (20 mL). The product was extracted with dichloromethane (3 × 20 mL) and dried with MgSO₄. The Cu₂O nanocubes were recovered by centrifugation, and the clean solution was analyzed by 300 MHz NMR spectroscopy.

¹H NMR Spectroscopic Data

Compounds **1A**,^[10a] **2A**,^[10a] **3A**,^[10b] **4A**,^[10c] **5A**,^[10d] **6A**,^[10e] and **7A**^[10a] are known compounds.

Diphenyl ether (1A): ¹H NMR (CDCl₃, 300 MHz): δ = 7.10–7.17 (m, 4 H), 7.19–7.22 (m, 2 H); 7.36–7.44 (m, 4 H) ppm.

1-Methyl-4-phenoxybenzene (2A): ¹H NMR (CDCl₃, 300 MHz): δ = 2.43 (s, 3 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 7.14–7.19 (m, 3 H), 7.22 (d, *J* = 8.1 Hz, 2 H), 7.40 (t, *J* = 7.8 Hz, 2 H) ppm.

1-Methoxy-4-phenoxybenzene (3A): ¹H NMR (CDCl₃, 300 MHz): δ = 3.78 (s, 3 H), 6.85–6.91 (m, 2 H), 6.94–6.99 (m, 4 H), 7.01–7.06 (m, 1 H), 7.26–7.32 (m, 2 H) ppm.

1-Nitro-4-phenoxybenzene (4A): ¹H NMR (CDCl₃, 300 MHz): δ = 6.81–6.83 (m, 2 H), 7.00–7.06 (m, 2 H), 7.22–7.25 (m, 1 H), 7.61–7.65 (m, 2 H), 8.06–8.09 (m, 2 H) ppm.

1-Methyl-3-phenoxybenzene (5A): ¹H NMR (CDCl₃, 300 MHz): δ = 2.20 (s, 3 H), 6.70–6.73 (m, 2 H), 6.79 (d, *J* = 9.6 Hz, 1 H), 6.90 (d, *J* = 7.8 Hz, 2 H), 6.94–6.99 (m, 1 H), 7.03–7.11 (m, 1 H), 7.17–7.20 (m, 2 H) ppm.

2-Naphthyl phenyl ether (6A): ¹H NMR (CDCl₃, 300 MHz): δ = 7.01–7.16 (m, 3 H), 7.25–7.27 (m, 1 H), 7.25–7.47 (m, 5 H), 7.69 (d, *J* = 7.5 Hz, 1 H), 7.80–7.83 (m, 2 H) ppm.

1-Methyl-2-phenoxybenzene (7A): ¹H NMR (CDCl₃, 300 MHz): δ = 7.22–7.30 (m, 3 H), 7.08–7.16 (m, 1 H), 6.92–6.99 (m, 2 H), 6.85–6.90 (m, 3 H), 2.29 (s, 3 H) ppm.

Supporting Information (see footnote on the first page of this article): Magnified TEM images of Cu₂O, XRD pattern of Cu₂O, and photo of the reaction vessel.

Acknowledgments

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