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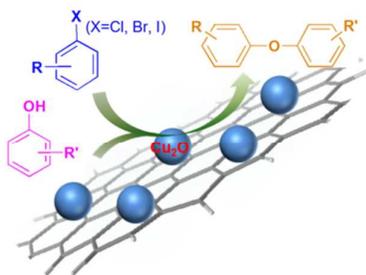
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Cu₂O/graphene as a heterogeneous catalyst can efficiently catalyze the C-O cross-coupling of aryl iodides with phenols.

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Graphene Supported Cu₂O Nanoparticles: an Efficient Heterogeneous Catalyst for C-O Cross-coupling of Aryl Iodides with Phenols

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Cu₂O/graphene as a heterogeneous catalyst can effectively ignite and catalyze the Ullmann C-O cross-coupling of aryl iodides with phenols at mild conditions. The yield of diphenyl ether from the cross-coupling of phenol and iodobenzene can get to 96% at 150 °C in 3 h, and the turnover frequency can be high up to 1282 h⁻¹. Meanwhile, the catalyst exhibits activity for varieties of C-O cross-coupling of aryl iodides, bromides and chlorides with phenol derivatives to form corresponding aryl ethers.

Diaryl ethers are widely employed as intermediates in organic synthesis, and thus their synthesis has attracted considerable attention for decades.^[1] Traditionally they are prepared through the Ullmann coupling of phenols with aryl halides promoted by copper reagents, which usually are stoichiometric and result in low or moderate yields.^[2] Homogeneous catalytic routes using palladium or copper complexes can greatly improve the efficiency of the coupling reactions.^[3] Taillefer et al. observed that the efficiency of the copper-catalyzed arylation of phenols from aryl chlorides could be greatly increased by addition of 2,2,6,6-tetramethyl-3,5-heptanedione as ligand.^[3c] However, the catalysts employed in the above routes are homogeneous and require ligands, and these lead to the difficulty in recycling and reuse of catalysts and increase the production cost.^[3e] Therefore more economical and flexible routes are still required to improve the synthesis processes. Comparing with the homogeneous processes, the routes employing recyclable heterogeneous catalysts would be efficient and environmentally friendly. Additionally, the improved technologies in material chemistry have furnished the availability of nanostructures and nanoporous solids with very large surface areas, which lead to increased yields.^[4] Indeed, more and more studies suggest that the coupling of phenols with aryl halides could be achieved by heterogeneous catalytic routes. Kim et al. reported that Cu₂O nanocubes with a size of ~ 45 nm can catalyze the formation of biaryl ethers.^[5] Ling et al. reported that CuO supported by solid oxides can catalyze the coupling reaction under

ligand-free conditions.^[6] Saberi et al. prepared carbon nanotube-supported α-Fe₂O₃@CuO composites and found that the magnetic feature of composites helped facile separation of the target ethers.^[7] These heterogeneous catalysts usually achieve a relatively low turnover frequency (TOF) from less than 1 up to 50 h⁻¹.^[7]

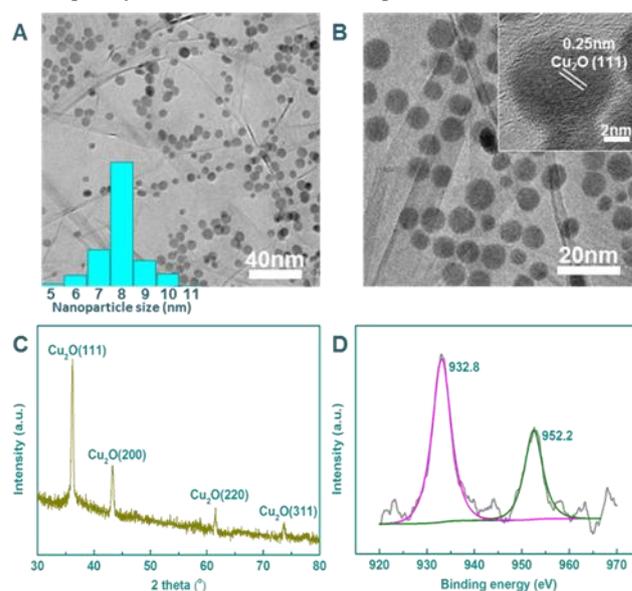


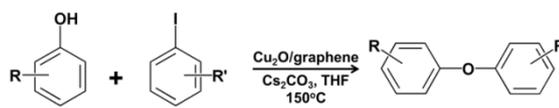
Fig.1 TEM images (A, B), XRD patterns (C) and XPS profiles (D) of a 5 wt.% Cu₂O/graphene catalyst, and the size distribution of Cu₂O nanoparticles (inset of A).

Cu₂O, CuO and Cu were found to be active for the Ullmann coupling reactions.^[5,6,8] According to the work of Buchwald and Bolm,^[9] trace amount of Cu₂O in salts of other metals can significantly increase the yield of target product and therefore Cu₂O could be the catalytically active phase for the reactions. It is well known that nanoparticles will have significantly increased surface area and thus catalytic activity when reducing their size to several nanometers. Unfortunately, nanosized Cu₂O particles are easily

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oxidized in air or moist conditions. Our recent work shows that graphene, a two-dimensional grid of sp^2 -bonded carbon atoms with highly delocalized electrons, can prevent the nanoparticles of Cu_2O and Cu from oxidation.^[10,11] The graphene-supported Cu_2O or Cu nanoparticles can exert stable catalytic functions for oxygen reduction reaction and coupling of nitrobenzene, respectively. It is therefore expected that nanosized Cu_2O particles may have higher activity for this type of Ullmann coupling reactions. Herein we report that the Cu_2O nanoparticles supported on graphene exhibit tremendous catalytic activity and recyclability for the Ullmann coupling reactions of phenols with aryl halides.

Table 1 C–O cross-coupling of aryl iodides with phenols over Cu_2O /graphene catalyst^[a].



Entry	Phenols	Aryl halides	Product	Yield (%) ^[b]	TOF (h ⁻¹)
1				96	1282
2				90	1202
3				87	1162
4				87	1162
5				98	1309
6				99	1322
7				97	1295
8				98	1309
9				85	1135
10				83	1108
11				82	1095

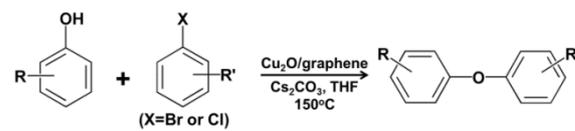
[a]: The reactions were conducted in a sealed argon atmosphere at 150 °C for 3 h using 0.014 mol aryl iodides, 0.014 mol phenols, 10 ml tetrahydrofuran (THF), 1.5 equiv Cs_2CO_3 , and 10 mg 5wt% Cu_2O /graphene catalyst. Conversions were based on the amount of substituted aryl halides used. TOF was calculated based the amount of Cu_2O ; [b]: Obtained from a Bruker GC-MS.

The Cu_2O /graphene catalyst with a Cu_2O loading of 5wt.% was prepared via a two-step method using liquid-phase diethylene glycol as the reduction agent (See Supporting Information). Transmission electron microscopy (TEM) images of the Cu_2O /graphene catalyst were presented in Fig.1A and B. Homogeneous Cu_2O nanoparticles are uniformly dispersed on the surface of graphene sheets; and their mean diameter is about 8 nm. The lattice fringe of the nanoparticles has an interplanar spacing of 0.25 nm, which is in agreement with the (111) plane of cubic Cu_2O . In the X-ray diffraction patterns

(XRD, Fig.1C), all the strong diffraction peaks can be indexed to the (111), (200), (220), (311) lattice planes of Cu_2O , confirming that Cu exists on the graphene sheets primarily as the cuprous phase. The X-ray photoelectron spectroscopy (XPS) of the catalyst can further confirm it. In Fig.1D, the binding energies of Cu 2p_{3/2} at around 932.8 eV and Cu 2p_{1/2} at 952.2 eV, respectively, can be attributed to the Cu⁺ and Cu⁰ states.^[12] The existence of metallic phase Cu indicates that the catalyst precursor was over-reduced in the preparation process. Our previous work has demonstrated that metallic Cu nanoparticles can stably exist on the graphene sheets.^[11] The XPS results presented here further suggest that some of metastable nanoparticles can be stabilized by using graphene as the support.

We tested several Cu_2O /graphene catalysts with different Cu_2O loadings, and found that the 5wt.% Cu_2O /graphene showed the best catalytic activity for the cross-coupling of phenol and iodobenzene. Therefore, all the reactions in the work were performed over the 5wt.% Cu_2O /graphene catalyst. The reaction results for the cross-coupling of phenols and iodides were summarized in Table 1. All the reactions were conducted in a sealed reactor under the protection of argon. The yield of diphenyl ether from the cross-coupling of phenol and iodobenzene is 96% and the TOF is high up to 1282 h⁻¹ (Table 1, entry 1). Saberi et al. had collected the TOF results over different catalysts and found that carbon nanotube supported $\alpha-Fe_2O_3@CuO$ nanocomposite had the highest TOF of 49.73 h⁻¹ for the cross-coupling of iodobenzene and phenol.^[7] Under the same reaction conditions, the TOF of Cu_2O /graphene catalyst is about 25 times higher than that one. No product was detected with the absence of Cs_2CO_3 . It is mainly because that the role of Cs_2CO_3 in the C–O cross-coupling is to enhance the nucleophilicity of phenols and then fasten the reaction.

Table 2 C–O cross-coupling of aryl bromides and chlorides with phenols over Cu_2O /graphene catalyst^[a].



Entry	Phenols	Aryl halides	Product	Yield (%) ^[b]	TOF (h ⁻¹)
1				26	347
2				57	761
3				20	267
4				5	67

[a]: The reactions conditions were the same as those in Table 1; [b]: Obtained from a Bruker GC-MS.

To explore the influences of different substituents on the coupling reactions of aryl halides with phenols, we employed various phenols to react with different iodobenzene derivatives. The presence of electron-donating groups such as methoxy or methyl in iodobenzene can slightly decrease the reaction yield (Table 1, entries 2–4). In contrast, the electron-withdrawing groups such as acetyl or nitro in

iodobenzene can increase the reaction yield (entries 5-6). However, the influences of electron-donating (entries 7-8) and electron-withdrawing groups (entries 9-10) in phenol are opposite to the aryl halides. When the electron-donating groups are simultaneously presented in iodobenzene and phenol, the reaction yield will further decrease (entry 11).

Besides aryl iodides, the catalyst can also catalyze the coupling reactions of aryl bromides and chlorides with phenol derivatives to produce corresponding aryl ethers. From the results shown in Table 2, the catalyst showed lower activity for aryl bromides and chlorides due to their low reactivity (entries 1-4).^[4]

For comparison, we also prepared graphene supported Cu and CuO nanoparticles as the catalysts for the cross-coupling reaction of phenol and iodobenzene. The CuO/graphene was prepared by a facile impregnation method. The Cu/graphene catalyst here was completely the same as that used in our previous work.^[11] Under the same reaction conditions, the TOF values over 5wt.% Cu/graphene and 5wt.% CuO/graphene are 291 (49% of iodobenzene conversion) and 393 (53%), respectively. When using only graphene as the catalyst, only 3% yield of diphenyl ether was detected. These results suggest that graphene supported Cu or CuO nanoparticles also possess considerable catalytic activity for the cross-coupling. However, the TOF values of both catalysts are further lower than that of the Cu₂O/graphene catalyst. Therefore, the active component in the catalyst for the Ullmann cross-coupling should be Cu₂O.

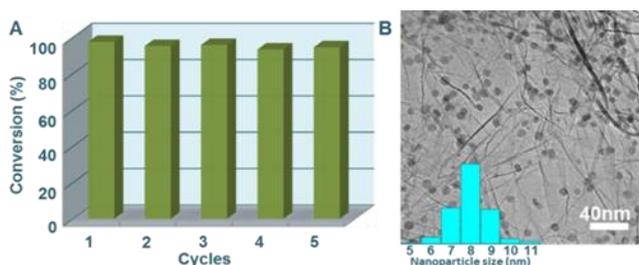


Fig.2 Recyclability of the 5wt% Cu₂O/graphene for the cross-coupling of phenol and iodobenzene in 5 rounds (A); and TEM image of the catalyst after 5-round test (B).

We investigated the yield of diphenyl ether from the reaction of phenol and iodobenzene at different time, and found that the reaction just reached its equilibrium at 3 h. Therefore, the product yield at 3h was monitored for five successive rounds to test the recyclability of the Cu₂O/graphene catalyst. A slight decrease in the catalytic activity was detected (Fig.2A). The product yield in the first round is 96%, and it can decrease to 94.4% after 5 rounds. The TEM image (Fig.2B) of the catalyst after 5-round usage shows no obvious change in morphology or aggregation of the Cu₂O nanoparticles. The mean diameter of the Cu₂O particles is still about 8 nm. The above results indicate that the Cu₂O/graphene has excellent catalytic stability in the reaction.

Conclusions

In summary, the present work demonstrates a new class of heterogeneous catalysts, graphene supported Cu₂O nanoparticles, which can efficiently catalyze the C-O cross-coupling reactions of aryl halides and phenols based on the

Ullmann method at mild conditions. Cu₂O nanoparticles with a mean size of 8 nm are homogeneously dispersed on the graphene sheets; and have very high stability during the catalytic reaction. The Cu₂O/graphene catalyst shows a very high turnover frequency of 1282 h⁻¹ for the cross-coupling of phenol and iodobenzene. The results for varieties of reaction substrates reveal the general applicability of the Cu₂O/graphene catalyst for this type of Ullmann cross-coupling. Therefore, the present work provides an efficient and green heterogeneously catalytic route for the production of diaryl ethers.

Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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