

Supporting Information

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

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Experimental

Cu₂O/graphene catalyst: The Cu₂O/graphene catalyst was prepared via a liquid-phase diethylene glycol reduction method. First, 47.5 mg graphite oxide (GO) and 7.0 mg copper acetate were dispersed into 50 mL absolute ethanol under sonication for 1 h; and then heated at 60 °C for 12 h. Second, the mixture was reduced by 80 mL diethylene glycol at 180 °C for 2 h. The final mixture changed from black to brick red indicating the formation of Cu₂O/graphene. The loading of Cu₂O is 5 wt.%, and the catalyst was marked as Cu₂O/graphene.

CuO/graphene catalyst: The CuO/graphene catalyst was prepared by an impregnation method. First, 47.5 mg graphene and 6.3 mg copper acetate were added into 20 mL aqueous solution with a small amount (5 mL) of ethanol under stirring for 24 h. Then the suspension was dried at 60 °C for 12 h. Finally, the mixture was calcined in the tube furnace at 400 °C under the protection of Ar for 4 h. The loading of CuO is 5 wt.%; and the catalyst was marked as CuO/graphene.

Cu/graphene catalyst: The Cu/graphene catalyst was prepared by the same method of Cu₂O/graphene catalyst; but the mass of graphite oxide (GO) and copper acetate was 47.5 mg and 7.9 mg respectively. When the Cu₂O/graphene was gotten, Cu/graphene catalysts were prepared by reducing Cu₂O/graphene composites in a mixture of H₂ (5 vol.%) and Ar at 500

°C for 4 h. The heating rate is 5 °C/min. The loading of Cu is 5 wt.%; and the catalyst was marked as Cu/graphene.

Catalyst Characterization: The metal loadings of different catalysts were determined by Perkin-Elmer ELAN 5000 inductively coupled plasma-mass spectroscopy (ICP-MS) instrument. The crystalline phases of the catalysts were characterized by X-ray diffractometer (XRD, Rigaku D-Max/RB). The microstructures of the catalysts were investigated by high-resolution transmission electron microscope (HRTEM, JEM-2010). X-ray photoelectron spectroscopy (XPS) was measured on a Kratos XSAM800 spectrometer, using Al Ka (hk=1486.6 eV) X-ray source as the excitation source.

C-O cross-coupling of aryl halides with phenols: The catalytic reactions were conducted in a 25 mL stainless steel reactor with a high-precision pressure gauge (0.4 %). The reactant mixture consisted of 0.014 mol benzene halides, 0.014 mol phenols, 10 ml tetrahydrofuran (THF), 1.5 equiv Cs₂CO₃, and 10 mg catalyst (CuO/graphene, Cu₂O/graphene or Cu/graphene). After purging the reactor by Ar 5 times, the reactor was immersed in a temperature-controlled oil bath, and the temperature was kept at 150°C under ambient pressure of Ar. The reaction time was 3 h. After reaction, 2 mL aliquots were collected, centrifuged, and then filtered through a Millipore filter (pore size 0.22 µm) to remove the catalyst particulates. The filtrates were analyzed by BRUKER SCION SQ 456 GC-MS to measure the concentration change of reactants and products. The quantitative analysis of specific analytes was detected by SIM mode in GC-MS. Conversions were based on the amount of substituted aryl halides used. The turn-over frequency (TOF) in our case was calculated as following:

$$\text{TOF} = \frac{\text{Amount of aryl halides (mol)} \times \text{conversion (\%)} \times \text{selectivity (\%)}}{\text{Mass of Cu}_2\text{O/graphene (g)} \times \text{Cu}_2\text{O loading (\%)} \times \text{reaction time (h)} / \text{M}[\text{Cu}_2\text{O}] \text{ (g/mol)}}$$

Supplement results

Table S1 The Cu loadings of CuO/graphene, Cu₂O/graphene and Cu/graphene catalysts.

Sample	Cu loading (ICP-MS) (wt. %)	
	fresh	used
Cu ₂ O/graphene	4.27	4.25
CuO/graphene	3.89	3.86
Cu/graphene	4.95	4.90

The Cu loadings of different catalysts measured by ICP-MS are listed in Table S1. The Cu loadings of Cu/graphene, Cu₂O/graphene and CuO/graphene are around 4.95, 4.27 and 3.89 wt.%. Accordingly, the Cu₂O and CuO loading are 4.80 and 4.86 wt.%, which is agreed with the theoretical value. From Table S1, the loadings of Cu in different catalysts only have slight decreases after reaction, suggesting that graphene as support can effectively stabilize the metal nanoparticles.

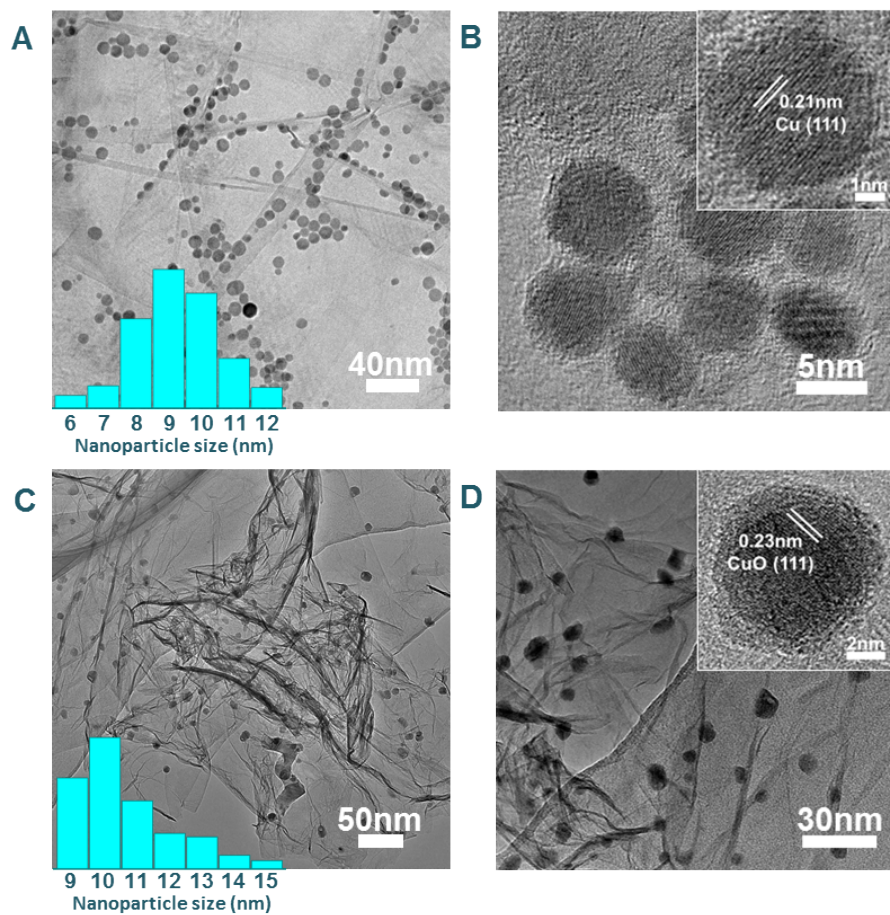


Fig.S1 TEM images of Cu/graphene (A and B) and CuO/graphene (C and D); and the size distribution of nanoparticles.

From Figure.S1, homogeneous Cu and CuO nanoparticles are uniformly dispersed on the surface of graphene sheets; and their mean diameter is about 9 and 11 nm, respectively. In these figures, the lattice spacings of nanoparticles are around 0.21 and 0.23 nm, which correspond to Cu (111) plane and CuO (111) plane, respectively.

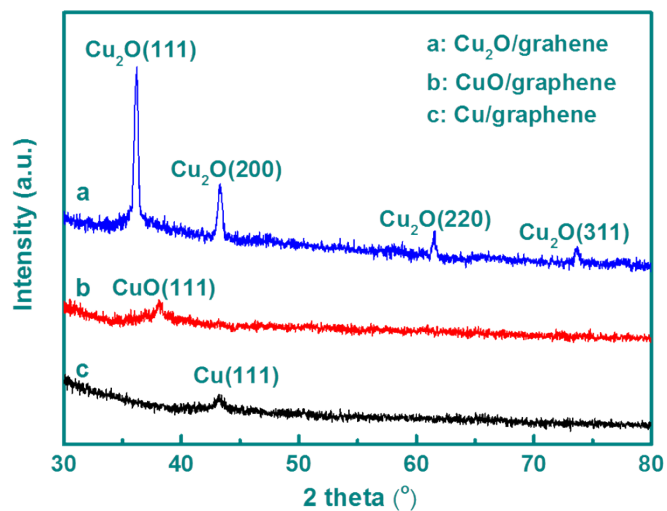


Fig.S2 XRD patterns of of CuO/graphene, Cu₂O/graphene and Cu/graphene catalysts.

In the X-ray diffraction patterns (XRD, Figure S2a), all the strong diffraction peaks can be indexed to the (111), (200), (220), (311) lattice planes of Cu₂O, confirming that Cu exists on the graphene sheets primarily as the cuprous phase. While the diffraction peaks at 38.1 and 43.3° in Figure S2 b and c, can be assigned to CuO (111) and Cu (111) plane respectively, which is agreed with the TEM results.

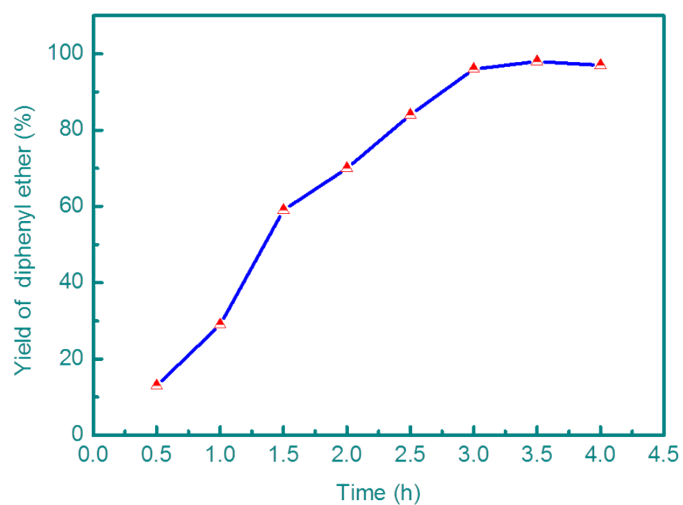


Fig.S3 Catalytic performance of Cu₂O/graphene for C-O cross-coupling of iodobenzene with phenol at different reaction time.

The yield of diphenyl ether increases with the reaction time increasing. The reaction can achieve equilibrium at 3 h. Therefore, we employ 3 h as the reaction time in our case.

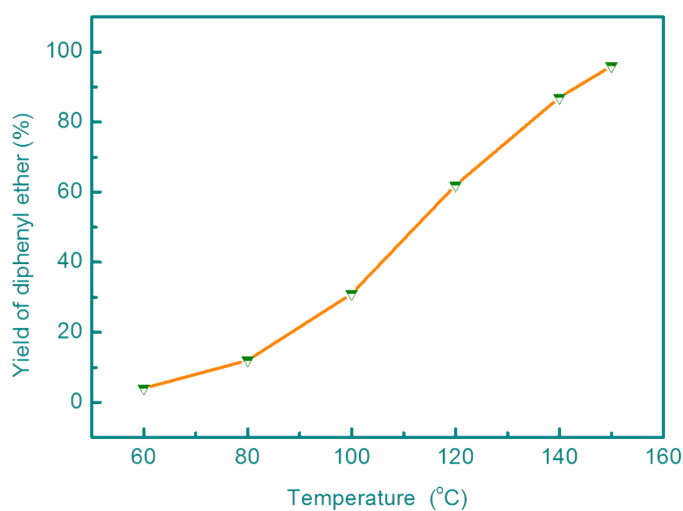
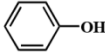

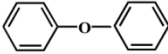
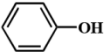
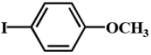
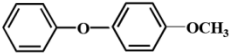
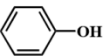
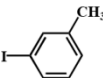
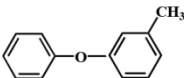
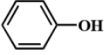
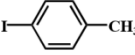
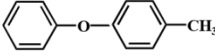
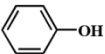
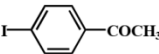
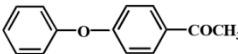
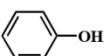
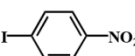
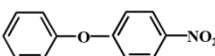
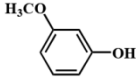

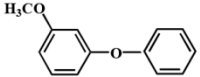
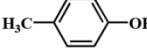

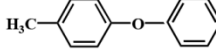


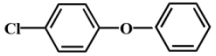
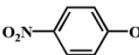

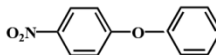
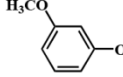
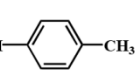
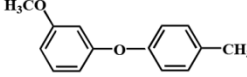


Fig.S4 The yields of diphenyl ether from C-O cross-coupling of iodobenzene with phenol at different temperatures.

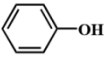
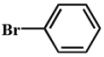
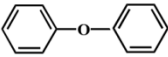
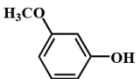
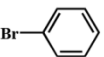
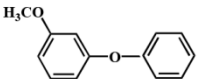
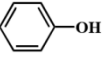
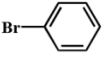
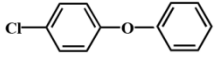
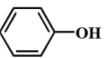
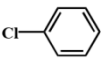
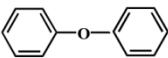
The yield of diphenyl ether decreases with the temperature decreasing. At 150°C, the yield of diphenyl ether reaches up to 96%, therefore we employ 150°C as the reaction temperature in our work.

Table S2 The conversion of aryl iodides and selectivity of corresponding diaryl ethers ^[a]

Entry	Phenols	Aryl halides	Product	Con. (%)	Sel. (%)
1				97	99
2				92	98
3				90	97
4				89	98
5				99	99
6				99	100
7				98	99
8				99	99
9				97	88
10				93	89
11				92	89

[a]: The reactions were conducted in an 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 Cs₂CO₃, and 10 mg 5wt% Cu₂O/graphene catalyst. Conversions were based on the amount of substituted aryl halides used. TOF was calculated based the amount of Cu₂O; [b]: Obtained from a Bruker GC-MS; [c]: The other products are corresponding aromatic compound from deiodination of aryl iodide.

Table S3 The conversion of aryl bromides or chlorides and selectivity of corresponding diaryl ethers ^[a]

Entry	Phenols	Aryl halides	Product	Con. (%)	Sel. (%)
1				26	99
2				58	99
3				24	83
4				5	99

[a]: The reactions conditions were the same as those in Table S2; [b]: Obtained from a Bruker GC-MS; [c]: The other products are corresponding aromatic compound from dehalogenation of aryl bromides or chlorides.

Table S4 Comparison of different catalysts for C–O cross-coupling of iodobenzene with phenol ^[a].

Entry	Catalyst	Time(h)	Yield(%)	TOF	Ref.
1	Polymer-Cu(Oac) ₂	12	95	3.04	1
2	CuFe ₂ O ₄ ^[b]	24	84	0.175	2
3	CuI	15	95	0.63	3
4	CuBr	20	97	0.48	4
5	CuO nanoparticles	15	93	2.48	5
6	CuO	24	87	36.25	6
7	CuO/γ-Al ₂ O ₃ ^[c]	10	76	0.038	7
8	CNT@α-Fe ₂ O ₃ @CuO	1	92	49.73	8
9	Cu ₂ O	24	93	3.87	9
10	Cu ₂ O nanocube	3	91	303	10
11	Cu ₂ O nannoparticles	3	96	1282	Present work

[a]: Condition: base/solvent/temp. For entries: (1) Cs₂CO₃/DMSO/120°C; (2) Cs₂CO₃/DMF/135°C; (3) Cs₂CO₃/DMF/110°C; (4) Cs₂CO₃/DMSO/60°C; (5) KOH/DMSO/110°C; (6) Cs₂CO₃/toluene/135°C; (7) K₃PO₄/DMSO/150°C; (8) Cs₂CO₃/DMF/130°C; (9) Cs₂CO₃/CH₃CN/80°C; (10) Cs₂CO₃/THF/150°C; (11) Cs₂CO₃/THF/150°C.

[b]: 4-Methyliodobenzene has compared instead of iodobenzene.

[c]: 3-Methyl phenol has compared instead of phenol.

The efficiency of the Cu₂O/graphene in comparison with some previously reported catalysts including supported and unsupported copper source is illustrated in Table S4. As can be seen, the Cu₂O/graphene exhibits the highest turnover frequency (TOF) in very short times (3h) among the works listed in Table S4. The above results show that the Cu₂O/graphene has an excellent catalytic activity in C–O cross-coupling reaction of iodobenzene with phenol.

References:

1. S. M. Islam, S. Mondal, P. Mondal, A. S. Roy., K. Tuhina, N. Salam and M. Mobarak, *J. Organomet. Chem.*, 2012, **696**, 4264–4274.
2. R. Zhang, J. Liu, S. Wang, J. Niu, C. Xia and W. Sun, *ChemCatChem*, 2011, **3**, 146–149.
3. H. Rao, Y. Jin, H. Fu, Y. Jiang and Y. Zhao, *Chem.–Eur. J.*, 2006, **12**, 3636–3646.
4. X. Lv and W. Bao, *J. Org. Chem.*, 2007, **72**, 3863–3867.
5. S. Jammi, S. Sakthivel, L. Rout, T. Mukherjee, S. Mandal, R. Mitra, P. Saha and T. Punniyamurthy, *J. Org. Chem.*, 2009, **74**, 1971–1976.
6. P. F. Larsson, A. Correa, M. Carril, P. O. Norrby and C. Bolm, *Angew. Chem., Int. Ed.*, 2009, **48**, 5691–5693.

7. P. Ling, D. Li and X. Wang, *J. Mol. Catal. A: Chem.*, 2012, **357**, 112–116.
8. D. Saberi, M. Sheykhan, K. Niknam and A. Heydari, *Catal. Sci. Technol.*, 2013, **3**, 2025-2031.
9. A. Y. Cheng and J. C. Hsieh, *Tetrahedron Lett.*, 2012, **53**, 71–75.
10. J. Y. Kim, J. C. Park, A. Kim, A. Y. Kim, H. J. Lee, H. Song and K. H. Park, *Eur. J. Inorg. Chem.*, 2009, **28**, 4219-4223.

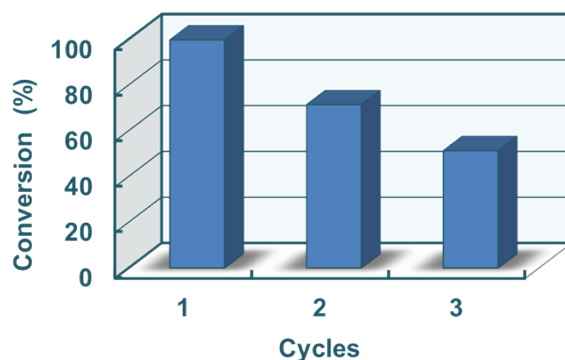


Fig.S5 Stability of the Cu_2O nanoparticles without any support in 3 catalytic rounds for C-O cross-coupling of iodobenzene with phenol.

For comparison, we also used 10 mg Cu_2O nanoparticles without any support as catalyst for the C-O cross-coupling of iodobenzene with phenol. The Cu_2O nanoparticles exhibit considerable catalytic activity to the Cu_2O /graphene in the first round, and the conversion of iodobenzene is nearly 100%. But the activity sharply decreases with the cyclic times. The conversion of iodobenzene decreases to only 51.2% after 3 reaction cycles mainly because of the oxidation of Cu_2O to CuO .