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Supporting Information

A novel Cu(II)-MOFs derived route for Cu/Cu_2O NPs @ graphene: electron transfer to lead the synergistic effect of Cu(0)-Cu(I) phase for efficiently catalytic the Sonogashira cross-coupling reactions

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Materials

Natural graphite powder (200 mesh, 99.9% purity), terephthalic acid (99% purity) was purchased from Alfa Aesar Chemical Co., Ltd. All other chemicals were analytical grade and were purchased from Aladdin Chemical Co., Ltd. All of the chemicals were used without further purification unless notified. Deionized water was used throughout the experiments.

Preparation of the catalysts

Preparation of graphene oxide (GO).

GO was prepared from natural graphite via acid-oxidation according to a modified Hummers method as reported in the previous papers[s1-s3].

Preparation of the Cu/Cu_2O-rGO: Cu/Cu_2O-rGO composites were prepared in a two steps process.

In the first step, the dispersed nano-Cu_2O on graphene (Cu_2O-rGO) was prepared by solvothermal method as follows: 100 mg $CuCl_2 \cdot 2H_2O$ and 200 mg terephthalic acid (TPA) were added into 10 mL water. The solution was stirred for 30 minutes. Then 50 mg of graphene oxide was dispersed in 30 mL of ethylene glycol (EG)-water (EG : water = 1 : 5(v/v)) solution. After that, the two new obtained solutions were mixed together and treated with ultrasonic for 1 h to obtain a homogeneous suspension. The pH value of the solution was adjusted to *ca*. 13 by the dropwise addition of *w. t.* 1% KOH/EG solution under vigorous stirring. The resulting solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave and sealed for solvothermal reaction at 160 ^{o}C for 10 h. The obtained suspension was washed with deionized water and ethanol three times. After being dried at 60 °C for 12 h, the sample was though a annealing operation at 350 °C for 2 hours in N_2 atmosphere. The obtained Cu_2O-rGO was dispersed in 100 mL of oxygen-free deionized water for further use.

In the second step, the Cu/Cu_2O-rGO was synthesized by in-situ reduction method. 0.25 mmol of CuCl was dissolved in 10 mL of deionized water. The solution was slowly added to the dispersion of Cu_2O-rGO with magnetic stirring. Afterward, a stoichiometric amount (0.5 mmol, 19 mg) of $NaBH_4$ was added dropwise into the solution. The obtained solution was stirred for 1 h. The Cu(I) was reduced to Cu(0) as Scheme R1. After all, the obtained suspension was washed with deionized water and ethanol five times, and was then applied to prevent the aggregation of graphene sheets by lyophilization process.

$$Cu_2O\text{-rGO-}Cu^+ + NaBH_4 \rightarrow Cu/Cu_2O\text{-rGO}$$

Scheme R1 Preparation of the Cu/Cu_2O-rGO

Preparation of the Cu_2O-rGO:

Cu_2O-rGO composites were prepared in a solvothermal process. 100 mg $CuCl_2{\cdot}2H_2O$ was added to the 10 mL water under magnetic stirring for 30 min, then the mixed solution was added into the system which 50 mg of graphene oxide flakes was exfoliated and dispersed in 30 mL of ethylene glycol (EG)-water (EG: water = 1:5 by volume). Then the mixed solvent was through ultrasonic treatment for 1 h. The resulting homogeneous solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave and sealed for solvothermal reaction at 160 ^oC for 10 h. The product (Cu_2O-rGO) was washed with deionized water and ethanol three times, and was then applied to prevent the aggregation of graphene sheets during drying process.

Preparation of the Cu-rGO:

The Cu-rGO was prepared by the following procedure: 50 mg of graphite oxide was exfoliated and dispersed in 100 mL of deionized water through ultrasonic treatment for 1 h. Then 50 mg of $CuCl_2{\cdot}2H_2O$ was dissolved in 10 mL of deionized water. The solution was slowly added to the dispersion of GO with stirring for 1 h. Then, a stoichiometric amount (50 mg) of $NaBH_4$ was added dropwise to 10 mL of the solution prepared in previous step and stirred for 1 h. The obtained product was washed with deionized water and ethanol five times, and and was then applied to prevent the aggregation of graphene sheets during drying process.

Preparation of the Cu_2O-rGO in the absence of TPA:

The composite of Cu/Cu_2O-rGO in the absence of TPA (Cu/Cu_2O-rGO free TPA) was prepared in a two steps process as Cu/Cu_2O-rGO. In the first step, the dispersed nano-

Cu_2O (Cu/Cu_2O-rGO free TPA) on graphene in the absence of TPA (Cu_2O-rGO free TPA) was prepared by solvothermal method as follows: 100 mg $CuCl_2 \cdot 2H_2O$ and 50 mg of graphene oxide was dispersed in 40 mL of ethylene glycol (EG)-water (EG : water = 1 : 4(v/v)) solution. After that, the two new obtained solutions were mixed together and treated with ultrasonic for 1 h to obtain a homogeneous suspension. The pH value of the solution was adjusted to *ca*. 13 by the dropwise addition of *w. t.* 1% KOH/EG solution under vigorous stirring. The resulting solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave and sealed for solvothermal reaction at 160 ^{o}C for 10 h. The obtained suspension was washed with deionized water and ethanol three times. After being dried at 60 °C for 12 h, the sample was though an annealing operation at 350 °C for 2 hours in N_2 atmosphere. The obtained Cu_2O-rGO free TPA was dispersed in 100 mL of oxygen-free deionized water for further use.

In the second step, the Cu/Cu_2O-rGO free TPA was synthesized by in-situ reduction method. 0.25 mmol of CuCl was dissolved in 10 mL of deionized water. The solution was slowly added to the dispersion of Cu_2O-rGO with magnetic stirring. Afterward, a stoichiometric amount (0.5 mmol, 19 mg) of $NaBH_4$ was added dropwise into the solution. The obtained solution was stirred for 1 h. The Cu(I) was reduced to Cu(0). After all, the obtained suspension was washed with deionized water and ethanol five times. The Cu_2O-rGO catalyst was gotten via lyophilization to prevent the aggregation of graphene sheets.

Preparation of the Cu/Cu_2O NPs in the absence of GO:

The composite of Cu/Cu_2O NPs in the absence of GO (Cu/Cu_2O NPs free GO) was prepared in a two steps process as Cu/Cu_2O-rGO. In the first step, the nano-Cu_2O NPs (Cu_2O free GO) was prepared by solvothermal method as follows: 100 mg $CuCl_2 \cdot 2H_2O$ and 200 mg terephthalic acid (TPA) were added 40 mL of ethylene glycol (EG)-water (EG : water = 1 : 5(v/v)) solution. After that, the solution was mixed together and treated with ultrasonic for 1 h to obtain a homogeneous suspension. The pH value of the solution was adjusted to *ca*. 13 by the dropwise addition of *w. t.* 1% KOH/EG solution under vigorous stirring. The resulting solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave and sealed for solvothermal reaction at 160 °C for 10 h. The obtained suspension was washed with deionized water and ethanol three times. After being dried at 60 °C for 12 h, the sample was though a annealing operation at 350 °C for 2 hours in N_2 atmosphere. The obtained Cu_2O NPs free GO was dispersed in 100 mL of oxygen-free deionized water for further use.

In the second step, the Cu/Cu_2O NPs free GO was synthesized by in-situ reduction method. 0.25 mmol of CuCl was dissolved in 10 mL of deionized water. The solution was slowly added to the dispersion of Cu_2O-rGO with magnetic stirring. Afterward, a stoichiometric amount (0.5 mmol, 19 mg) of $NaBH_4$ was added dropwise into the solution. The obtained solution was stirred for 1 h. The obtained solution was stirred for 1 h. The Cu(I) was reduced to Cu(0) as Scheme R1. After all, the obtained suspension was washed with deionized water and ethanol five times, and was then applied to prevent the aggregation of graphene sheets by lyophilization process.

Catalyst characterization

X-ray diffraction (XRD) analysis: The crystal structures were characterized with XRD on a Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu Kα radiation source at 40 kV and 40 mA.

X-ray photoelectron spectroscopy (XPS): XPS datas were recorded with a Perkin Elmer PHI 5000C system. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode (Mg Kα, hν = 1253.6 eV) was used. The C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BE).

Scanning electron microscopy (SEM): The scanning electron microscopy (SEM) measurements were carried out on a Nova Nano SEM 450 field-emission scanning electron microscope. X-ray energy dispersive spectroscopy (EDS) was used to analyze the element composition and distribution.

Transmission electron microscopy (TEM): A JEOL 2011 microscope operating at 200 kV equipped with an EDX unit (Si(Li) detector) was used for the TEM investigations. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids. The size distribution of the metal nanoparticles was determined by measuring about 100 random particles on the images.

Emmett–Teller surface area (BET):): The BET catalysts was obtained by N_2 adsorption–desorption using an Automated Gas Sorption Analyzer (Quadrasorb IQ, Quantachrome Instrument Corp).

HPLC charts of the products

Agilent Hypersil ODS column (4.6 × 250 mm) and UV detector (at 256 nm), was used to analyze the concentrations of the products. The eluent was 0.01 mol L^{-1} KH_2PO_4 in an acetonitrile-water mixture.

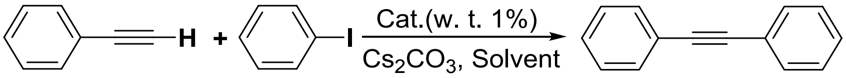
The yield and selectivity of the reaction were also recorded by HPLC analytical method. The yield and selectivity based on isolated yields vs those based on biphenyl are as the reference.

Typical Procedure for the Sonogashira Reaction

Under a nitrogen atmosphere, an oven-dried, round-bottomed flask was charged with the Cu/Cu_2O-rGO (10 mg), Cs_2CO_3 (1.3 g, 4.0 mmol), aryl halide (2 mmol), terminal alkyne (2 mmol) and DMF (1 mL). The reaction mixture was refluxed at 80 °C for 8 h. After cooling to the room temperature, the reaction mixture was vacuum filtered using a sintered glass funnel and washed with ethyl acetate (25mL). The combined organic phases were dried over Na_2SO_4, filtered, concentrated, and the residue was purified by flash chromatography on silica gel to give the desired cross-coupling product.

1,2-Diphenylethyne: ^{1}H-NMR (400 MHz, δ ppm, $CDCl_3$): δ = 7.36-7.41 (m, 6H) 7.54-7.58 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 89.6, 123.8, 128.5, 131.5.

Table S1. Effect of solvent on the Sonogashira cross-coupling reaction[a].



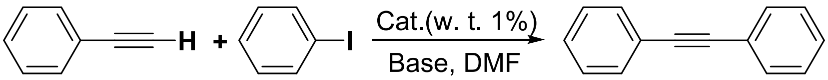
Entry	Solvent	Yield[b](%)
1	CH_3OH	50
2	C_2H_5OH	63
3	Dioxane	69
4	CH_3CN	61
5	THF	73
6	DMF	91
7	DMA	90
8	Benzene	hence
9	Toluene	hence

[a] Phenylacetylene (2.00 mmol), iodobenzene (2.00 mmol), catalyst (w. t. 1 %), K_2CO_3 (4.00 mmol) in solvent (1 mL) stirring for 8 h. Reaction temperature: 80 °C

[b] Isolated yields.

We then turned our attention to investigate the effect of solvent on the cross-coupling reaction. When the reactions were conducted in EtOH, DMF and DMA, excellent yields (80%, 91% and 90%, respectively) of products were isolated. Use of MeOH, dioxane, THF and CH_3CN as solvents led to slower reactions, and no desired cross-coupling products were observed while reactions run in benzene and toluene (Entries 1-9, Table S1) because of the very poor solubility of Cs_2CO_3 in unipolar solvents such as benzene and toluene. These studies suggest that the polar protic media is more suitable for carrying out the Sonogashira cross-coupling reactions.

Table S2. Effect of base on the Sonogashira cross-coupling reaction[a].



Entry	Base	Yield[b](%)
1	Black	hence
2	Na_2CO_3	67
3	K_2CO_3	76
4	Cs_2CO_3	90
5	K_3PO_4	hence
6	NaOH	39
7	Triethylamine	20
8	Piperidine	32
9	Diethylamine	18

[a] Phenylacetylene (2 mmol), iodobenzene (2 mmol), catalyst (w. t. 1%), base (4 mmol) in DMF (1 mL) at 80 °C stirring for 8 h.

[b] Isolated yields.

Furthermore, the model reaction remained sensitive by a change in the species of base (Entries 1-9, Table S2). When Cs_2CO_3 was selected as the base the catalytic efficiency was higher than others, the organic base shown terrible catalytic efficiency because the strong interaction between organic base and Cu NPs leading to the reduction and even Loss of the hot spots. Also, the same reaction when carried out in the absence of Cs_2CO_3 showed almost no conversion (Entry 1, Table S2). Thus, a basic medium is essential for carrying out these reactions.

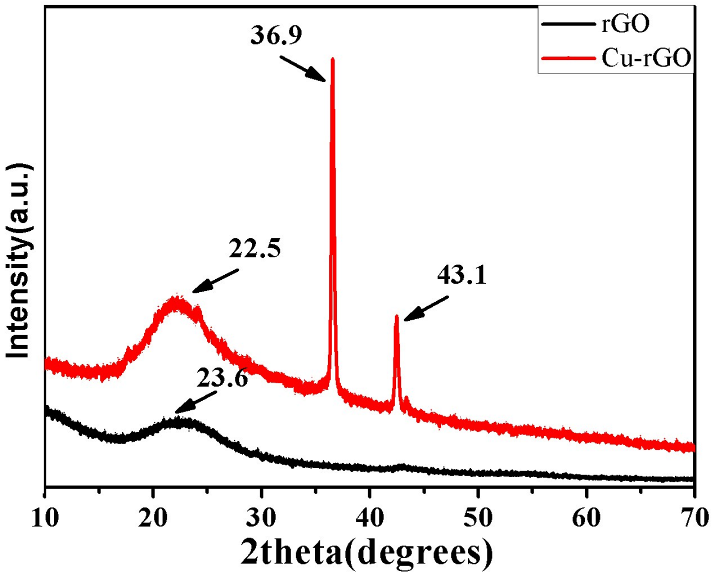


Fig. S1. XRD plots of the rGO and Cu-rGO materials.

The samples of reduced graphene oxide (rGO) and Cu-rGO were also confirmed using a power X-ray diffraction (XRD). As shown in Fig. S1, it is found that rGO were crystalline and a peak could be found at $2\theta = 23.5^\circ$ belong to the graphene. After being coated with Cu NPs, the peak of rGO still existed, and some new peaks that were attributed to the Cu appear, these new diffraction peaks were located at $2\theta = 39.6^\circ$ and 43.1°, which could be indexed to the (1 1 1) and (3 1 1) planes of the face centered cubic structure of Cu.

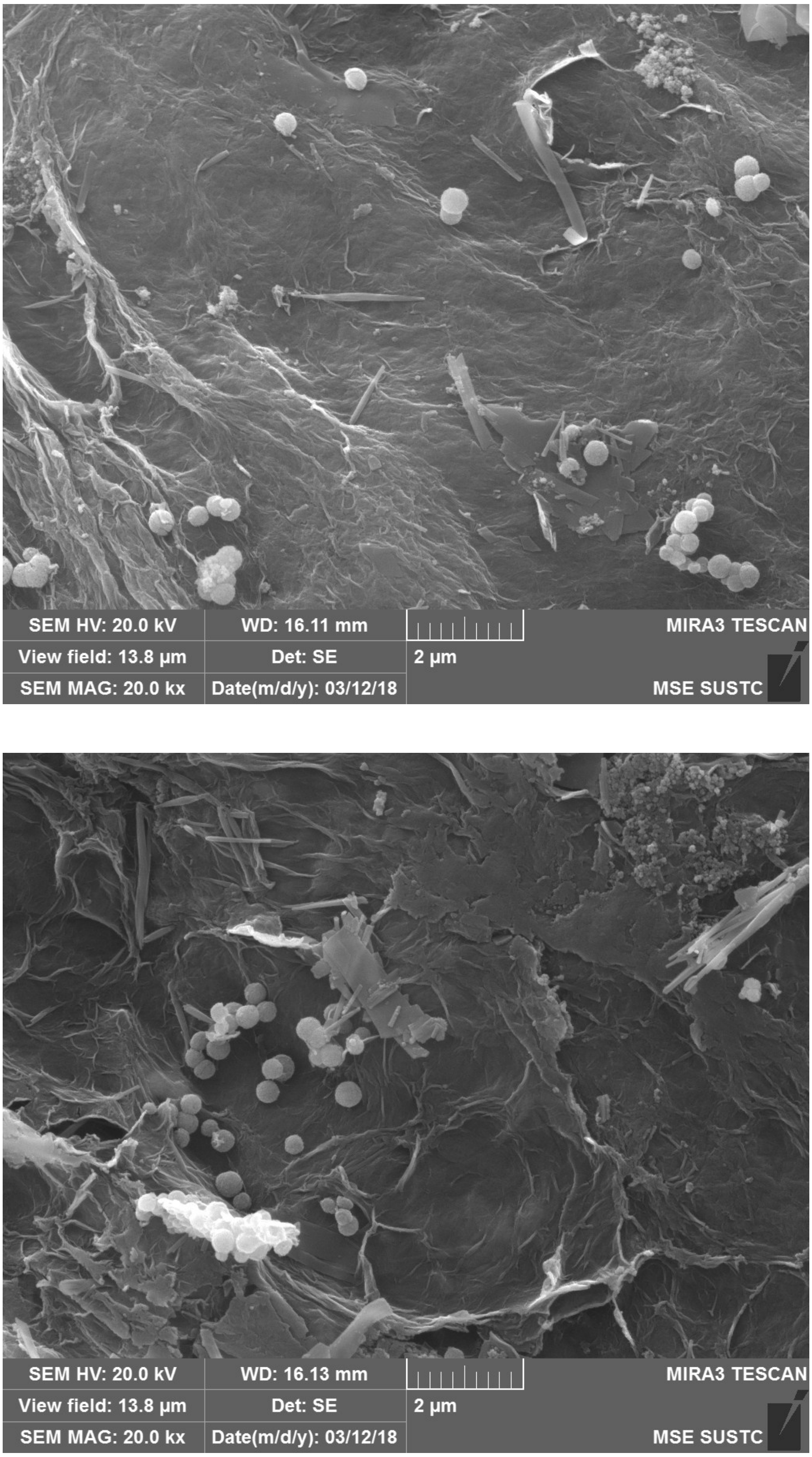


Fig. S2 SEM images of obtained Cu_2O-rGO and Cu/Cu_2O-rGO.

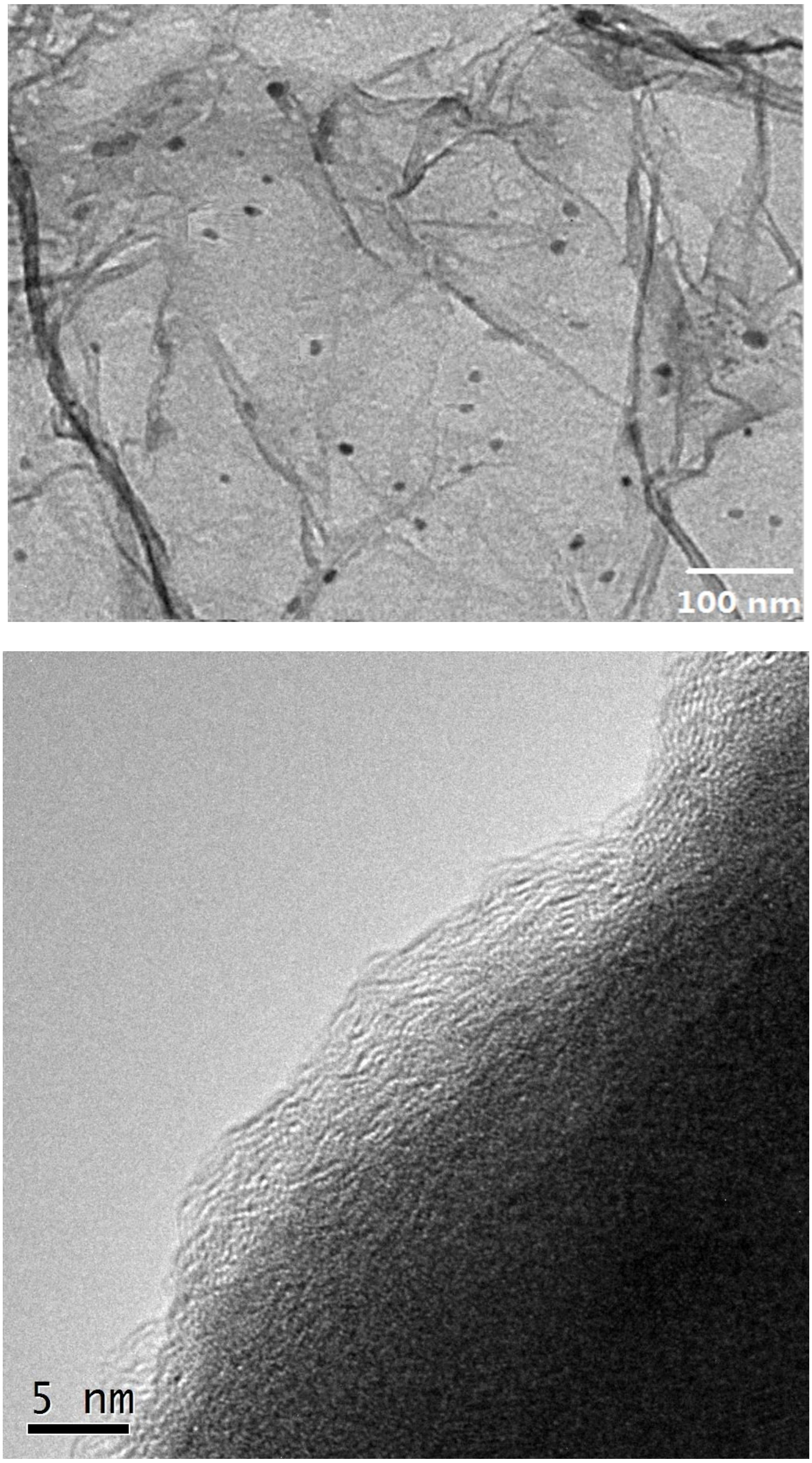


Fig. S3 TEM and HR-TEM image of Cu NPs on Cu/Cu_2O-rGO sheets.

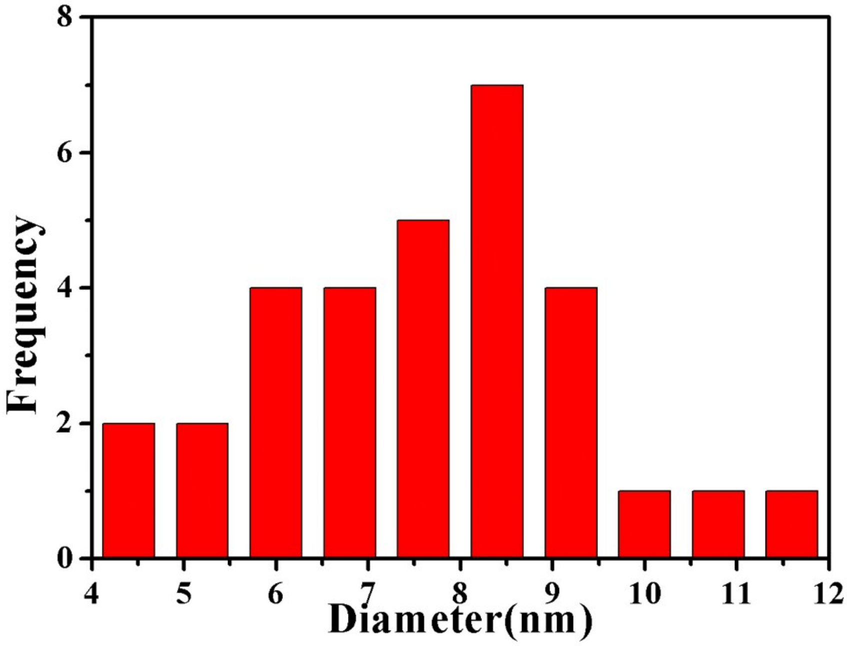


Fig. S4 Particle size distributions in the Cu/Cu_2O-rGO sheets.

In order to elucidate the size and morphology of Cu species an electron microscopy study of the samples has been performed. As seen from Fig. S3 and S4, the catalysts Cu/Cu_2O-rGO contain Cu particles with the mean size of 8.55 ± 2.92 nm, respectively. The particle size distributions for the samples presented in Fig. S4 demonstrate not substantial differences in the samples. In the case of the catalyst (Fig. S4), the size distribution is broad. This could be related to the porous structures of the substrates.

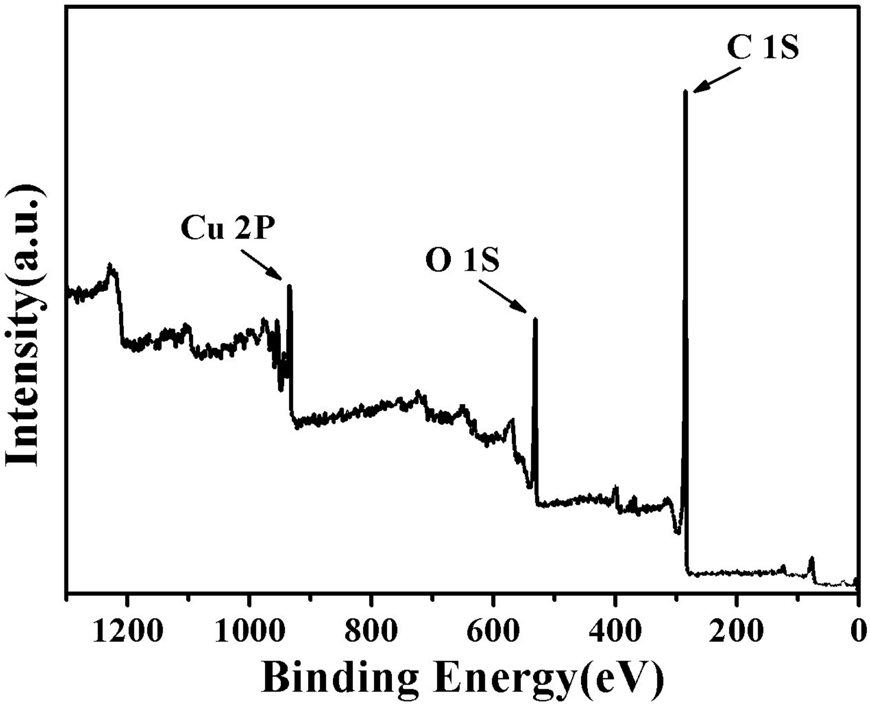


Fig.S5 The XPS survey spectrum of the Cu_2O-rGO.

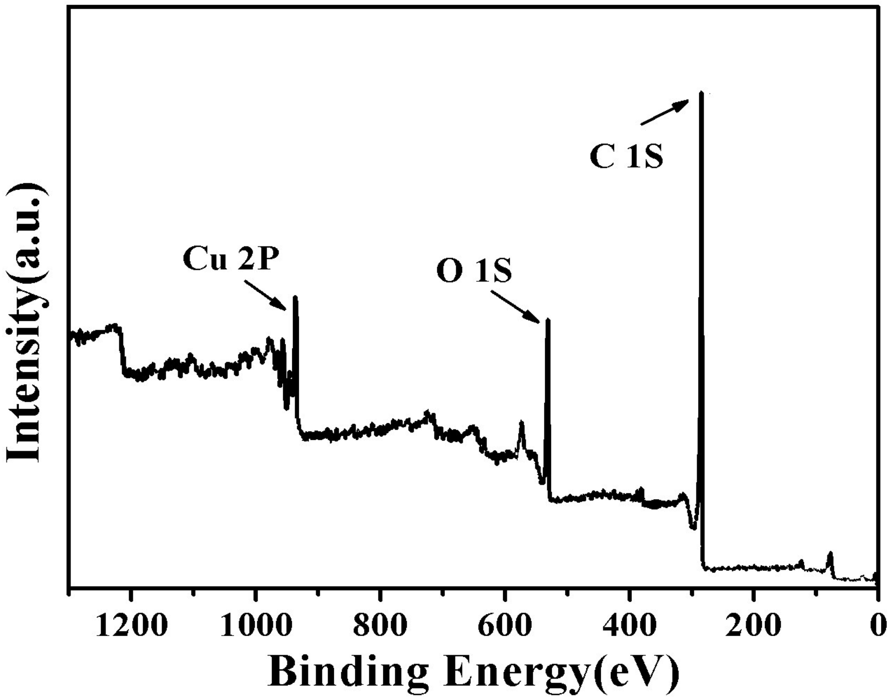


Fig.S6 The XPS survey spectrum of the Cu/Cu_2O-rGO.

Table S3: The Peak table and amount analysts by XPS

Name	C %	O %	Cu %
Cu_2O-rGO	74.4	15.1	10.5
Cu/Cu_2O-rGO	71.8	13.2	15.0

Leaching study and hot filtration test of Cu/Cu_2O-rGO

Copper leaching was studied after the first run of a standard reaction (12 h) of Phenylacetylene and iodobenzene: the resulting solution was filtered through celite and a 10 μL aliquot of the filtrate was diluted with 5 mL nalysed by ICP-MS. The copper content of this solution was determined to be 0.01 w. t. % of the original amount.

The poisoning tests of Cu/Cu_2O-rGO

Table S4: The poisoning tests the Sonogashira cross-coupling reaction

Entry	additive	Yield (%)
1	mercury (2 equiv.)	Trace
2	CS_2 (0.25 equiv.)	Trace

From the poisoning tests, that the addition of either mercury (2 equiv.) or CS_2 (0.25 equiv.) was added to the standard reaction between iodobenzene and phenylacetylene, almost no product was find after reaction for 8 hours. This is highly evidences the heterogeneous catalysis reaction on the nanoparticle surface.

Reutilization of Cu/Cu_2O-rGO catalyst

The resulting suspension from a standard Sonogashira reaction was subjected to centrifugation in order to precipitate the Cu/Cu_2O-rGO catalyst, which was washed with distilled water and ethyl acetate, to remove the remnants of the starting materials and, finally, dried in air. The catalyst was used in subsequent reactions under the same standard condition

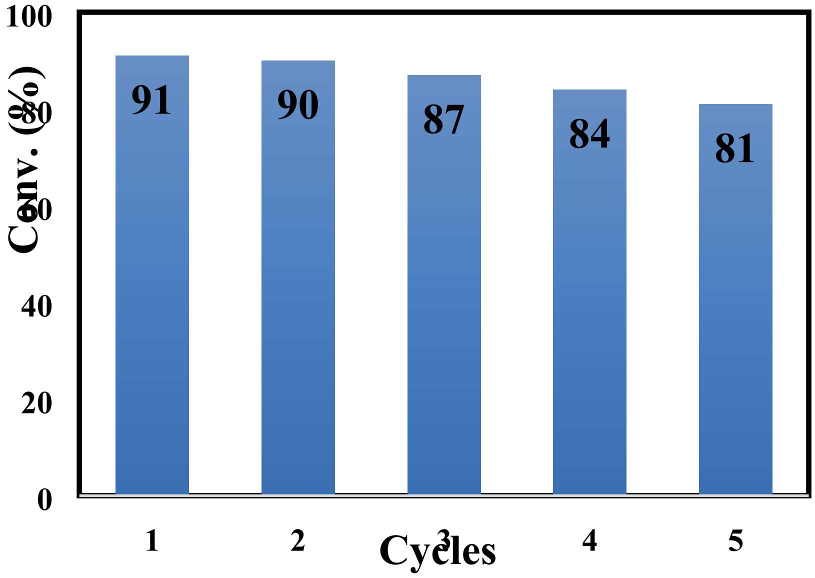


Fig. S7 Recycling of Cu/Cu_2O-rGO in the reaction.

Control experiments

After that, the more controlled experiments for the Sonogashira cross-coupling were carried out under the optimal reaction conditions (Table R1). In the absence of any catalysts, the reaction gave no cross-coupling product (entry 4, Table R1). GO as the only catalyst, the reaction also gave very poor cross-coupling yield (entry 2, Table R1). In addition, graphene and TPA did not catalyze the reaction at all (entry 3, Table R1), which ruled out the possibility that trace amounts of TPA and graphene template in Cu/Cu_2O-rGO catalyzed the reaction. Furthermore, application of Cu/Cu_2O NPs and Cu/Cu_2O-rGO free TPA as the catalysts in this reaction was also carried out. The Cu/Cu_2O-rGO free TPA gave the yield for the Sonogashira cross-coupling reaction for 56% (entries 6, Table R1). The TPA-MOFs structure in the catalyst just as the shell protection that could prevent the serious agglomeration of Cu_2O NPs during the preparation process, and more active sites were exposed then the catalyst exhibited higher catalytic efficiency. [s4] In addition, Cu/Cu_2O NPs free of GO as catalyst could improve the reaction performance giving the desired Sonogashira cross-coupling product in the yield of 84% (entry 6, Table R1). However, the Cu/Cu_2O NPs could not be recycling because the inherent drawback of conventional copper-based catalysts is the deactivation by metal-particle growth and unstable surface Cu(0)-Cu(I) active species in the strongly reaction atmosphere. And the graphene could coordinate surface charge distribution and promote the electron transfer process for the good electric conduction could also improve the catalytic efficiency. [s5] So that the Cu-MOFs derived synthetic strategy for two phases Cu/Cu_2O-rGO allows the Cu species to be reversibly oxidized and reduced through electron transfer between Cu phase and Cu_2O phase, the graphene can promote the electric conduction, leading to the material works as excellent catalyst for the Sonogashira cross-coupling reactions.

Table R1 Control experiments for Sonogashira cross-coupling reaction [a].

Entry	Deviation from standard conditions	Yield[b](%)
1	Balck	hence
2	GO	hence
3	Graphene	hence
4	TPA	hence
5	Cu/Cu_2O-rGO free TPA	56
6	Cu/Cu_2O NPs	84

[a] Reaction conditions: phenylacetylene (2 mmol, 1 equiv.), iodobenzene (2 mmol, 1 equiv.), catalyst (w. t. 1%), Cs_2CO_3 (4 mmol, 2 equiv.), DMF (1 mL), 80 ^oC, 8 h. [b] Isolated yields.

Reaction mechanism proposed for the Sonogashira cross-coupling reaction

From the catalytic cycle: Cu_2O phase is more possible than Cu phase to act as catalyst in this catalytic system, the electron transfer process on the graphene promoted the reaction process to construct the final cross-coupling product. As shown in Fig. R11, in one route, the Cu(I) sites could function as electrophilic or Lewis acidic sites to polarize the C-H bond, thus the C-H bond could be activated and facilitated the terminal alkyne proton abstraction leading to formation of the intermediate (I), [s6] and then the proton was neutralized by the base in solution. [s7] In another route, with the presence of Cu(I) phase, iodide displacement by the Cu(I) from the intermediate (II). Subsequent, the intermediate (I) and (II) followed by the single electron transfer (SET) of the electron transfer from Cu(I) to Cu(0), and to afford the final cross-coupling product and reduced Cu(I) species with regeneration of Cu(0). [s8] This indicated that the Cu(0) species were oxidized to Cu(I) species, and as the reaction went on, these Cu (I) was gradually back to Cu(0). So that, the newly fabricated Cu/Cu_2O-rGO catalyst allows the electron transfer between Cu phase and Cu_2O phase, the graphene can promote the good electric conduction. The synergistic effect of between Cu phase and Cu_2O phase phases to lead the material works as excellent heterogeneous noble metal free catalysts for the Sonogashira cross-coupling reactions.

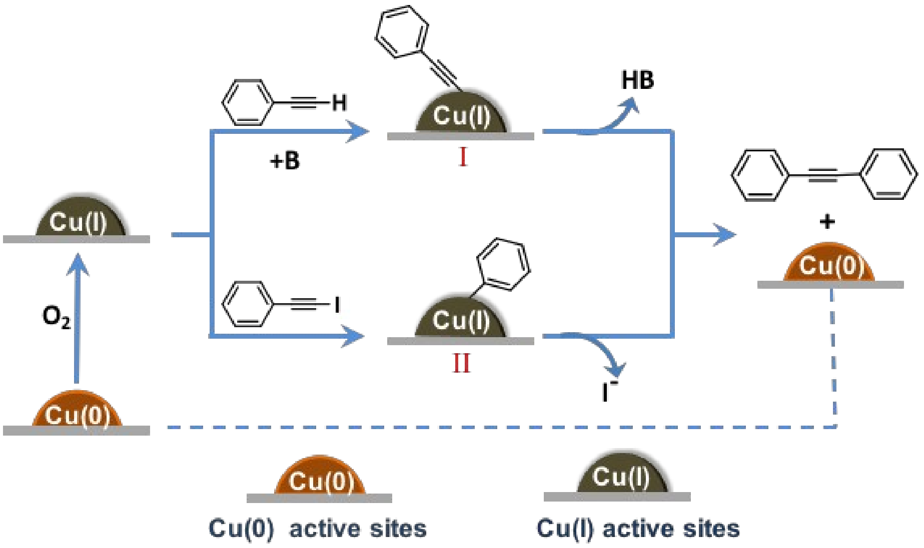


Fig. S7 Reaction mechanism proposed for the Sonogashira cross-coupling reaction catalyzed by Cu/Cu_2O-rGO

[s1] Y. Li, Y. Zhao, H. Cheng, Y. Hu, G. Q. Shi, L. M. Dai and L. T. Qu, *J. Am. Chem. Soc*. 2012, **134**, 15.

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[s5]. D. J. Guo, Z. Y. Wei, B. Shi, S. W. Wang, L. Z. Wang, W. Tan and S. M. Fang, *J. Mater. Chem. A*, 2016, **4**, 8466.

[s6]. J. L. Gong, H. R. Yue, Y. J. Zhao, S. Zhao, L. Zhao, J. Lv, S. P. Wang and X. X. Ma, *J. Am. Chem. Soc*. 2012, **134**, 13922.

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[s8]. J, J Ge, P. Wei, G. Wu, Y. D; Liu, T. W. Yuan, Z. J. Li, Y. T. Qu, Y. Wu, H. Li, Z. B. Zhuang, X. Hong and Y. D. Li, *Angew. Chem. Int. Ed*., 2018, **57**, 1836.

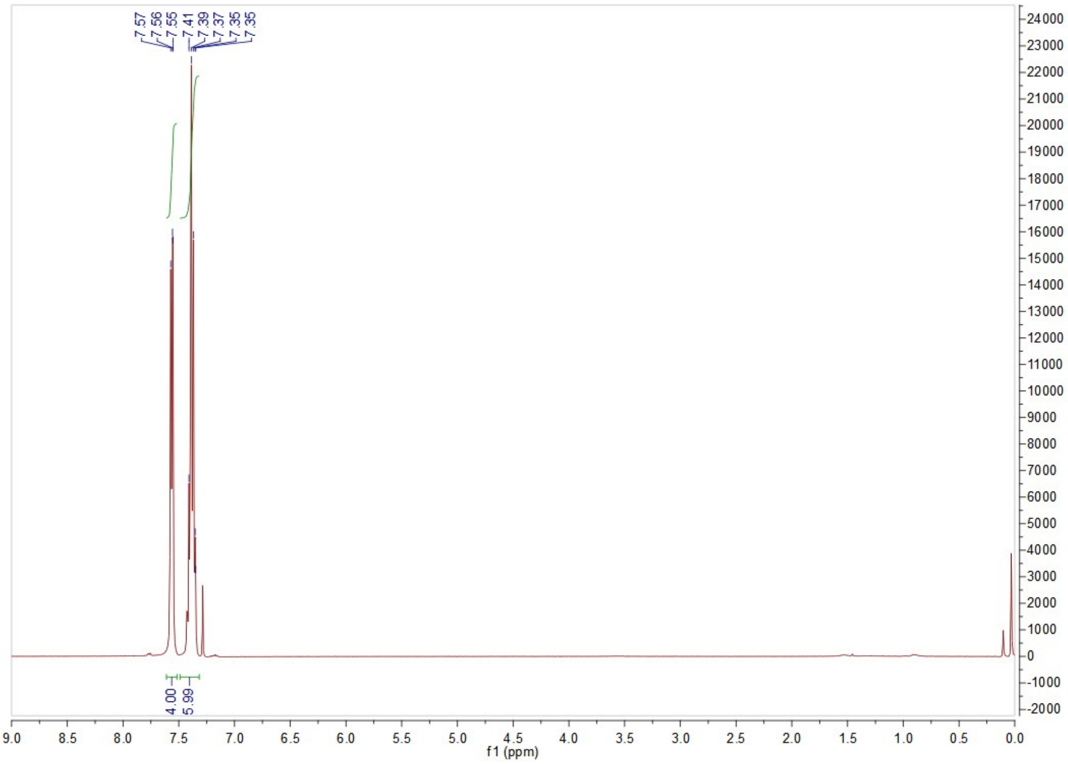

Figure S14. ^{1}H NMR spectrum of 1,2-diphenylethyne in $CDCl_3$.

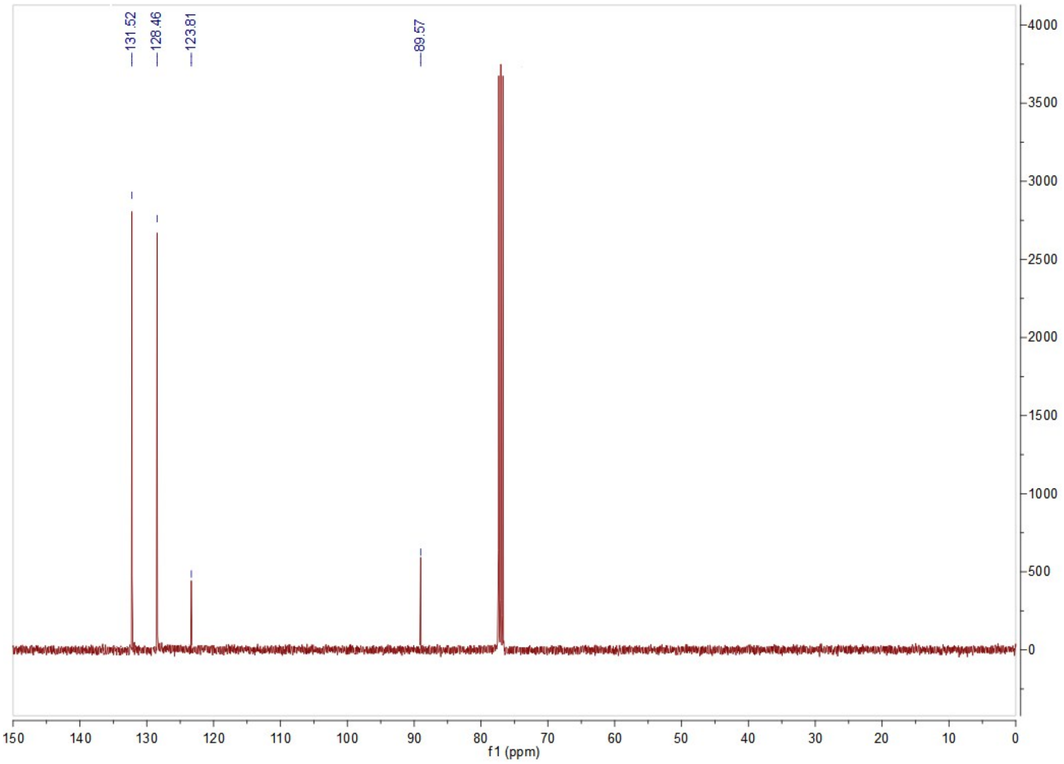

Figure S17. ^1H NMR spectrum of 1,2-diphenylethyne in $CDCl_3$.

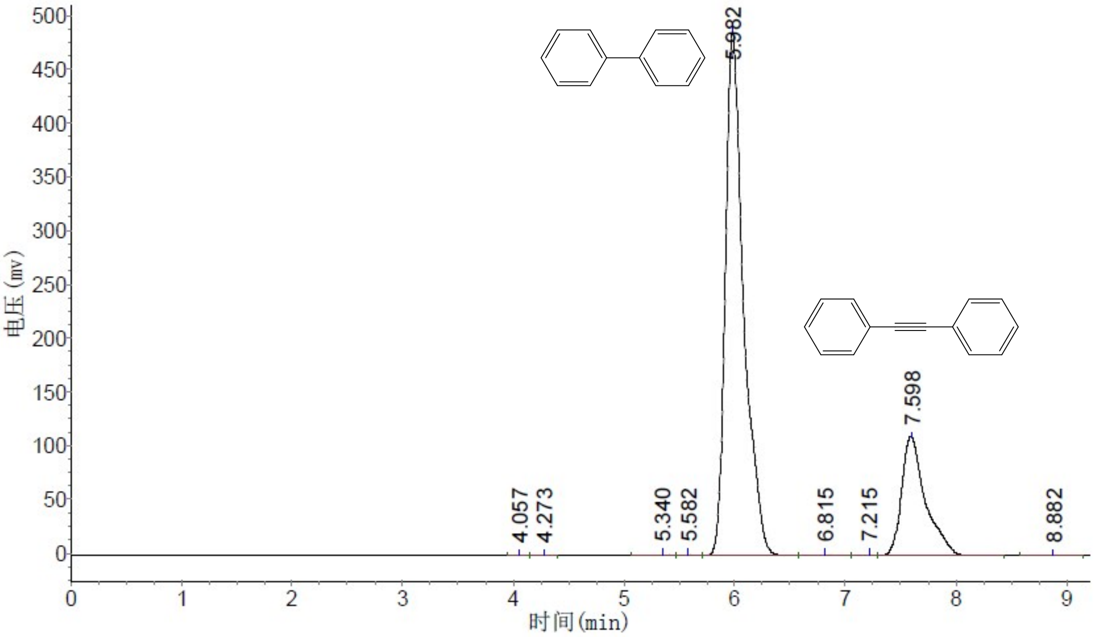

Figure. S18 HPLC chromatograms of 1,2-Diphenylethyne.

Based on above results, the yield and selectivity based on HPLC analytical method are consistent with those based on isolated yields, which further confirm the selectivity of the reaction.