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Please cite this article as: B. Wang, L. Gao and G. Zheng, Leaf-like CuO nanosheets on rGO as an efficient heterogeneous catalyst for Csp-Csp homocoupling of terminal alkynes, *Catalysis Communications* (2020), https://doi.org/10.1016/j.catcom.2020.106260

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Leaf-like CuO nanosheets on rGO as an efficient heterogeneous catalyst for C_{sp} - C_{sp} homocoupling of terminal alkynes

Bin Wang^a, Lingfeng Gao^{a,*}, Gengxiu Zheng^{a,*}

^a School of Chemistry and Chemical Engineering, University of Jinan, 336 Nanxinzhuang West Road, 250022, Jinan (China)

Abstract

In this work, the economic and well-defined leaf-like CuC nanosheets on rGO (CuO nanosheets/rGO) was synthesized by a convenient hydrothermal method. The morphology and chemical composition of CuO nanosheets/rGO were confirmed by XRD, SEM-EDS, TEM, HR-TEM, and XPS techniques. The CuO nanosheets/rGO was successfully applied as a high-performance heterogeneous catalyst in the homocoupling of 12 terminal alkynes, and the nonlated yield of each product was more than 80%, except for propargyl alcohol. This catalyst could be reused five times with little activity loss. Thus, it is beneficial for green and sustainable development of organic synthetic chemistry.

Keywords: Homocoupling; Terminal alkynes; CuO nanosheets; rGO; Heterogeneous catalysis

Corresponding authors: Tel.: +86053182765841

* E-mail address: gaolf108@mail.ustc.edu.cn; chm_zhenggx@ujn.edu.cn

1. Introduction

Graphene is a type of carbon nanomaterial that possesses a single layer of sp²-bonded carbon atoms.^[1] During the past few years, most of the chemical engineering processes utilizing graphene-based nanomaterials are catalytic reactions to meet the increasing demand of sustainable development.^[2] Naturally, the progress of graphene-based nanomaterials was motivated by its advantages, including large specific surface area, excellent thermal stability, and interesting chemical and e.ectronic properties.^[3] Most importantly, the oxygen-containing functional groups of r duc d graphene oxide (rGO) can interact strongly with the supported metal nanomaterials, thereby realizing heterogeneous catalysis.

The synthesis and application of size and morphology-controlled Cu-based nanomaterials have always been recognized as important subjects in the fields of both chemistry and materials science. In particular, CuO-based nanomaterials offer distinct advantages such as ease of synthesis, low cost, and intrinsic stability, which makes it a promising candidate for practical applications.^[4-5] Although significant progress was achieved in the development of CuO/rGO nanomaterials^[3,4-5,6-10], their applications in heterogeneous catalytic o ganic reactions need further exploration.^[3,4-5,7-8] Thus, CuO nanomaterials with will-defined morphology on rGO are required to investigate its catalytic properties and establish a highly efficient heterogeneous organic catalytic system.

1,3-Diyne, a type of carbon skeleton with high rigidity, has been well utilized in many fields, involving fluorescent probes, organic building blocks, pharmaceuticals, and organogelators.^[11-14] As known, Glaser coupling is a good approach for the preparation of symmetrical 1,3-diynes.^[15] In recent years, several catalytic systems were

reported for the C_{sp} - C_{sp} homocoupling of terminal alkynes.^[16-34] Among these previous works, a series of efficient and recyclable catalysts were explored, such as $Cu_3(BTC)_2$ $MOF^{[16]}$, meso Cu/MnOx^[21], metallomicelles^[23], Cu/C₃N₄^[26], MCM-41-2N-CuI^[27], CuO/TiO₂^[28], and CuOx NPs^[29]. Nevertheless, there are still some disadvantages such as the use of noble metals as the catalytic centre^[19-20, 22], which are difficult to recycle as the catalyst^[17, 24-25, 31-34]. By contrast, the C=C bond of terminal alkynes can be well activated by Cu(II) species through the coordination^[16, 18, 31-55], which indicates the CuO nanomaterials can be an economic catalytic center for the C_{sp}-C_{sp} homocoupling of terminal alkynes. Thus, the exploration of a mild catalytic nethod for homocoupling of terminal alkynes that is catalysed by CuO nanome erials on rGO is highly important not only for the development of organic synutetic chemistry but also for carbon nanomaterials.

In the present work, well-defined leaf-like CuO nanosheets/rGO was prepared through a simple hydrothermal n et a. J. The nanocomposites were characterized by the XRD, SEM-EDS, TEM, HP- $_{r}$ ^TM and XPS techniques to explore its morphology and chemical composition. The cocellent synergy between CuO nanosheets and rGO made the CuO nanosheets/r $_{r}$ ^TO an economic and efficient heterogeneous catalyst for the C_{sp}-C_{sp} homocoupling of various terminal alkynes. Furthermore, this catalyst was reused five times with little loss of its catalytic activity. All these indicate that this work will expand the application scope of CuO nanosheets/rGO and promote green and environmentally friendly development of organic synthetic chemistry.

2. Experimental

2.1. Synthesis of graphene oxide (GO)

GO was prepared through a modified Hummer's method.^[S1] The manufactured GO was subjected to a freeze-drying process and yielded a dark brown solid. Then, the obtained GO was preserved for subsequent characterization and usage.

2.2. Synthesis of CuO nanosheets/rGO

In the present work, the CuO nanosheets/rGO was prepared using the hydrothermal method. In a typical synthesis of CuO nanosheets/rGO, 100 mg GO was added to 80 mL purified water and sonicated (3 h) to obtain a homogeneous cuspension at 20 °C. Next, 1 mL CuSO₄ solution (0.125 g/mL) and 50 mg sodium gluta nate were added to the above suspension. Subsequently, the pH of the system was d_{1} solution 11 using NH₃·H₂O and stirred for 4 h. The suspension was then transferred into a 100 mL Teflon-lined autoclave and hydrothermally treated at 105 °C. Nine hours later, the system was centrifuged and washed with ethanol and purified water for three times. Finally, the CuO nanosheets/rGO was obtained using a freeze-drying process and preserved carefully for further characterization application.

In addition, CuO nanosherts without rGO was also synthesized using the same method for further comparison (Supporting Information).

3. Results and discussion

3.1. Characterization of CuO nanosheets/rGO

[Insert Fig. 1]

The synthesized CuO nanosheets/rGO was characterized by powder X-ray diffraction (XRD) to perform crystal structure and phase analysis. The XRD patterns of GO, rGO, CuO nanosheets and CuO nanosheets/rGO are shown in Fig. S1b and Fig. 1a. In Fig. S1a, graphite showed a characteristic sharp reflection peak centered around $2\theta = 26^{\circ}$ (002 graphitic plane).^[S2] After the oxidation, a new peak centered at 10.8° appeared,

which is the expanded plane (001) of GO due to the intercalation of oxygen-containing functional groups between the graphene layers (Fig. S1b).^[S2] When the hydrothermal treatment for GO was completed, a broad peak centered at 24.5° was detected and rGO was formed.^[S2] For the prepared CuO nanosheets (Fig. 1a), the peaks at 32.4°, 35.5°, 38.7°, 48.7°, 53.5°, 58.2°, 61.6°, 66.2°, 68.2°, 72.4°, and 75.1° corresponded to the (110), (-111), (111), (-202), (020), (202), (-113), (-311), (220), (311), and (004) planes of monoclinic CuO (JCPDS 48-1548), respectively. The share diffraction peaks of XRD pattern also indicated the high crystalline structure of CuO nanosheets.^[3,5] Similarly, the XRD data of CuO nanosheets/rGO (Fig. 1a) agreed with the XRD data of CuO nanosheets but without the peak at 24.5° (002 place) from rGO. This was because of the growth of CuO nanosheets on the rGO sheets at Sunctionalized sites, which mitigated its restacking during the freeze-drying process, hence, the interplanar diffraction signal of rGO was too weak to observe. All these results proved that CuO was formed and GO was reduced to rGO during the hydrochermal process.

The surface chemical composition and bonding information of the CuO nanosheets/rGO were obtained by X-ray photoelectron spectra (XPS) analysis (Fig. 1b, S2). The measured ICPS spectrum (Fig. S2a) confirmed that CuO nanosheets/rGO contain the elements of Cu, O and C, which is consistent with the EDS mapping results (Fig. S5d). The Cu element belonged to CuO nanosheets, C was attributed to rGO, and O was mainly ascribed to the oxygen-containing group on rGO and the incorporated CuO nanosheets. The survey spectrum of CuO nanosheets/rGO revealed the presence of Cu 2s, Cu 2p, Cu LLMd, Cu LLMb, Cu LLMc, Cu LLMa, O 1s, C 1s, Cu 3s, and Cu 3p photoelectrons (Fig. S2a).^[3, S3-S4] As shown in C 1s spectrum (Fig. S2b), three types fitted peaks located at 284.8, 285.9, and 288.6 eV were observed and were assigned to

C=C, C-O, and O-C=O bond, respectively.^[S5] This further proved the existence of an oxygen-containing functional group on the surface of rGO. The high-resolution spectrum of Cu 2p showed the presence of Cu 2p1/2 and Cu 2p3/2 peaks with binding energies of 953.5 and 933.6 eV, respectively, accompanied with their corresponding satellite peaks (Fig. 1b).^[S5] The distance between Cu 2p1/2 and Cu 2p3/2 peak was 20 eV, which is in agreement with the standard XPS spectrum of CuO.^[S5-S9] Furthermore, the binding energy of 568.8 eV in Cu LMM spectrum proved the characteristic Cu(II) oxidation state of CuO nanosheets/rGO (Fig. S2d).^[S4, S10-S(2)] The O 1s spectrum can be deconvoluted into four peaks at 529.8, 531, 531.8, a a 532.1 eV (Fig. S2c), which are assigned to the C=O, Cu-O, O=C-OH and C-O bends, respectively. Therefore, the XPS results fully illustrated the chemical status of CO nanosheets/rGO catalyst, and it was found to be 18.45 wt%.

[Insert Fig. 2]

As shown in Fig. 2, the morphology of as-prepared CuO nanosheets/rGO was characterized using SEM and TEM techniques. The rGO showed a classic wrinkle structure (Fig. 2a and S3). The well-defined leaf-like CuO nanosheets was distributed uniformly on the surface of rGO (Fig. 2a, S4), which indicated the oxygen functional groups of rGO could effectively hinder the excessive recrystallization of the CuO nucleus.^[5] The elemental mapping and energy-dispersive X-ray (EDS) elemental analysis (Fig. S5) of CuO nanosheets/rGO were performed to evaluate the distribution of elements. Fig. S5a-c shows the homogeneous distribution of C, O, and Cu elemental signals and good spatial correspondence within the CuO nanosheets/rGO. Likewise, Fig. S5d shows the distribution of C, O, and Cu elements, which were consistent with

the elemental mapping results. The TEM images of CuO nanosheets/rGO (Fig. 2b, S6) also shows that leaf-like CuO nanosheets were uniformly dispersed on rGO and they were well consistent with the SEM images. After the loading of leaf-like CuO nanosheets (Fig. 2b, S6a), the highly wrinkled transparent surface of the rGO nanosheets could still be observed. The HR-TEM image (Fig. S6b) shows the (020) face of CuO nanosheets with a lattice space of 0.17 nm, suggesting crystal growth along that direction.^[5] All these characterizations demonstrated that the CuO nanosheets/rGO was successfully prepared by the hydrothermal method.

3.2. Catalytic homocoupling of terminal alkynes

After the characterization of the CuO nanoshec s/rCO, it was then used as a catalyst for the C_{sp} - C_{sp} homocoupling of terminal alky at a Phenylacetylene (1a) was treated as a model substrate to obtain the optimal reaction conditions (Table S1, 1). The progression of the reaction was determined by thin-lay r chromatography.

For the initial investigation, various catalysts including GO, rGO, bulk CuO powder, different copper salts, and C. O nanosheets were first tested (Table S1). The reaction hardly proceeded without any catalyst (entry 1, Table S1). The performances of GO and rGO were also quite bool (entries 2 and 3, Table S1). The common copper salts and bulk CuO powder also provided a fair yield (entries 4-8, Table S1). Though the CuO nanosheets catalyzed the reaction to some extent and higher than the abovementioned copper salts under the same conditions, the yield were also far from satisfactory (entry 9, Table S1). However, the excellent results obtained by CuO nanosheets/rGO illustrate the synergic catalytic effect of CuO and rGO at the interface.^[19, S13-S14] This showed that CuO nanosheets/rGO was an efficient catalyst for the homocoupling of phenylacetylene.

[Insert Table 1]

To estimate the catalytic performance of CuO nanosheets/rGO under the designated reaction conditions, different kinds of solvents were first investigated (Table 1). An exciting aspect was that the isolated yield of 2a reached 98% in ethanol and 96% in isopropanol with NaOH as the base, which was higher than other solvents (entries 1-10). Toluene and some polar solvents, such as 1,4-dioxane, CH₃CN and DMSO, were also examined and lower yields were obtained (entries 4-C and 8, Table 1).^[18,26] The good solubility of NaOH in alcoholic solvents probably acilitated this reaction. Inhibition was almost observed when the reaction val carried out in water (entry 7, Table 1). The effect of various bases on the perfermance of CuO nanosheets/rGO was also studied. Different yields of 2a were obtained under these bases, while trace amount of **2a** was produced without any bases (controls 9 to 14, Table 1). This revealed that the existence of bases was necessary to promote the homocoupling reaction.^[34] Though a moderate yield was achieved by No CtBu, it remained lower than NaOH. Moreover, the poor yield of 2a (entry 15) indicated that the homocoupling reaction is aerobic.^[16] Likewise, obvious effects of reaction temperature and time were observed on the homocoupling reaction (1 ble S2 and S3). Lastly, the hot filtration and leaching study of CuO nanosheet/rGC showed it was stable and catalyzed the homocoupling reaction in a heterogeneous manner. Hence, the combination of CuO nanosheets/rGO (3 mg) with NaOH (1.2 equivalent) in ethanol and reaction at 80 °C for 12 h was considered as the optimized conditions for the homocoupling reaction.

[Insert Table 2]

Having established the optimized conditions, terminal alkynes with different substituents were evaluated to verify the versatility of CuO nanosheets/rGO (Table 2,

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eq.2). Generally, the homocoupling products could be easily isolated. The homocoupling of phenylacetylene with electron-donating/withdrawing substituents at para-position could be proceeded efficiently (entries 2, 3, 5, and 6, Table 2). For larger substituents such as n-butyl, n-pentyloxy, and t-butyl, a good result could be achieved after the reaction time was prolonged to 18 h (entries 4, 7, and 8, Table 2). Interestingly, in the case of meta-position substituted phenylacetylenes (entries 9 and 10, Table 2), a good yield was also realized. The yield for the hon coupling products of o-chlorophenylacetylene was 81% (entry 11, Table 2). Hex v-2, e-diyne-1,6-diol was also obtained, and the yield was 43% (entry 12, Table 2). Moreover, no dehalogenation was detected for both *m*-chloro and *o*-chlorophenyla etyl me. Thus, CuO nanosheets/rGO could be considered as a versatile catalyst for the C_{sp} - C_{sp} homocoupling of terminal alkynes.

Generally, the sustainability of one callyst was determined by its reusability during the heterogeneous catalytic process. For this assessment, CuO nanosheets/rGO was reused for catalyzing the homocoupling of phenylacetylene under the optimized conditions. In Fig. S7, a ml/d decrease (9%) in the yield was observed after five runs. The TEM technique was used to characterize the morphology of the recycled CuO nanosheets/rGO (Fig '.8). By comparing the TEM image of the recycled catalyst with the fresh one, the morphology and structure of the recycled catalyst showed no obvious change. These indicated that CuO nanosheets/rGO shows excellent recyclability for the homocoupling of phenylacetylene.

[Insert Fig. 3]

Based on the experimental results and by analogy with previous reports, a possible pathway (Fig. 3) was proposed for the C_{sp} - C_{sp} homocoupling of terminal alkynes

catalyzed by CuO nanosheets/rGO.^[30-34, S15-S22] First, alkynes were adsorbed on the active sites of the CuO nanosheets/rGO, and the π - π stacking between alkynes and rGO increased its concentrations. The C=C bond was activated by Cu(II) species, and deprotonation of terminal alkynes then occurred with the assistance of bases (I). Consequently, the C=C bond could interact with Cu(II) species to yield the key intermediate copper acetylide (II).^[31-34, S15-S21] The copper acetylide species then underwent a dimerization process (III).^[16, 31-34] The dimeric species underwent the electron transfer process promoted by CuO nanosheets/rGO and C-C bond formation step to yield the homocoupling product. During the product of the transformation of Cu(II) species was achieved by O₂ (IV). Finally, the CuO nanosheets/rGO was regenerated and a new cycle was started.

4. Conclusions

The CuO nanosheets/rGO was successfully prepared through a facile hydrothermal method. The well-defined CuO n ir osmeets/rGO showed the layer structure of rGO with an evenly distributed leaf-nive CuO nanosheets. More importantly, the CuO nanosheets/rGO was successfully applied as an economic and efficient heterogeneous catalyst for the C_{sp} - C_{s_p} homocoupling of terminal alkynes. This catalyst showed little activity loss after reuse for five times, and its morphology showed no obvious change. Thus, this work broadens the application of CuO/rGO nanocomposites and promotes green and sustainable development of organic synthetic chemistry.

Acknowledgment

This work was financially supported by the Natural Science Foundation of Shandong Province (2019GGX104021).

Appendix A. Supplementary data

Supplementary data to this article can be found online at: please add the website.

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Table captions

Table 1. Screening condition for estimating the catalytic performances of CuOnanosheets/rGO a

 Table 2. Substrate scope^a

Figure captions

Fig. 1. (a) XRD patterns of CuO nanosheets and CuO nanosheets/rGO; (b) The high-resolution XPS survey spectrum of Cu 2p.

Fig. 2. (a) SEM and (b) Low-magnification TEM image. of CuO nanosheets/rGO.

Fig. 3. A possible mechanism for the homocoup ing of terminal alkynes catalyzed by CuO nanosheets/rGO.

South



Fig. 1.



Fig. 2.





| Entry | Solvent | Base | 2a Yield $(\%)^b$ |
|-------|--------------------------------------|--|--------------------------|
| 1 | CH ₃ OH ^c | NaOH | 76 |
| 2 | C ₂ H ₅ OH | NaOH | 98 |
| 3 | (CH ₃) ₂ CHOH | NaOH | 96 |
| 4 | Toluene | NaOH | 24 |
| 5 | 1,4-Dioxane | Nath | 68 |
| 6 | CH ₃ CN | HCe.1 | 52 |
| 7 | H ₂ O | NaOH | Trace |
| 8 | DMSO | NaOH | 49 |
| 9 | С2Н3СЧ | / | Trace |
| 10 | C ₂ h ₅ OH | Na ₂ CO ₃ | 53 |
| 11 | C ₂ H₅OH | K_2CO_3 | 74 |
| 12 | C ₂ H ₅ OH | NaOtBu | 84 |
| 13 | C ₂ H ₅ OH | DBU | 69 |
| 14 | C ₂ H ₅ OH | N(C ₂ H ₅) ₃ | 60 |
| 15 | $C_2H_5OH^d$ | NaOH | trace |

Table 1. Screening condition for estimating the catalytic performances of CuOnanosheets/rGO a

^{*a*} Reaction condition: CuO nanosheets/rGO (3 mg), solvent (2 mL), 1 mmol **1a**, base (1.2 mmol), 80 °C, 12 h, O₂ (a balloon filled with oxygen). ^{*b*} Isolated yield. ^{*c*} Reflux. ^{*d*} Under a nitrogen atmosphere.

 Table 2. Substrate scope^a

| R | CuO nanosheets/rGO | |
|----------------|---|-----------------------|
| Alkynes | NaOH, EtOH, O_2 , 80 °C $^{\sim}$ $^{\sim}$ | Dialkynes |
| | | |
| Entry | Substrate | Yield(%) ^b |
| 1 | | 98 |
| 2 | Н₃С-√ | 91 |
| 3 | С2Н5 | 89 |
| 4 ^c | n-Bu | 82 |
| 5 | F- | 88 |
| 6 | н ₃ со- | 92 |
| 7 ^c | $n-C_5H_{11}O$ | ≡ 84 |
| 8 ^c | t-Bu | 81 |
| 9 | | 86 |
| 10 | | 87 |
| 'n | | 81 |
| 2 | но — | 43 |

^{*a*} Reaction conditions: alkynes (1 mmol), CuO nanosheets/rGO (3 mg), NaOH (1.2 mmol), EtOH (2 mL), 80 °C, O₂ (a balloon filled with oxygen), 12 h. ^b Isolated yield. ^c 18 h.



South

Highlights

The economic and well-defined leaf-like CuO nanosheets/rGO was synthesized.

The CuO nanosheets/rGO catalyzed the homocoupling of terminal alkynes efficiently.

The well synergy between CuO nanosheets and graphene.

This catalyst was reused five times with little activity loss.

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Author Contributions

Bin Wang: Conceptualization, Data curation, Investigation, Methodology, Writing-original draft.

Lingfeng Gao: Formal analysis, Funding acquisition, Methodology, Project administration, Supervision, Writing-review & editing.

Gengxiu Zheng: Funding acquisition, Project administration, Resources, Validation, Writing-review & editing.

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: