Catalysis Communications 132 (2019) 105806

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Stabilized Cu_2O nanoparticles on rGO highly catalyzed direct oxidative coupling synthesis of α-ketoamides with molecular oxygen

Weiyang Lu[a], Wei Sun[a], Xiaofeng Tan[a], Bin Wang[a], Hua Yang[b], Lingfeng Gao[a,*], Gengxiu Zheng[a,*]

[a] *School of Chemistry and Chemical Engineering, University of Jinan, Jinan, Shandong 250022, China*
[b] *Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, 252059 Liaocheng, China*

ARTICLE INFO

Keywords:
Cu_2O nanoparticles
Reduced graphene oxide
Oxidative coupling
Heterogeneous catalyst
α-Ketoamides

ABSTRACT

In this study, a green, efficient, recyclable Cu_2O nanoparticles on reduced graphene oxide (Cu_2O-NPs@rGO) carbon-based composite catalyst was synthesized by facile one-pot hydrothermal method. And Cu_2O-NPs@rGO catalyst was characterized by XRD, XPS, TEM, SEM, SEM-EDS and ICP-OES to explore its morphology, structure and chemical composition. The heterogeneous catalyst shows great catalytic performance and excellent functional group tolerance in the oxidative coupling of aryl methyl ketones and secondary amines leading to α-ketoamides with O_2 and N-iodosuccinimide (NIS) under room temperature. Furthermore, Cu_2O-NPs@rGO exhibits good recyclability, which was reused seven times without obvious decline in the catalytic activity.

1. Introduction

The α-ketoamides are important synthetic intermediates in numerous natural products [1] and pharmaceutical drugs [2] with the relevant biological activities. They are also irreplaceable precursors [3,4] for further transformation of various functional groups. Some appealing methods have been developed for synthesizing α-ketoamides including oxidative amidation-diketonization of terminal alkynes [5], double carbonylation of aryl halides [6,7], oxidation of arylacetamides [8], and cross coupling of formamides and α-oxocarboxylic acids [9,10]. These synthetic methodologies are still involved in expensive substrates, harsh reaction conditions and hazardous reagents. Recently, the oxidative coupling of aryl methyl ketones and secondary amines leading to α-ketoamides [11] was reported as an alternative strategy due to its properties of environmental friendly, cost-efficient and mild reaction conditions. These methodologies were mostly carried out on homogeneous reaction system, generally catalyzed by Cu salts (CuBr, CuI and $CuBr_2$) [12,13]. Inherent drawbacks of homogeneous catalytic systems were the product contamination caused by metal residues and the difficulties in the recovery of catalysts, which limited their widespread application in practice. In order to surmount these difficulties, some high-efficient heterogeneous catalysts have been developed for synthesizing the α-ketoamides, such as CuI@TiO_2 [14], SBA-16-pro-Cu (I) [15]. These heterogeneous catalysts suffered from multi-step synthesis methods and low yields. Developing high-efficient heterogeneous catalyst with facile synthetic methods and green catalytic system remains an important challenge.

Cu-containing composite materials were widely used as catalysts in organic catalysis for the copper's high earth-abundance, outstanding physical and chemical properties and low cost [16]. Developing some applications of Cu_2O nanoparticles in the oxidative coupling of aryl methyl ketones and secondary amines leading to α-ketoamides is very significant. However, the widespread use of Cu_2O nanoparticles is restricted by their inherent instability since Cu_2O nanoparticles were easily oxidized [17]. Therefore, the development of solid support materials for Cu_2O nanoparticles with stability and high catalytic performance is really in demand. Graphene, as a new developed 2D carbon material with the properties of large surface area, great electronic conductivity and thermal stability [18,19], was applied in many fields such as energy storage [20], chemical sensor [21], photoelectric devices [22], as well as ideal supports for multi-type catalysts [23,24]. Especially in organic transformations, graphene-based Cu nanoparticles catalysts were widely used in reduction and oxidation reactions, C—H functionalization and cross coupling and other miscellaneous reactions [17]. For example, Movahed et al. reported that Cu@Cu_2O NPs supported on rGO was used as an efficient catalyst for the N-arylation of N-heterocycles [25]. Sun et al. developed an efficient Cu/Cu_2O NPs@graphene for Sonogashira cross-coupling reactions [26]. Therefore, the advantages of graphene and Cu_2O nanoparticles inspired us to combine the two materials to form Cu_2O-NPs@rGO as an efficient heterogeneous

---

* Corresponding authors.
E-mail addresses: gaolf108@mail.ustc.edu.cn (L. Gao), chm_zhenggx@ujn.edu.cn (G. Zheng).

https://doi.org/10.1016/j.catcom.2019.105806
Received 20 May 2019; Received in revised form 23 August 2019; Accepted 27 August 2019

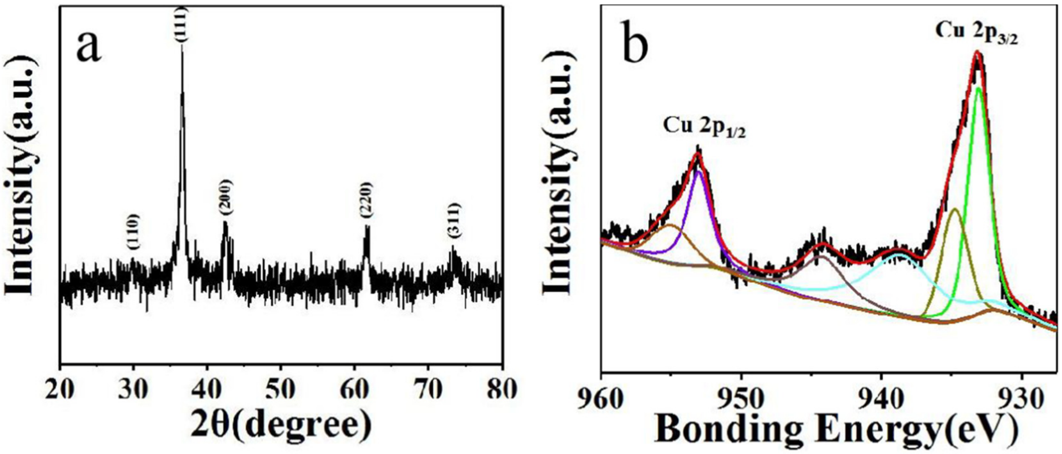


Fig. 1. Characterization of Cu_2O-NPs@rGO (a) XRD pattern; (b) XPS survey spectra.

catalyst through facile one-pot hydrothermal reduction of graphene oxide and copper salts. In this case, Cu_2O nanoparticles were endowed with excellent dispersion and stability on the rGO, which inhibited the agglomeration of Cu_2O nanoparticles and the further oxidation [27]. Meanwhile the Cu_2O nanoparticles were exposed more active sites to accelerate catalytic process.

In our previous studies, an efficient Cu-based catalyst was developed for oxidizing alcohols to aldehydes, which exhibited excellent catalytic performance and recyclability [28]. Herein, we developed an efficient and green heterogeneous catalyst Cu_2O-NPs@rGO for the synthesis of α-ketoamides from aryl methyl ketones and secondary amines with O_2 under room temperature. The catalytic activities were significantly enhanced, which attributed to the charge transfer across the graphene-metal surface because of the graphene-metal spacing and Fermi level difference [29]. Through the synergistic catalysis of Cu_2O nanoparticles and rGO, the new developed Cu_2O-NPs@rGO catalyst shows excellent catalytic performance for the synthesis of α-ketoamides from aryl methyl ketones and secondary amines. Moreover Cu_2O-NPs@rGO was easily separated by centrifugation and recycled seven times without obvious decrease of its catalytic activity.

2. Experimental

2.1. Synthesis of graphene oxide(GO)

Graphene oxide (GO) was synthesized via intense oxidation and exfoliation of natural graphite powder by the modified Hummers method [30,31]. More details about the synthetic method were provided in Supporting Information.

2.2. Synthesis of Cu_2O-NPs@rGO

The Cu_2O-NPs@rGO was synthesized by a facile and economical strategy. Firstly, the 0.16 g of the prepared GO was added into 20 mL deionized water, and sonicated for 1 h to obtain uniformly dispersed GO solution (8 mg/mL). Then 20 mL $Cu(CH_3COO)_2 \cdot H_2O$ (0.8 M) aqueous solution was added into GO solution under vigorously stirring to form a well-dispersed mixture. The mixed solution was transferred into a 50 mL Teflon-lined stainless steel autoclave under continuous stirring for 1 h. After the completion of stirring, the Teflon-lined stainless steel autoclave was kept at 180 °C in oven for 12 h and then cooled down to room temperature naturally. The final Cu_2O-NPs@rGO was separated by centrifugation, washed several times by ethanol and oxygen-free water, and freeze-dried in lyophilizer. Cu_2O nanoparticles and rGO were synthesized by the same method without GO or $Cu(CH_3COO)_2 \cdot H_2O$.

2.3. Characterization

The Cu_2O-NPs@rGO catalyst was characterized by XRD, XPS, TEM, SEM, SEM-EDS, ICP-OES. More parameters about the characterization were shown in Supporting Information.

2.4. Specific experimental conditions for the synthesis of α-ketoamides

The α-ketoamides was synthesized in a round-bottomed flask under continuous stirring. Initially, aryl methyl ketones (1 mmol), secondary amines (2 mmol), additive (1 mmol), catalyst (2 mg), solvent (2 mL) were added into round-bottomed flask. Subsequently, the reaction solution was stirred for 32 h at room temperature under O_2 atmosphere. After the reaction, the solid catalyst was collected by centrifugation and the crude products solution were extracted with ethyl acetate. The α-ketoamides were obtained by further purification of column chromatography and calculated the exact yields. Also, the products were identified by ^1H NMR and ^{13}C NMR spectra.

3. Results and discussion

3.1. Characterization of the catalyst Cu_2O-NPs@rGO

The crystal structure of the synthesized Cu_2O-NPs@rGO was investigated by X-ray diffraction (XRD). The result was shown in Fig. 1a. For Cu_2O diffraction peaks observed at $2\theta = 29.6$, 36.5, 42.4, 61.5 and 73.6 that were assigned to (110), (111), (200), (220) and (311) planes of the cubic structure of Cu_2O crystal (JCPDS No. 65-3288). The XRD result clearly demonstrated the formation of Cu_2O crystals without the diffraction peaks of other metallic copper and impurities in the XRD pattern. It was suggested that Cu_2O nanoparticles were equipped with high crystallinity on the surface of rGO. The chemical states of Cu_2O nanoparticles supported on the rGO were further analyzed by XPS characterization (Fig. 1b). The binding energies at 933.0 and 952.9 eV respectively corresponds to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of Cu^+. Meanwhile, the weak peaks at 934.7 and 955.0 eV were assigned to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of Cu^{2+} in the Cu_2O-NPs@rGO. The tiny existence of Cu^{2+} can also be confirmed by the satellite peaks at 944.1 eV, which could be attributed to the partial surface oxidation of Cu_2O nanoparticles exposed in humid air [32–34]. Moreover, the total content of Cu in the Cu_2O-NPs@rGO detected by ICP-OES was 36.31 wt%. The results of the above characterizations demonstrated that Cu_2O-NPs@rGO was successfully synthesized with highly crystalline of Cu_2O nanoparticles on the surface.

The SEM and TEM images (Fig. 2) show the morphology and structure of the Cu_2O-NPs@rGO. It could be seen that Cu_2O nanoparticles were evenly dispersed on rGO and no free nanoparticles were

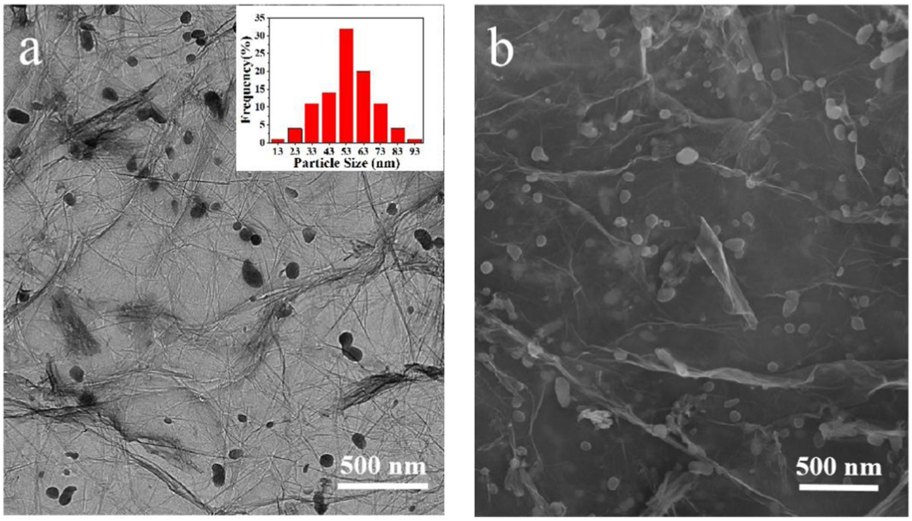
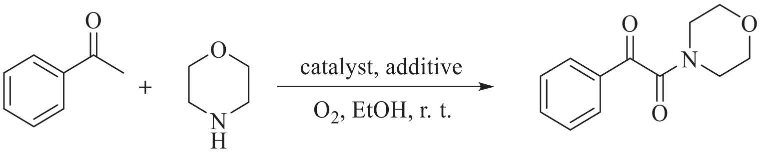


Fig. 2. Characterization of Cu_2O-NPs@rGO (a) TEM image; (b) SEM image.

Table 1
The catalytic performance of different catalysts and additives for the synthesis of α-ketoamides[a].



1 **2** **3**

Entry	Additive	Catalyst	Conv.(%)	Select.(%)	Yield[b]/%
1	NBS	Cu_2O-NPs@rGO	51	64	33
2	TBAB	Cu_2O-NPs@rGO	Trace	Trace	Trace
3	TBAI	Cu_2O-NPs@rGO	21	71	15
4	I_2	Cu_2O-NPs@rGO	51	91	47
5	NaI	Cu_2O-NPs@rGO	22	72	16
6	KI	Cu_2O-NPs@rGO	32	61	22
7	NIS	Cu_2O-NPs@rGO	99	96	95
8[c]	NIS	Cu_2O-NPs@rGO	96	97	93
9	NIS	Cu-NPs[d]	57	90	51
10	NIS	Cu_2O-NPs	60	95	57
11	NIS	rGO	60	81	49
12	NIS	blank	49	84	41

[a] Reaction conditions: **1** (1 mmol), **2** (2 mmol), additive (1 mmol), catalyst (2 mg), EtOH (2 mL), r. t., O_2, 32 h.
[b] Isolated yields.
[c] **1** (10 mmol).
[d] Commercial.

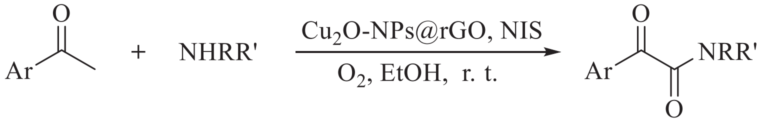
generated outside according to the TEM image (Fig. 2a). The particle sizes of Cu_2O nanoparticles on the rGO were in the range of 45–60 nm by TEM image. Further, the typical folds and wrinkles were still observed on the surface of Cu_2O-NPs@rGO, which increased the contact area of reaction and exposed more active sites for catalysis. The result of SEM image showed that the rGO nanosheets were uniformly decorated with Cu_2O nanoparticles (Fig. 2b). The corresponding SEM elemental mapping shown in Fig. S4 proved that C, O and Cu elements were evenly distributed in the whole catalyst. The above characterizations demonstrated that Cu_2O nanoparticles evenly loaded on the surface of rGO.

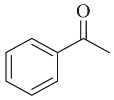
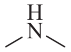
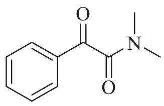
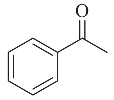
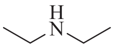
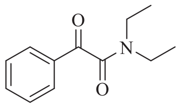
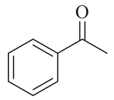
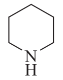
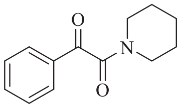
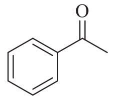
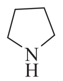
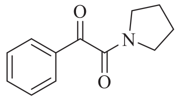
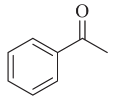
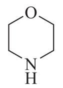
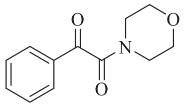
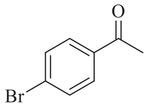
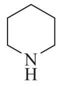
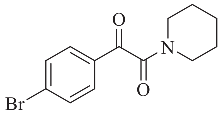
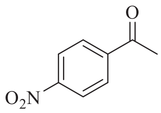
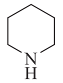
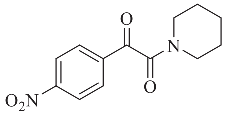
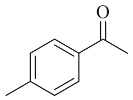
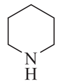
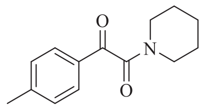
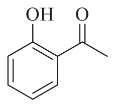
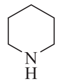
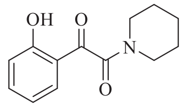
3.2. Catalytic performance

In initial study, we investigated a series of additives and catalysts under O_2 atmosphere by employing acetophenone (1 mmol) and morpholine (2 mmol) as model substrates. The corresponding catalytic performance was shown in Table 1. When NBS, TBAB were utilized as additives with Cu_2O-NPs@rGO as catalyst, the desired α-ketoamide was obtained in low conversion and selectivity (Table 1, entries 1,2). When Cu_2O-NPs@rGO was utilized as catalyst, some iodine-containing additives (TBAI, I_2, NaI, KI, NIS) were investigated in the oxidative coupling reaction. Among these additives, NIS was found as the best choice as the additive with the excellent conversion and selectivity of the desired α-ketoamide (Table 1, entries 3–7). Then different catalysts were also investigated in the synthesis of the desired α-ketoamide including Cu-NPs, Cu_2O-NPs and rGO. All of the reactions gave moderate yields of 49–57% (Table 1, entries 9–11). In the absence of any catalyst, only 41% yield of α-ketoamide was obtained (Table 1, entry 12). It was revealed that the catalyst is an essential part in the oxidative coupling synthesis of α-ketoamides. In addition, when the usage of acetophenone reached 10 mmol, the desired α-ketoamide gave the yield of 93% and no obvious decline in the yield and selectivity was observed (Table 1, entry 8). It was indicated that the catalyst system has excellent potential in practical application. Notably, Cu_2O-NPs@rGO exhibited much higher catalytic performance than Cu_2O nanoparticles and rGO

Table 2

Cu_2O-NPs@rGO catalyzed oxidative coupling synthesis of various α-ketoamides[a].



Entry	Methyl ketone	Amine	Product	Yield[b]/%	TONs/TOFs[c]
1				68	59.9/1.9
2				79	69.6/2.2
3				96	84.6/2.6
4				89	78.4/2.5
5				95	83.7/2.6
6				91	80.2/2.5
7				90	79.3/2.5
8				84	74.0/2.3
9				81	71.4/2.2

[a] Reaction conditions: methyl ketone (1 mmol), amine (2 mmol), Cu_2O-NPs@rGO (2 mg), NIS (1 mmol), EtOH (2 mL), r. t., O_2, 32 h. [b] Isolated yields. [c] TON is the number of moles of product per mol of Cu loading and TOF = TON per hour.

respectively indicating the synergistic catalysis of rGO and Cu_2O nanoparticles dramatically increased the catalytic efficiency for the oxidative coupling reaction. Finally, NIS and Cu_2O-NPs@rGO were chosen as the additive and catalyst for their efficient synergic catalytic performance.

Next, the reaction solvent was optimized for the synthesis of α-ketoamides by employing acetophenone (1 mmol) and morpholine (2 mmol) as model substrates. The reaction result was shown in Table S2. EtOH and i-PrOH were proved as the good solvents with the yields of 95% and 91% respectively (Table S2, entries 1,2). DMSO, DMF solvents gave low catalytic activities with the yields of 22% and 37% (Table S2, entries 3,4). When CH_3CN, 1,4-dioxane, toluene were utilized as solvents respectively, the reaction afforded the 1-morpholino-2-phenylethane-1,2-dione in moderate yields of 63–84% (Table S2,

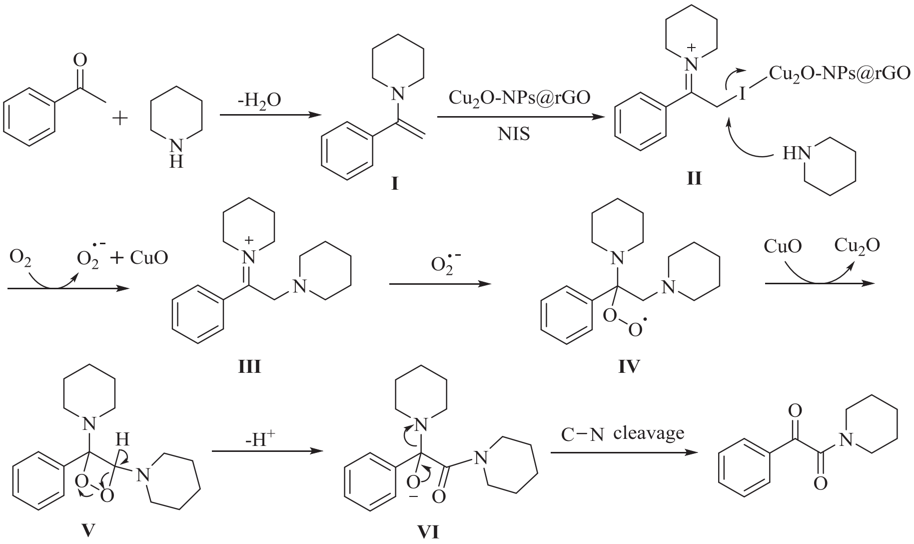


Fig. 3. Proposed mechanism for Cu$_2$O-NPs@rGO catalyzed oxidative coupling synthesis of α-ketoamides.

entries 5–7). With CH$_2$Cl$_2$, THF as the solvents, the reaction gave low yields of 4%, 57% respectively (Table S2, entries 8,9). The above results indicated that EtOH was the optimized solvent. For easy handing, 2 mL of EtOH was then applied as a solvent in further research.

Moreover, the different usages of NIS and Cu$_2$O-NPs@rGO were investigated in the oxidative coupling reaction from acetophenone (1 mmol) and morpholine (2 mmol). The optimal amounts were 1 mmol NIS and 2 mg Cu$_2$O-NPs@rGO (Table S3). Therefore, the optimized reaction conditions were as follows: acetophenone (1 mmol), morpholine (2 mmol), NIS (1 mmol) and Cu$_2$O-NPs@rGO (2 mg) in 2 mL EtOH at room temperature under O$_2$ atmosphere.

In order to investigate the generality of the catalytic system, a series of secondary amines were examined in the synthesis of the α-ketoamides. Several aliphatic secondary amines such as dimethylamine and diethylamine were reacted with acetophenone to afford corresponding α-ketoamides with good yields of 68% and 79% respectively (Table 2, entries 1,2). Several cyclic secondary amines such as piperidine, pyrrolidine and morpholine that reacted with acetophenone gave excellent yields of 96%, 89% and 95% (Table 2, entries 3–5). It was noteworthy that cyclic secondary amines were obtained better yields than aliphatic secondary amines. Some functional groups (Br−, NO$_2$−, CH$_3$− and HO−) on acetophenone that reacted with piperidine were also investigated in the oxidative coupling synthesis of α-ketoamides. All of these acetophenone derivatives afforded the desire α-ketoamides in good yields of 81–91% (Table 2, entries 6–9). And the corresponding TONs/TOFs value of different substrates were shown in the Table 2. It could be seen that the oxidative coupling of acetophenone and piperidine gave relatively higher TONs/TOFs of 84.6/2.6 (Table 2, entries 3). The above results demonstrated that the Cu$_2$O-NPs@rGO showed excellent catalytic performance and great functional groups tolerance for the direct oxidative coupling synthesis of various α-ketoamides.

One of the most important properties of the heterogeneous catalysts was their recyclability. Hence, the cycle experiments of the Cu$_2$O-NPs@rGO were carried out by using acetophenone and piperidine as standard substrates under optimum reaction condition. After the reaction finished, Cu$_2$O-NPs@rGO was recovered by centrifugation, washed with ethanol and water, and finally dried under vacuum. The desired product was obtained by column chromatography and calculated the exact yields. And the concrete experimental results were shown in the Fig. S5. It could be seen that no apparent decline in the yield after recycling seven times (89%). Furthermore, the recycled Cu$_2$O-NPs@rGO was characterized by TEM to observe its morphology and structure. The corresponding image was displayed in Fig. S6. Through the comparison of the TEM images of the recycled and fresh catalyst, no obvious change in the morphology and structure of the catalyst was observed. It was indicated that Cu$_2$O-NPs@rGO possesses excellent recyclability in the synthesis of α-ketoamides.

Based on the previous research results [12,13,35] and our studies, a possible mechanism for the formation of α-ketoamides was proposed in Fig. 3. With great electrical conductivity and huge specific surface area of graphene, the electron transfer between Cu$_2$O nanoparticles and graphene was more easily proceeding, which facilitated the transfer of electron in the catalytic process. Firstly, acetophenone and piperidine generated enamine **I**. Intermediate **II** was then formed by the iodination of NIS catalyzed by Cu$_2$O-NPs@rGO. Piperidine took placed nucleophilic substitution with intermediate **II** to generate the α-piperidinyl substituted iminium **III**. During the process, the carbon-iodine bond cleavage was promoted by Cu$_2$O-NPs@rGO. Meanwhile, superoxide radical O$_2^{\cdot -}$ was formed from O$_2$ promoted by the value state change from Cu$_2$O to CuO in the Cu$_2$O-NPs@rGO, which accelerated the process of the iminium **III** to radical intermediate **IV**. Then, intramolecular cyclization took place to form pivotal aminodioxetane intermediate **V** accomplished with the single electron transfer process of CuO to Cu$_2$O in the Cu$_2$O-NPs@rGO. Through O−O bond heterolysis, ring opening reaction took place to generate intermediate **VI**. Finally, α-ketoamide was obtained by C−N bond cleavage. Cu$_2$O-NPs@rGO continued to attend for the next catalysis cycle.

4. Conclusions

In conclusion, we developed a novel, efficient and recyclable Cu$_2$O-NPs@rGO material to catalyze the direct oxidative coupling of aryl methyl ketones and secondary amines to synthesize α-ketoamides with O$_2$ as clean oxidant. The Cu$_2$O-NPs@rGO was systematically characterized by XRD, XPS, TEM, SEM, SEM-EDS, ICP-OES, which proved that Cu$_2$O nanoparticles evenly and firmly supported on the rGO. But more important, the heterogeneous synthetic methodology using facilely prepared Cu$_2$O-NPs@rGO, green oxidant and mild reaction conditions, provides a simple and efficient approach to synthesize various α-ketoamides in good to excellent yields. We believed that our study could provide a reliable approach to develop copper-based carbon catalysts and promote the application of heterogeneous catalyst into organic reaction.

Acknowledgement

This study was supported by the Natural Science Foundation of Shandong Province (2019GGX104021, ZR2016BQ10) and the National Natural Science Foundation of China (No. 21601064, 21701078).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2019.105806.

References

[1] M. Hagihara, N.J. Anthony, T.J. Stout, J. Clardy, S.L. Schreiber, Vinylogous polypeptides: an alternative peptide backbone, J. Am. Chem. Soc. 114 (1992) 6568–6570.

[2] Y. Chen, Y. Zhang, H. Zhang, Design, synthesis, and biological evaluation of isoquinoline-1,3,4-trione derivatives as potent caspase-3 inhibitors, J. Med. Chem. 49 (2006) 1613–1623.

[3] Q. Liu, S. Perreault, T. Rovis, Catalytic asymmetric intermolecular stetter reaction of glyoxamides with alkylidenemalonates, J. Am. Chem. Soc. 130 (2008) 14066–14067.

[4] D. Tomita, K. Yamatsugu, M. Kanai, M. Shibasaki, Enantioselective synthesis of SM-130686 based on the development of asymmetric Cu(I)F catalysis to access 2-oxindoles containing a tetrasubstituted carbon, J. Am. Chem. Soc. 131 (2009) 6946–6948.

[5] C. Zhang, N. Jiao, Dioxygen activation under ambient conditions: Cu-catalyzed oxidative amidation-diketonization of terminal alkynes leading to a-ketoamides, J. Am. Chem. Soc. 132 (2010) 28–29.

[6] J. Liu, R. Zhang, S. Wang, W. Sun, C. Xia, A general and efficient copper catalyst for the double carbonylation reaction, Org. Lett. 11 (2009) 1321–1324.

[7] M. Iizuka, Y. Kondo, Remarkable ligand effect on the palladium-catalyzed double carbonylation of aryl iodides, Chem. Commun. (16) (2006) 1739–1741.

[8] B. Song, S. Wang, C. Sun, H. Deng, B. Xu, Cesium carbonate promoted aerobic oxidation of arylacetamides: an efficient access to N-substituted α-keto amides, Tetrahedron Lett. 48 (2007) 8982–8986.

[9] D. Li, M. Wang, J. Liu, Q. Zhao, L. Wang, Cu(II)-catalyzed decarboxylative acylation of acyl C-H of formamides with α-oxocarboxylic acids leading to α-ketoamides, Chem. Commun. 49 (2013) 3640–3642.

[10] H. Wang, L. Guo, X. Duan, Copper-catalyzed oxidative condensation of α-oxocarboxylic acids with formamides: synthesis of α-ketoamides, Org. Biomol. Chem. 11 (2013) 4573–4576.

[11] M. Lamani, K.R. Prabhu, NIS-catalyzed reactions: amidation of acetophenones and oxidative amination of propiophenones, Chem. Eur. J. 18 (2012) 14638–14642.

[12] J. Zhang, Y. Wei, S. Lin, F. Liang, P. Liu, Copper-catalyzed aerobic oxidative synthesis of α-ketoamides from methyl ketones, amines and NIS at room temperature, Org. Biomol. Chem. 10 (2012) 9237–9242.

[13] F. Du, J. Ji, Copper-catalyzed direct oxidative synthesis of α-ketoamides from aryl methyl ketones, amines, and molecular oxygen, Chem. Sci. 3 (2012) 460–465.

[14] P.K. Dutta, B. Dhar, S. Sen, Aerobic oxidative amidation of alkynes using titanium oxide encapsulated cuprous iodide nanoparticles (CuI@TiO$_2$), New J. Chem. 42 (2018) 12062–12071.

[15] X. Zhang, H. Yang, Y. Huo, J. Li, J. Ma, J. Ma, Cu(I)-Functionalized SBA-16: an efficient catalyst for the synthesis of α-ketoamides under moderate conditions, Dalton Trans. 45 (2016) 8972–8983.

[16] J. Zhang, J. Liu, Q. Peng, X. Wang, Y. Li, Nearly monodisperse Cu$_2$O and CuO nanospheres: preparation and applications for sensitive gas sensors, Chem. Mater. 18 (2006) 867–871.

[17] M.B. Gawande, A. Goswami, F.X. Felpin, T. Asefa, X. Huang, R. Silva, X. Zou, R. Zboril, R.S. Varma, Cu and Cu-based nanoparticles: synthesis and applications in catalysis, Chem. Rev. 116 (2016) 3722–3811.

[18] Y. Yao, Y. Cai, F. Lu, F. Wei, X. Wang, S. Wang, Magnetic recoverable MnFe$_2$O$_4$ and MnFe$_2$O$_4$-graphene hybrid as heterogeneous catalysts of peroxymonosulfate activation for efficient degradation of aqueous organic pollutants, J. Hazard. Mater. 270 (2014) 61–70.

[19] P. Kumar, F. Shahzad, S. Yu, S.M. Hong, Y.H. Kim, C.M. Koo, Large-area reduced graphene oxide thin film with excellent thermal conductivity and electromagnetic interference shielding effectiveness, Carbon 94 (2015) 494–500.

[20] Y. Yang, L. Li, H. Fei, Z. Peng, G. Ruan, J.M. Tour, Graphene nanoribbon/V$_2$O$_5$ cathodes in lithium-ion batteries, ACS Appl. Mater. Interfaces 6 (2014) 9590–9594.

[21] G.J. Rani, K.J. Babu, G.G. kumar, M.A.J. Rajan, Watsonia meriana flower like Fe$_3$O$_4$/reduced graphene oxide nanocomposite for the highly sensitive and selective electrochemical sensing of dopamine, J. Alloys Compd. 688 (2016) 500–512.

[22] Y. Zhou, E. Yiwen, L. Zhu, M. Qi, X. Xu, J. Bai, Z. Ren, L. Wang, Terahertz wave reflection impedance matching properties of graphene layers at oblique incidence, Carbon 96 (2015) 1129–1137.

[23] M. Hu, Z. Yao, K.N. Hui, K.S. Hui, Novel mechanistic view of catalytic ozonation of gaseous toluene by dual-site kinetic modelling, Chem. Eng. J. 308 (2017) 710–718.

[24] M.A. Al-Daous, Graphene-MoS$_2$ composite: hydrothermal synthesis and catalytic property in hydrodesulfurization of dibenzothiophene, Catal. Commun. 72 (2015) 180–184.

[25] S.K. Movahed, M. Dabiri, A. Bazgir, A one-step method for preparation of Cu@Cu$_2$O nanoparticles on reduced graphene oxide and their catalytic activities in N-arylation of N-heterocycles, Appl. Catal. A Gen. 481 (2014) 79–88.

[26] W. Sun, L. Gao, X. Sun, G. Zheng, A novel route with a Cu(II)-MOF-derived structure to synthesize Cu/Cu$_2$O NPs@graphene: the electron transfer leads to the synergistic effect of the Cu(0)-Cu(I) phase for an effective catalysis of the Sonogashira cross-coupling reactions, Dalton Trans. 47 (2018) 5538–5541.

[27] P. Bhanja, S.K. Das, A.K. Patra, A. Bhaumik, Functionalized graphene oxide as an efficient adsorbent for CO$_2$ capture and support for heterogeneous catalysis, RSC Adv. 6 (2016) 72055–72068.

[28] X. Feng, P. Lv, W. Sun, X. Han, L. Gao, G. Zheng, Reduced graphene oxide-supported Cu nanoparticles for the selective oxidation of benzyl alcohol to aldehyde with molecular oxygen, Catal. Commun. 99 (2017) 105–109.

[29] L. Li, J. Zhang, Y. Liu, W. Zhang, H. Yang, J. Chen, Q. Xu, Facile fabrication of Pt nanoparticles on 1-pyrenamine functionalized graphene nanosheets for methanol electrooxidation, ACS Sustain. Chem. Eng. 1 (2013) 527–533.

[30] W.S. Hummers Jr., R.E. Offeman, Preparation of Graphitic Oxide, J. Am. Chem. Soc. 80 (1958) 1339.

[31] D. Li, M.B. Mueller, S. Gilje, R.B. Kaner, G.G. Wallace, Processable aqueous dispersions of graphene nanosheets, Nat. Nanotechnol. 3 (2008) 101–105.

[32] C. Cheng, C. Zhang, X. Gao, Z. Zhuang, C. Du, W. Chen, 3D network and 2D paper of reduced graphene oxide/Cu$_2$O composite for electrochemical sensing of hydrogen peroxide, Anal. Chem. 90 (2018) 1983–1991.

[33] S. Deng, V. Tjoa, H.M. Fan, H.R. Tan, D.C. Sayle, M. Olivo, S. Mhaisalkar, J. Wei, C.H. Sow, Reduced graphene oxide conjugated Cu$_2$O nanowire mesocrystals for high-performance NO$_2$ gas sensor, J. Am. Chem. Soc. 134 (2012) 4905–4917.

[34] J. Pan, W. Liu, L. Quan, N. Han, S. Bai, R. Luo, Y. Feng, D. Li, A. Chen, Cu$_2$O and rGO hybridizing for enhancement of low-concentration NO$_2$ sensing at room temperature, Ind. Eng. Chem. Res. 57 (2018) 10086–10094.

[35] X. Zhang, L. Wang, TBHP/I$_2$-promoted oxidative coupling of acetophenones with amines at room temperature under metal-free and solvent-free conditions for the synthesis of α-ketoamides, Green Chem. 14 (2012) 2141–2145.