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#### WILEY Applied Organometallic Chemistry

## Copper(I) complex covalently anchored on graphene oxide as an efficient and recyclable catalyst for Sonogashira reaction

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### **Funding information**

Yasouj University Research Council, Grant/Award Number: Gryu-89131303; Iranian Nanotechnology Initiative Council In this study, the organosilane-functionalized graphene oxide as a stabilizer was prepared by a facile one-step silylation approach.  $[Cu(PPh_3)_3Cl]$  complex was successfully immobilized onto the graphene oxide surface through coordination interaction with organosilane ligand spacers. The supported catalyst showed enhanced catalytic performance toward Sonogashira reaction of aryl halides with phenylacetylene in water solvent compared with the homogeneous analogues, and it could be readily recycled and reused several times without discernible loss of its activity.

### KEYWORDS

catalyst, graphene oxide, nanohybrid, organosilane, Sonogashira reaction

## **1** | INTRODUCTION

Transition metal catalyzed reactions have evolved as general and powerful tools in organic chemistry for the synthesis of many agrochemicals and pharmaceuticals because of easy carbon–carbon (C-C) bond formation.<sup>[1]</sup> In particular, the Sonogashira reaction involves the formation of a C–C bond between aryl halides and terminal acetylene in presence of a palladium-based catalyst, copper(I) salt as a co-catalyst and a base to form an aryl acetylene, as shown in Figure 1.<sup>[2]</sup>

Due to the high cost of Pd metal, the use of Sonogashira reaction in large scale production is limited and consequently alternative catalyst systems are searched for. So replacing Pd metal with more abundant, cheaper and less toxic Cu has become an area of active research.<sup>[3]</sup> Despite high activity and selectivity, industrial applications of these catalysts are still limited because of their high costs with the problem of separating them from product containing solutions. So, the recovery of these catalysts is important for both ecological and economical reasons. Heterogeneous catalysts can be easily recycled. In fact, strategies to immobilize these homogeneous catalysts on separable supports have been pursued for decades.  $\ensuremath{^{[4]}}$ 

Numerous reports have been published in the recent years with respect to the excellent catalytic properties including recyclability of different copper complexes immobilized on different supports.<sup>[5]</sup> Recently, Mureseanu et al., have reported the immobilization of Cu(II) complexes on functionalized mesoporous silica as catalysts for biomimetic oxidations.<sup>[5e]</sup> The copper complex of 1,2bis(4-aminophenylthio)ethane was immobilized on gra phene oxide (GO) nanosheets to obtain a novel heterogeneous Cu catalyst for epoxidation of olefins with tert-butyl hydroperoxide, have been studied by Moghadam et al.<sup>[5f]</sup> Mononuclear complexes of CuL and Cu(2 L), where L is propyl-thiazol-2-ylmethylene-amine, covalently immobili zed onto SiO<sub>2</sub>, which can catalyze efficiently the oxidation of 3,5-di-t-butylcatechol to 3,5-di-t-butylquinone by utilizing ambient O<sub>2</sub> as oxidant, have been studied by Deligiannakis *et al.*<sup>[5g]</sup> It is worth noting that Lu *et al.* have reported the cross-coupling catalytic activity of novel Pd complexes with fluorous bipyridyl ponytails with high turnover number (TON).<sup>[6]</sup> Here we show that a copper(I) complex immobilized on functionalized GO can be readily



FIGURE 1 General representation of Pd/Cu-catalyzed Sonogashira reaction

recycled and shows enhanced activity in the Sonogashira reaction.

Graphene and graphene derivatives are currently the most intensively studied material. A graphene derivative, such as GO, offers a wide range of possibilities to synthesize the novel functional catalysts owing to its abundant containing carboxyl, carbonyl, epoxy and hydroxyl functional groups functionalities.<sup>[7]</sup> The two-dimensional structure with a huge surface area makes it a promising support for different complexes and nanoparticles (NPs).<sup>[8]</sup> In particular, the two-dimensional structure may allow reactive species immobolized on this surface readily accessed with limited mass transfer resistance. Based on these considerations, we predict that GO may be used as a desirable support for anchoring copper(I) complex.

The organosilane-functionalized GO was prepared by reaction between GO and (3-aminopropyl)triethoxysilane (APTES) (shown as APTES-f-GO). Copper(I) complex [Cu (PPh<sub>3</sub>)<sub>3</sub>Cl], was synthesized and the copper(I) complex was covalently anchored onto the GO surface through coordination interaction by employing APTES ligand spacers. The catalytic performance of the [Cu(PPh<sub>3</sub>)<sub>3</sub>Cl] complex and the supported copper(I) complex on GO (shown as Cu(I)-f-GO) were investigated in Sonogashira reaction in water (Figure 2).

### 2 | EXPERIMENTAL SECTION

All of the chemical compounds were purchased from Sigma-Aldrich and Merck companies. Scanning electron microscopic (SEM) images and energy dispersive X-ray spectroscopy (EDS) mapping were recorded using a Mira 3-XMU. Transmission electron microscopy (TEM) images were taken with a Philips CM-10 microscope operated at 100 kV. The surface atomic concentration and chemical composition of the samples were investigated by X-ray photoelectron spectroscopy (XPS) equipped with an Al Kax-ray source at energy of 1486.6 eV in an ultrahigh vacuum (UHV) system with a base pressure lower than  $2 \times 10^{-9}$  Torr. Raman spectra were recorded from 4250  $\text{cm}^{-1}$  to 100  $\text{cm}^{-1}$  on a high resolution dispersive Raman Thermonicolet (LabRAM HR UV/Vis/NIR, Electrooptics). The loading amount of copper was determined using an inductively coupled plasma (ICP) analyzer (Varian, Vista-Pro). A BET surface analyzer (SA 3100, Beckman Coulter) is used to measure nitrogen adsorption isotherm at 77 K and the specific surface area was determined using the Brunauer Emmett Teller (BET) equation. NMR spectra were taken with a Bruker 400 MHz ultra-shield spectrometer using CDCl<sub>3</sub> as the solvent. FT-IR spectra were taken with a Jasco FT/IR-



**FIGURE 3** FT-IR spectra of (a) GO, (b) APTES-*f*-GO and (c) Cu(I)-*f*-GO nanohybrid



**FIGURE 2** Schematic illustration of the preparation of Cu(I)-*f*-GO nanohybrid

680 plus spectrometer. The  $[Cu(PPh_3)_3Cl]$  complex was synthesized using reported procedure.<sup>[9]</sup>

### 2.1 | Preparation of APTES-f-GO

GO was prepared by the previously reported modified Hummers method.<sup>[8a-c,10]</sup> The as-prepared GO (12.0 mg ml<sup>-1</sup>, 16.7 mL) was dispersed in 120 ml ethanol, and placed for 0.5 h under ultrasonic waves. The APTES-*f*-GO was processed by stirring the suspension with excess APTES (852.3 mg, 3.85 mmol) and refluxed at 70 °C for 6 h, after which the mixture was centrifuged and black crystals were separated, washed with ethanol, distilled water and anhydrous toluene, and air-dried.



**FIGURE 4** Raman spectra of (a) GO, (b) APTES-*f*-GO and (c) Cu(I)-*f*-GO nanohybrid



FIGURE 5 EDAX spectrum of Cu(I)-f-GO nanohybrid



 $\label{eq:FIGURE 6} \begin{array}{l} \text{XPS spectra of Cu(I)-$f$-GO nanohybrid, (a) the survey} \\ \text{curve, (b) C 1 s, (c) Si 2p, (d) Cu $p_{1/2}$ and (e) Cu $p_{3/2}$ \end{array}$ 

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# 2.2 | Preparation of Cu(I)-*f*-GO nanohybrid

200 mg of the as-prepared APTES-*f*-GO (100 ml) was added to a dry toluene solution of  $[Cu(PPh_3)_3Cl]$  (141.7 mg, 0.16 mmol). The reaction mixture was heated under a reflux condenser at 80 °C under nitrogen atmosphere for 24 h, after which the mixture was centrifuged and black crystals were separated, washed with dry toluene and air-dried.

# 2.3 | General procedure for Sonogashira coupling reaction

Aryl halide (0.5 mmol), phenylacetylene (0.75 mmol), K<sub>2</sub>CO<sub>3</sub> (1 mmol), catalyst, and 5 mL of H<sub>2</sub>O were charged in a round-bottom flask. Reaction was carried out at 80 °C. After completion of the reaction (monitored by Thin Layer Chromatography (TLC)), the mixture was cooled and then, dichloromethane  $(3 \times 5 \text{ ml})$  was added to the reaction vessel and separated solid catalyst. The organic phase was extracted and dried by anhydrous MgSO<sub>4</sub>. Evaporation of the solvent gave the desired organic product. The unknown products were also characterized by comparing the <sup>1</sup>H NMR data with authentic samples and the details are given in the supporting information. The TON (= mol of product/mol of catalyst) and turnover frequency (TOF (= TON/time (h))) were calculated on the basis of the amount of diarylacetylene product formed.

## 3 | RESULTS AND DISCUSSION

## 3.1 | Structure characterization

The Cu(I)-f-GO nanohybrid synthesized according to method titled in the experimental section and graphically summarized in Figure 2. FT-IR spectra of GO, APTES-f-GO and Cu(I)-f-GO nanohybrid are shown in Figure 3. The FT-IR spectroscopy in Figure 3a revealed that the pristine GO displayed three strong bands at 3376, 1729 and 1226 cm<sup>-1</sup> characteristic of the hydroxyl, carboxyl and epoxy groups, respectively.<sup>[11]</sup> The representative APTES-f-GO exhibited two additional bands at 2860 and 2925 cm<sup>-1</sup>, indicative of the symmetric and asymmetric stretching modes of C - H bonds from  $CH_2 - CH_2$  groups connecting with the NH<sub>2</sub> group. One other additional band at 1548 cm<sup>-1</sup> could be ascribed to the symmetric N - H stretching band from the  $NH_2$  group.<sup>[12]</sup> Also, the appearance of two new bands at 696 and 1110 cm<sup>-1</sup> were assigned to the Si - O - C stretching and Si - O - Si asymmetric stretching vibration.<sup>[13]</sup> Furthermore, the intensity of the absorption band around 3413 cm<sup>-1</sup> characteristic of the surface OH groups significantly decreased, suggesting that the silvlanization mainly occurred via reaction with surface OH (Figure 3b). The FT-IR spectrum of Cu(I)-f-GO nanohybrid is shown in Figure 3c. Due to the weak signal and overlapping of absorption by other groups, hardly evident additional peaks or shifts can be observed in the spectrum of Cu(I)f-GO nanohybrid. Nevertheless, the weak signal at



FIGURE 7 (a and b) SEM images of Cu(I)-f-GO nanohybrid, and corresponding quantitative EDS mapping of (c) N, (d) Si, (e) Cl and (f) Cu

457 cm<sup>-1</sup> which might be one of the characteristic absorptions of triphenylphosphine (PPh<sub>3</sub>) implies the introduction of  $[Cu(PPh_3)_3Cl]$ . All of these indicate that  $[Cu(PPh_3)_3Cl]$  complex moiety has been successfully grafted on the surface of APTES-*f*-GO.

Raman spectroscopy has been widely used to probe structural and electronic characteristics of graphite materials, providing useful information on the defects (D band) and in plane vibration of  $sp^2$  carbon atoms (G band). Raman spectra of GO, APTES-*f*-GO and Cu(I)-*f*-GO nanohybrid show an obvious and step-by-step blue shift of the G band from 1583 to 1592 and 1599 cm<sup>-1</sup>, probably due to the gradually increased compressive local stress induced by the attached amine-terminal silanes and the final copper complexes (Figure 4). One other peak was observed at 2698 cm<sup>-1</sup>, corresponding to the 2D combinational mode for GO.

The surface areas of GO, APTES-*f*-GO and Cu(I)-*f*-GO nanohybrid are 89, 28 and 25 m<sup>2</sup> g<sup>-1</sup>, respectively. The subsequent decrease is attributed to the successful immobilization of metal complex.

The composition of the Cu(I)-*f*-GO nanohybrid was further examined by energy dispersive analysis of X-ray (EDAX) where the Cu, Cl, P, Si, N, O and C elements were observed (Figure 5). The copper loading of the Cu(I)-*f*-GO nanohybrid catalyst was determined to be 15.57 µg by ICP.

XPS analysis was used to analyze the chemical compositions of the Cu(I)-f-GO nanohybrid surface. As expected the presence of Cu, Si, Cl, P, N, O and C is evident in the general spectrum (Figure 6a). In the C1s XPS spectrum of the Cu(I)-f-GO nanohybrid, the first main peak at a binding energy of 282.49 eV is assigned to the C-Si bonds of the APTES (Figure 6b). As shown in Figure 6b, the intensity of the C-O (epoxy) and C-OH groups in Cu(I)-f-GO nanohybrid at 286.77 eV was significantly lower compared to the C-O (epoxy) and C-OH groups in GO,<sup>[14]</sup> which means a structure deprived of hydroxy groups. Also, the Si 2p XPS can be divided into two components, including a Si-O-C and Si-C bond at 102.28 eV, and a Si-O-Si bond at 103.5 eV (Figure 6c). The Cu 2p spectra exhibited the presence of Cu(I) and Cu(0) species (Figures 6d and e). The XPS spectra were characterized by two pairs of Cu 2p peaks: the binding energies of 953.69 and 933.79 eV were assigned to Cu(I) and the binding energies of 951.79 and 931.45 eV were assigned to Cu(0), for  $2p_{1/2}$  (Figure 6d) and  $2p_{3/2}$ (Figure 6e), respectively. The contents of Cu(I) and Cu(0) are 81.65% and 18.35%, respectively.

 $[Cu(PPh_3)_3Cl]$  complexes were immobilized on APTES-*f*-GO by forming a stronger coordination bond between the terminal NH<sub>2</sub> and the copper metallic centers,  $[Cu(PPh_3)_3Cl]$  was firmly anchored onto APTES-*f*-GO by substituting one ligand PPh<sub>3</sub> of WILEY-Organometallic 5 of 9 Chemistry

 $[Cu(PPh_3)_3Cl]$ . The morphology of the as-synthesized Cu(I)-*f*-GO nanohybrid was characterized by SEM and TEM analysis. SEM images present the two-dimensional planar structure with heavy crumpling features of Cu(I)-*f*-GO nanohybrid (Figure 7a and b). As shown in Figure 7, EDS mapping of Cu(I)-*f*-GO nanohybrid displays a homogeneous distribution of copper element on the whole surface of GO, implying a desirable anchoring of a large amount of copper complexes. EDS mapping of the rest elements also shows well-defined distributions (Figure S1, Supporting Information).

Also, Figure 8 shows TEM images of Cu(I)-*f*-GO nanohybrid. As shown in Figure 8, the presence of folds on the sheet indicates that Cu(I)-*f*-GO exhibits a nanosheet structure.



FIGURE 8 (a and b) TEM images of Cu(I)-f-GO nanohybrid

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**TABLE 1**Sonogashira cross-coupling of aryl halides with phenylacetylene catalyzed by the  $[Cu(PPh_3)_3Cl]$  complex and Cu(I)-f-GOnanohybrid

$ \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $								
		Y = C, N G = H, M G' = H, M X = CI, E	/le, NO <sub>2</sub> , CN, OMe /le Jr, I	a; Y = C, G' = H 1a; G = H, 2a; 4a; G = CN, 5a 1b; Y = C, G' = 1c; Y = N, G =	H G = Me, 3a; G = NO <sub>2</sub> , ; G = OMe Me, G = H H			
Entry	Substrate	Product	Cat.	Time (min)	Yield (%) <sup>a</sup>	TON <sup>b</sup>	$TOF^{b}(h^{-1})$	
1	$C_6H_5I$	1a	[Cu(PPh <sub>3</sub> ) <sub>3</sub> Cl] <sup>c</sup> Cu(I)- <i>f</i> -GO <sup>d</sup>	50 33	91 95	67 1939	80 3525	
2	2-MeC <sub>6</sub> H <sub>4</sub> I	1b	[Cu(PPh <sub>3</sub> ) <sub>3</sub> Cl] Cu(I)- <i>f</i> -GO	101 71	85 89	63 1816	37 1535	
3	$4-MeC_6H_4I$	2a	[Cu(PPh <sub>3</sub> ) <sub>3</sub> Cl] Cu(I)- <i>f</i> -GO	90 62	89 92	66 1877	44 1816	
4	$4\text{-}\mathrm{NO}_2\mathrm{C}_6\mathrm{H}_4\mathrm{I}$	3a	[Cu(PPh <sub>3</sub> ) <sub>3</sub> Cl] Cu(I)- <i>f</i> -GO	39 28	93 97	69 1979	106 4241	
5	$C_6H_5Br$	1a	[Cu(PPh <sub>3</sub> ) <sub>3</sub> Cl] Cu(I)- <i>f</i> -GO	70 46	85 90	63 1837	54 2396	
6	4-MeC <sub>6</sub> H <sub>4</sub> Br	2a	[Cu(PPh <sub>3</sub> ) <sub>3</sub> Cl] Cu(I)- <i>f</i> -GO	147 78	69 75	51 1531	21 1178	
7	$C_6H_5Cl$	1a	[Cu(PPh <sub>3</sub> ) <sub>3</sub> Cl] Cu(I)- <i>f</i> -GO	205 103	65 71	48 1449	14 844	
8	$4\text{-}\mathrm{NO}_2\mathrm{C}_6\mathrm{H}_4\mathrm{Cl}$	3a	[Cu(PPh <sub>3</sub> ) <sub>3</sub> Cl] Cu(I)- <i>f</i> -GO	165 80	70 82	52 1673	19 1255	
9	4-CNC <sub>6</sub> H <sub>4</sub> Cl	4a	[Cu(PPh <sub>3</sub> ) <sub>3</sub> Cl] Cu(I)- <i>f</i> -GO	165 79	73 87	54 1775	20 1348	
10	4-MeOC <sub>6</sub> H <sub>4</sub> Cl	5a	[Cu(PPh <sub>3</sub> ) <sub>3</sub> Cl] Cu(I)- <i>f</i> -GO	450 216	58 66	43 1347	6 374	
11	C <sub>5</sub> H <sub>4</sub> NCl	1c	[Cu(PPh <sub>3</sub> ) <sub>3</sub> Cl] Cu(I)- <i>f</i> -GO	595 333	69 81	51 1653	5 298	

<sup>a</sup>Isolated yields.

<sup>b</sup>See Experimental section for the calculation of TONs and TOFs.

<sup>c</sup>[Cu(PPh<sub>3</sub>)<sub>3</sub>Cl] (1.35 mol% of Cu).

<sup>d</sup>Cu(I)-*f*-GO (0.049 mol% of Cu).

## 3.2 | Catalytic activity

The formation of C-C bond is one of the most fundamental reactions for the construction of molecular frameworks in organic chemistry. So, in the present project, we studied the role of the prepared catalysts toward the Sonogashira reaction. The heterogeneous catalysts are used in the present project.  $K_2CO_3$  was used as a base for optimizing the reaction conditions. Reaction conditions such as solvents and reaction temperature have been optimized. According to the results, when  $H_2O$  was used as solvent at high temperature (80 °C), an excellent yield was detected. Further investigations were focused on application of the optimized reaction conditions to



FIGURE 9 Proposed reaction pathway

Sonogashira coupling reactions of aryl halides. The results for related experiments are summarized in Table 1.

The Sonogashira reaction of activated aryl iodide and bromide with different substituents also gave good yields

**TABLE 2** Recycling result for the coupling reaction ofbromobenzene with phenylacetylene

$ \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $							
Run	1st	2nd	3rd	4th	5th	7th	
Yield (%)	84	82	85	81	83	80	
mol% of Cu	0.049	0.049	0.049	0.049	0.049	0.049	
Final TOF $(h^{-1})$	2236	2180	2261	2152	2205	2127	

ranging from 69 to 97% (Table 1, entries 1–6). In addition, the yields for chlorobenzene, 1-chloro-4-nitrobenzene, 4-chlorobenzonitrile, 1-chloro-4-methoxybenzene and 2-chloropyridine were low, ranging from 58 to 87% in (Table 1, entries 7–11). The results showed that the aryl iodide and bromide are more suitable substrates for diarylacetylene synthesis.

The mechanism of Cu-catalyzed Sonogashira coupling in presence of different catalysts was reported by several research groups.<sup>[13,15]</sup> A similar mechanism for Sonogashira reaction catalyzed by [Cu(PPh<sub>3</sub>)<sub>3</sub>Cl] complex or Cu(I)-*f*-GO nanohybrid catalysts proposed in the Figure 9. According to this mechanism, in the presence of a base, the reaction of Cu(I) complex with the alkyne would proceed to yield a Cu(I) acetylide intermediate.

TABLE 3 Catalytic performance of different Cu-based catalysts in the coupling of phenylacetylene with bromobenzene and iodobenzene

Entry	Х	Catalyst	Solvent	Ligand	Base	Temp (°C)	Time (h)	Yield (%)	Ref
1	Ι	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O <sup>a</sup>	solvent-free	DAB-Ph <sup>b</sup>	TBAF <sup>c</sup>	130-135	14	85	[16]
2	Ι	Cu(OAc) <sub>2</sub> <sup>d</sup>	DMF	Acetylacetone <sup>e</sup>	$K_2CO_3$	120	36	85	[17]
3	Ι	CuI <sup>f</sup>	DMF	DABCO <sup>g</sup>	$Cs_2CO_3$	135-140	10	94	[18]
4	Ι	CuI <sup>f</sup>	dioxane	ethylene diamine <sup>h</sup>	K <sub>2</sub> CO <sub>3</sub>	100	24	89	[19]
5	Ι	CuI <sup>i</sup>	DMF	$L^j$	K <sub>2</sub> CO <sub>3</sub>	140-145	6	90	[20]
6	Ι	[cu(PPh <sub>3</sub> ) <sub>3</sub> Cl]	$H_2O$	ligand-free	K <sub>2</sub> CO <sub>3</sub>	80	0.83	91	This work
7	Ι	Cu(I)-f-GO	$H_2O$	ligand-free	K <sub>2</sub> CO <sub>3</sub>	80	0.55	95	This work
8	Br	[ChCl][CuCl] <sup>k</sup>	DMF	ligand-free	КОН	140	9	80	[21]
9	Br	CuI <sup>i</sup>	DMF	$L^j$	K <sub>2</sub> CO <sub>3</sub>	140-145	48	35	[20]
10	Br	CuI <sup>d</sup>	DMF	DABCO <sup>g</sup>	Cs <sub>2</sub> CO <sub>3</sub>	135-140	15	91	[18]
11	Br	CuI <sup>1</sup>	dioxane	ethylene diamine <sup>m</sup>	K <sub>2</sub> CO <sub>3</sub>	110	24	62	[19]
12	Br	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O <sup>a</sup>	solvent-free	DAB-Ph <sup>b</sup>	TBAB <sup>n</sup>	130-135	20	57	[16]
13	Br	Cu(OAc) <sub>2</sub> .2H <sub>2</sub> O <sup>o</sup>	solvent-free	DAB-Ph <sup>p</sup>	TBAB <sup>n</sup>	140-145	26	72	[16]
14	Br	[Cu(PPh <sub>3</sub> ) <sub>3</sub> Cl]	$H_2O$	ligand-free	K <sub>2</sub> CO <sub>3</sub>	80	1.17	85	This work
15	Br	Cu(I)-f-GO	H <sub>2</sub> O	ligand-free	K <sub>2</sub> CO <sub>3</sub>	80	0.77	90	This work

<sup>a</sup>Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (10 mol%).

<sup>b</sup>DAB-Ph: 1,4-Diphenyl-1,4-diazabuta-1,3-diene (20 mol%).

<sup>c</sup>TBAF: Tetra-*n*-butylammonium fluoride (3 equiv).

<sup>d</sup>Cu(OAc)<sub>2</sub> (2 mmol).

eAcetylacetone (0.6 mmol).

<sup>f</sup>CuI (10 mol %).

<sup>g</sup>DABCO (20 mol %).

<sup>h</sup>Ethylene diamine (15 mol%).

<sup>i</sup>CuI (20 mol %).

<sup>j</sup>L: N,N'-dibenzyl BINAM (20 mol %).

<sup>k</sup>[ChCl][CuCl] (20 mol%).

<sup>1</sup>CuI (30 mol %).

<sup>m</sup>Ethylene diamine (45 mol%).

<sup>n</sup>TBAB (1 equiv).

°Cu(OAc)2.2H2O (50 mol%).

<sup>p</sup>DAB-Ph (100 mol%).

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Next, a Cu(III) complex was generated by the oxidative addition of aryl halide to the acetylide. Finally, the formation of a new C-C bond would proceed by reductive elimination.

Oxidative addition and reductive elimination are key steps in Sonogashira coupling reactions. The oxidative addition of copper into a C-X bond decreases in the order I > Br > > Cl > > F, based mainly on the strength of the C-X bond. As expected, electron withdrawing groups (EWGs) on the aryl ring enhance reactivity compared to electron donating groups (EDGs). As shown in Table 1, entries 5 and 6, bromobenzene is faster than 4-bromotoluene in the Sonogashira reaction because CH<sub>3</sub> is EDG and reduces oxidative addition step speed. As shown in Table 1, entries 7 and 8, chlorobenzene is slower than 1-chloro-4-nitrobenzene due to NO<sub>2</sub> group that is EWG and cause weaken  $C(sp^2)$ -Cl bond and increase the speed of oxidative addition.

For the reactions of phenylacetylene with aryl halides in the presence of Cu(I)-*f*-GO nanohybrid catalyst, TON or TOF factors are higher than that for the [Cu(PPh<sub>3</sub>)<sub>3</sub>Cl] complex and shorter times are seen, as shown in Table 1. The enhanced activity of Cu(I)-*f*-GO nanohybrid is attributed to nanostructure of the catalyst and the presence of graphene sheets that these properties increase the surface to volume ratio of the catalyst to accelerate the reactions.

To further evaluate the stability of the used catalyst, inductively coupled plasma, was also employed to determine the copper content before and after the Sonogashira reaction and no discernible leaching of Cu was observed, attributed to the strong coordination bonds. We found that Cu(I)-*f*-GO nanohybrid after seven cycles showed no discernible difference in the copper content with the fresh one (Table 2).

As shown in Table 3, we compared our results with those of the Cu-based catalysts reported in the past few years for Sonogashira reaction, taking the reactions of phenylacetylene with bromobenzene and iodobenzene as two examples.<sup>[16-21]</sup> Although some of them can also obtain high yields, the following factors make our catalysts superior to the others for these reactions. (i) Organic solvents are less favorable than H<sub>2</sub>O solvent used in this work, (ii) well-dispersed [Cu(PPh<sub>3</sub>)<sub>3</sub>Cl] complexes over the support are strongly bound with the NH<sub>2</sub> moiety which offers excellent repeatability without loss of catalytic activity, (iii) good results were obtained in short reaction times using water as the green medium and low catalyst loading, (iv) the low-cost Cu-based catalysts were prepared by a facile and efficient method, and (v) large TON for catalyst indicates that the catalyst is stable and very long-lived.

## 4 | CONCLUSIONS

In summary, we have successfully developed a facile and efficient strategy for the synthesis of a GO supported copper(I) complex catalyst. The Cu(I)-f-GO nanohybrid was used as efficient catalyst in the Sonogashira coupling reaction, with the lowest loading of 0.0049 mol%, the reaction was completed after 33 min in H<sub>2</sub>O solvent. These results demonstrate the remarkable catalytic activity of Cu(I)-f-GO nanohybrid with a TOF of 4241  $h^{-1}$ (Table 1, entry 4). To our knowledge, this is one of the highest TOF observed in copper-catalyzed Sonogashira coupling reactions.<sup>[22]</sup> We also demonstrated that the copper complexes immobilized on GO could be used repeatedly, showing good potential for industrial applications. Compared to classical reactions, this method consistently has the advantages of well dispersed Cu(I) complex over the support, low catalyst loading, short reaction times, green solvent, high yields and reusability of the catalyst. The Cu(I)-f-GO nanohybrid showed highly improved catalytic activity toward aryl chloride derivatives as compared with other catalysts that have been reported. The above results demonstrate that GO is a suitable and promising support for anchoring of metal complexes as remarkable catalysts. Notably, strategy reported here may open new avenues to coordination catalysis with graphene materials.

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