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Graphene oxide/poly(vinyl imidazole) nanocomposite: an effective support for preparation of highly loaded heterogeneous copper catalyst

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A heterogeneous polymeric catalyst was synthesized by immobilization of copper ions in a graphene oxide/poly(vinyl imidazole) nanocomposite. This catalyst has proven to be highly active in a practical protocol for click synthesis of 1,2,3-triazole via one-pot three-component cycloaddition of halides, terminal alkynes and sodium azide. The reaction was carried out in water medium and good to excellent yields of products were obtained using only 1.0 mol% of catalyst. The catalyst can be readily recovered and reused eight times under the described reaction conditions without significant loss of activity. The reaction also proceeded well with only 0.002 mol% of catalyst, which shows the high activity of the resulting copper-loaded nanocomposite. Copyright © 2015 John Wiley & Sons, Ltd.

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Keywords: graphene oxide; poly(vinyl imidazole); 1,2,3-triazoles; copper catalyst

Introduction

One of the notable reactions within the click chemistry concept is the copper-catalyzed azide–alkyne cycloaddition (CuAAC) which was originated by pioneering Sharpless and Meldal in 2001.^[1-4] The regioselective and high-yield 1,2,3-triazole is obtained in the presence of Cu(I) catalyst under the benign reaction conditions in comparison with the former Huisgen method which produced a mixture of 1,4- and 1,5-disubstituted products at high temperature.^[5,6] These five-membered nitrogen heterocycles are involved in various research areas including biological chemistry,^[7] pharmaceutical science,^[8] material science^[9] and organic synthesis.^[10] Scheme 1 shows the structure of a protease inhibitor for HIV disease, which has a triazole group.^[8]

Up to now, several methods have been developed for the synthesis of 1,2,3-triazole. These methods are based on using various homogeneous copper catalytic systems such as Cu(I) salts in the presence of base or ligands,^[11] Cu(II)/Cu(0) comprotonation,^[12] Cu/Cu oxide nanoparticles^[13] and direct reduction of Cu(II)^[14] in the reaction medium typically by ascorbate. However, these methods suffer from some drawbacks such as recyclability and recovery issues, the use of stoichiometric and relatively expensive reagents, prolonged maintenance, requirements of solvent mixture and tedious work-ups leading to generation of large amounts of toxic waste which restrict its utilization on a practical scale. To overcome the separation problem, a reasonable choice is metal immobilization on a solid support. Some distinctive solid supports have been reported like zeolites,^[15] polymer backbones,^[16] silica,^[17] magnetic nanoparticles^[18] and carbon-based materials.^[19] However, small amount of metal loading, metal leaching, difficulties in synthesis process and recovery are some disadvantages of these solid supports.

Graphene, a two-dimensional aromatic material, has received great attention in a broad category of applications based on its outstanding chemical, thermal and mechanical stability in electronics, energy storage, solar cells, optical imaging, biology and drug delivery.^[20-27] Graphene with a high specific area has great potential in the development of new kinds of composite materials especially in catalytic applications.^[28-31] Graphene oxide (GO), a single-layered oxidized form of graphene, is an alternative substrate of carbon which could serve as a significant supporting material to stabilize transition metals or active species due to its high surface area, biocompatibility and efficient adsorption capacity.[32-36] However, only a limited number of reports have dealt with the immobilization of transition metals onto GO because of its weak chelation towards metals which causes metal leaching problems. Modification of GO with chelating materials improves its metal absorbency, but low loading of metal is still an issue.[29,30]

Herein, we report the synthesis of a recyclable heterogeneous copper catalyst. In this catalytic system, GO is entrapped into a cross-linked poly(vinyl imidazole) matrix and then copper is adsorbed onto the nanocomposite support by complexation with the imidazole rings in the polymer chains. The multi-layered nature of the cross-linked polymer increases the copper loading onto the

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Scheme 1. Protease inhibitor

catalyst. The catalyst was used in the synthesis of triazole using one-pot three-component cycloaddition of sodium azide, benzyl bromide and phenylacetylene in water medium.

Materials and Methods

GO was prepared according to the Hummers method with slight modification from flake graphite. 1-Vinylimidazole was obtained from Sigma-Aldrich and was distilled before use. 1,4-Dibromobutane was obtained from Aldrich. 2,2'-Azobisisobutyronitrile (AIBN; Kanto, 97%) was recrystallized from ethanol.

Thin-layer chromatography (TLC) was performed using silica gel 60 F254 plates and UV light was used for visualization. FT-IR spectra of samples were obtained using an ABB Bomen MB-100 FT-IR spectrometer. The samples were powdered and mixed with KBr to make pellets. NMR spectra of samples were recorded with a Bruker 500 MHz NMR instrument. Thermogravimetric analysis (TGA) was conducted under a nitrogen atmosphere with a TGA Q 50 thermogravimetric analyzer. Transmission electron microscopy (TEM) images were obtained with a TOPCON-002B electron microscope. The morphology of the catalyst was observed using a MIRA3 TESCAN scanning electron microscopy (SEM) instrument.

Synthesis of GO

GO was prepared from natural graphite powder by oxidation with KMnO₄ in concentrated H₂SO₄ according to the Hummers method.^[37] In brief, 1 g of purified graphite was mixed with 13 ml of H₃PO₄ and 120 ml of H₂SO₄ in a 1 I flask at 50°C under vigorous stirring. KMnO₄ (6 g) was slowly added to the mixture and stirred for 8 h. When the color of the solution changed to brown, the flask was placed in an ice bath and 200 ml of distilled water was added to the solution. An amount of 2 ml of H₂O₂ (30%) was slowly added until no gas was produced. The mixture was centrifuged and washed with HCl solution (10%) to remove residual ions. Then, the GO was washed with distilled water to neutralize the solution and to remove excess acid. The GO solution was centrifuged at 8000 rpm for 15 min; the obtained yellow-brown powder was dried at 60°C in an oven. A TEM image of GO is presented in the supporting information.

Synthesis of Cross-linker

Cross-linker was prepared as previously reported.^[38] Amounts of 10 mmol of 1-vinylimidazole and 5 mmol of 1,4-dibromobutane were added to 30 ml of methanol in a 100 ml round-bottom flask. The mixture was stirred at room temperature overnight and heated to 60°C for 16 h. The reaction mixture was cooled to room temperature and it was added slowly to 250 ml of diethyl ether. The obtained white participate was placed in a refrigerator for 5 h and then washed three times with diethyl ether and dried under vacuum at 50°C.

Synthesis of Catalyst

GO (0.2 g), 1-vinylimidazole (1 g) and cross-linker (0.4 g) were loaded into a 100 ml round-bottom flask and 10 ml of methanol was added. The mixture was sonicated for 20 min and then deoxygenated under argon for another 20 min. Afterwards, AIBN (3 wt%) was added to initiate polymerization. The flask was equipped with a condenser and placed in an oil bath at 70°C for a day. The solid product (GO/Pim) was washed several times with methanol to eliminate excess reactants and was dried under vacuum at 50°C. Amounts of 0.50 g of the resulting GO/Pim powder and 0.40 g of CuSO₄ were added into 5 ml of water in a 50 ml round-bottom flask and placed at 50°C overnight. The reaction product (GO/Pim/Cu) was filtered and washed several times with water and methanol and then the catalyst was dried at 50°C in an oven.

General Procedure for CuAAC Reaction Catalyzed by GO/Pim/Cu

Phenylacetylene (1 mmol), benzyl bromide (1 mmol), sodium azide (1.3 mmol) and water (2 ml) were added into a 10 ml round-bottom flask and stirred for 10 min at room temperature. Then, 4.7 mg of GO/Pim/Cu (1.0 mol%) was added with 10 mol% of sodium ascorbate to reduce Cu(II) to Cu(I). The mixture was stirred for an appropriate time at 50°C as indicated in Table 1. After completion of the reaction, which was monitored with TLC (using silica gel with ethyl acetate and *n*-hexane (1:4) as eluent), the catalyst was removed by filtration and was washed three times with 5 ml of methanol and dried for another run. The resulting product was extracted using hot ethyl acetate and dried under reduced pressure to afford the desired triazole as a white crystalline solid.

Results and Discussion

The desired catalyst was synthesized in the following steps. Step one: GO was synthesized by exfoliation of graphite based on the Hummers method.^[37] This method produces GO with sufficient hydroxyl and carboxyl groups to give it an amphiphilic character such that it can perform as a phase transfer substrate between organic materials and aqueous solvent. Step two: GO was entrapped in cross-linked poly(vinyl imidazole) prepared by free radical initiation polymerization of 1-vinylimidazole, GO and cross-linker agent. The polymerization was initiated by AIBN and the cross-linked insoluble copolymer was precipitated from the solution. Step 3: copper was loaded using complexation of copper sulfate and imidazole groups (Scheme 2).

Such an approach for the preparation of the heterogeneous catalyst improves the loading level of copper ions onto the catalyst surface due to multi-layered structure of cross-linked poly(vinyl imidazole) in comparison with traditional supported materials. Therefore, a low weight percentage of the catalyst could be used compared to the substrates. It is certainly beneficial for large-scale application to avoid using large amounts of catalyst and solvent. Moreover, the presence of GO as an inexpensive and abundant material with high surface area can enhance the activity of the supported material which facilitates synthetic transformation. Also, defects in the GO structure endow it with unpaired spins, which is helpful for activation of small molecules by the spin flip process.

FT-IR spectroscopy was employed to characterize the catalyst structure. Figure 1 shows the FT-IR spectra of GO, GO/Pim and GO/Pim/Cu. The FT-IR spectrum of GO (Fig. 1(a)) shows stretching vibration of O–H as a broad peak at 3300–3500 cm⁻¹. The peaks

Table 1. Optimization of synthesis of 1,2,3-triazole catalyzed by GO/Pim/Cu^a

+ NaN ₃ , Sodium ascorbate									
Entry	Catalyst	Solvent	Catalyst loading (mol%)	T (°C)	Time (h)	NaN ₃ (eq.)	Yield (%) ^b	TOF (h^{-1})	
1	—	H ₂ O	_	r.t.	24	1	<1 ^c	_	
2	—	H ₂ O	_	70	8	1	<3 ^c	—	
3	CuSO ₄	H ₂ O	5.0	50	10	1	23	0.46	
4	GO/Pim	H ₂ O	10 mg	50	10	1	<3 ^c	—	
5	GO/Pim/Cu	H ₂ O	2.0	r.t.	3	1	80	13.33	
6	GO/Pim/Cu	H ₂ O	1.5	r.t.	3	1	77	17.11	
7	GO/Pim/Cu	H ₂ O	1.0	r.t.	3	1	76	25.33	
8	GO/Pim/Cu	H ₂ O	1.0	r.t.	4	1	84	21	
9	GO/Pim/Cu	H ₂ O	0.5	r.t.	3	1	64	42.66	
10	GO/Pim/Cu	H ₂ O	0.3	r.t.	3	1	43	47.77	
11	GO/Pim/Cu	H ₂ O	1.0	80	0.5	1	99	198	
12	GO/Pim/Cu	H ₂ O	1.0	50	0.5	1	94	188	
13	GO/Pim/Cu	H ₂ O	1.0	50	0.5	1.3	99	198	
14	GO/Pim/Cu	H ₂ O	0.7	50	0.5	1.3	77	220	
15	GO/Pim/Cu	H ₂ O	0.3	50	0.5	1.3	54	360	
16	GO/Pim/Cu	Neat	1.0	50	3	1.3	40	13.33	
17	GO/Pim/Cu	t-BuOH	1.0	50	3	1.3	71	23.66	
18	GO/Pim/Cu	DMF	1.0	50	3	1.3	62	20.66	
19	GO/Pim/Cu	CH₃CN	1.0	50	3	1.3	21	7	
20	GO/Pim/Cu	CH ₂ Cl ₂	1.0	50	3	1.3	<1 ^c	_	
21	GO/Pim/Cu	THF	1.0	50	3	1.3	10	3.33	
22	GO/Pim/Cu	Toluene	1.0	50	3	1.3	33	11	
23	Pim/Cu ^d	H ₂ O	1.0	50	1	1.3	84	84	
24	GO/Pim/Cu ^e	H ₂ O	0.002	50	20	1.3	93	2325	

^aReaction condition: phenylacetylene (1 mmol), benzyl bromide (1 mmol), sodium ascorbate (10 mol%), solvent (2 ml). ^bIsolated yield.

^cMainly recovery of the starting materials.

^dCross-linked poly(vinyl imidazole) was used. Loading amount of copper on Pim is 0.61 mmol g^{-1} .

^e10 mmol scale of reactant.



Scheme 2. Synthesis and structure of GO/Pim/Cu

at 1730 and 1623 cm⁻¹ correspond to C=O and C=C stretching vibrations, respectively. Also, the weak peaks at 1084 and 1387 cm⁻¹ are related to C-O stretching. In the FT-IR spectrum of GO/Pim (Fig. 1(b)), characteristic peaks of imidazolium ring are observed at 1565 and 1640 cm⁻¹ attributed to C=C and C=N bonds. The

aliphatic C–H band at 2930 cm⁻¹ clearly indicates the presence of imidazole rings. The FT-IR spectrum of GO/Pim/Cu (Fig. 1(c)) shows a new strong band at 1120 cm⁻¹ which is attributed to stretching vibration of S=O bond, indicating the presence of CuSO₄ in the catalyst structure.

Thermal stability and organic content of GO/Pim/Cu were investigated using TGA (Fig. 2(II)). In both curves, weight loss below 150°C is attributed to the loss of adsorbed water molecules. The TGA curve of GO (Fig. 2(Ia)) shows two weight losses: the first is attributed to loss of hydroxyl and carboxyl groups and the second to GO sheet decomposition. The TGA curve of the catalyst (Fig. 2(Ib)) shows a main weight loss at 340°C which is attributed to dissociation of imidazole groups from the main alkyl chains. It is necessary to emphasize that the loading amount of the monomer and the cross-linker cannot be calculated individually using TGA due to the identical nature of the monomer and the cross-linker. DTG analysis of the catalyst (Fig. 2(II)) also shows a main strong peak at 340°C. These results indicate that the catalyst is thermally stable and can be used under harsh reaction conditions at high temperature (lower than 340°C).

Surface morphologies of Pim/Cu and GO/Pim/Cu were visualized using SEM, as shown in Figs. 3(a) and (b), respectively. As can be seen, Pim/Cu has a smooth surface without any porosity but



Figure 1. FT-IR spectra of (a) GO, (b) GO/Pim and (c) and GO/Pim/Cu

GO/Pim/Cu shows a layered structure due to the presence of GO. Catalytic surface area and catalytic activity could be improved due to such a layered structure. Energy-dispersive X-ray spectroscopy (EDS) analysis of GO/Pim/Cu can confirm the presence of copper in the catalyst (Fig. 3(c)).

A TEM image of the GO/Pim/Cu catalyst is shown in Fig. 4. The TEM image of the catalyst shows the presence of GO sheets in the copolymer matrix.

The loading amount of Cu(II) ions in GO/Pim/Cu was calculated with atomic absorption spectroscopy using standard samples. It is found that the loading amount of Cu(II) ions in the catalyst is 2.10 mmol g^{-1} which is quite high for such a metal-supported catalyst. To investigate the complexation of copper to Pim chains, the loading level of imidazole groups in the catalyst structure was calculated by titration of GO/Pim with HCI (0.1 M). The result of titration shows that the loading level of imidazole groups is about 5.60 mmol g^{-1} . This result indicates that most of the copper ions are coordinated to two imidazole rings (Scheme 2). Moreover, it can be concluded that copper ions do not penetrate into the interior layers of the catalyst and some of the imidazole rings of polymer chains are uncoordinated.

The catalytic activity of GO/Pim/Cu was investigated by choosing the reaction between benzyl bromide, sodium azide and phenylacetylene as a model reaction. In order to obtain the best catalytic conditions for synthesis of *N*-benzyl-4-phenyl-1,2,3triazole, several parameters such as catalyst loading, NaN₃ amount, solvent and temperature were examined. Considering the green chemistry concept in the synthesis of triazoles, we focused our attention on the development of this reaction in water as a green solvent. Water, a universal solvent with low cost and environmental



Figure 3. SEM images of (a) Pim/Cu and (b) GO/Pim/Cu. (c) EDS analysis of GO/Pim/Cu

acceptability, can be chosen as a green alternative to reduce the production of toxic waste. Therefore, the optimization of the reaction was mainly conducted in water (Table 1). The results show that no product is produced when using no catalyst even at higher temperature (entries 1 and 2). When 5 mol% of copper sulfate is used as a catalyst, the reaction yield is 23%. GO/Pim has no catalytic activity in the absence of copper (entry 4). But using 2 mol% of GO/Pim/Cu gives 80% yield at room temperature. It is found that a reduction in the amount of catalyst reduces the yield of products (entries 5–10). Moreover, reducing the reaction temperature from 80 to 50°C slightly reduces the yield of triazole product (entries 11 and 12). Due to the importance of avoiding consumption of energy and time, the use of 1 mol% of GO/Pim/Cu at 50°C was chosen for further optimization of the model reaction (entry 12). It is found that increasing the amount of NaN₃ from 1 to 1.3 eq. has a positive effect on the yield of product (entry 13). In solvent-free condition no







Figure 4. TEM image of GO/Pim/Cu catalyst

significant yield is obtained (entry 16). Also, various kinds of solvents were assessed which can be categorized to aprotic polar and non-polar (entries 17–22). Aprotic solvents give lower yields which can be attributed to their less capability of dissolving NaN₃. However, polar aprotic solvents give higher yields, more than

Table 2. Three-component click synthesis of 1,2,3-triazoles using GO/ Pim/Cu catalyst ^a Pim/Cu catalyst ^a						
R-X + NaN ₃ + R'—≡		GO/Pim/Cu		→ N=N R-N R'		
Entry	R	R'	Time (h)	Yield of 3 (%) ^b		
1	PhCH ₂	Ph	0.5 (X = Br)	3a : 94		
			1.5 (X = Cl)	3a : 93		
2	4-BrPhCH ₂	Ph	1 (X = Br)	3b : 90		
3	4-MePhCH ₂	Ph	0.5 (X = Br)	3c : 91		
			1.5 (X = Cl)	3d : 88		
4	NH ₂ COCH ₂	Ph	0.5 (X = Br)	3e : 96		
5	C ₄ H ₉	Ph	0.5 (X = Br)	3f : 87		
6	C_4H_8	Ph	1 (X = Br)	3g : 88		
7	Allyl	Ph	1.5 (X = Br)	3h : 83		
			2 (X = CI)	3h : 80		
8	PhCOCH ₂	Ph	1.5 (X = Br)	3i : 90		
9	C ₂ H₅OCOCH ₂	Ph	2 (X = Br)	3j : 91		
10	CH ₃ C(CH ₃)CHCH ₂	Ph	0.5 (X = Br)	3k : 92		
			1 (X = CI)	3k : 90		
11	1-(Chloromethyl)	Ph	2.5	3I : 90		
	naphthalene					
12	PhCH ₂	Ph	2 (X = OTs)	3a : 95		
13	PhCH ₂	4-NO ₂ Ph	3 (X = Br)	3m : 90 ^c		
14	PhCH ₂	4-MeOPh	3.5 (X = Br)	3n : 91 ^c		
15	PhCH ₂	EtO ₂ C	3.5 (X = Br)	3o : 93		
16	PhCH ₂	C_5H_{11}	2.5 (X = Br)	3p : 86		
17	Allyl	C_5H_{11}	2 (X = Br)	3q : 90		
18	PhCOCH ₂	C_5H_{11}	3 (X = Br)	3r : 87		
19	4-BrPhCH ₂	C_5H_{11}	3 (X = Br)	3s : 91		
20	4-BrPhCH ₂	OHCH ₂	2.5 (X = Br)	3t : 90		
21	PhCH ₂	OHCH ₂	1.5 (X = Br)	3u : 91		
³ Dearting and times all ad halida (1 game) NaN (1 2 game)						

⁴Reaction conditions: alkyl halide (1 mmol), NaN₃ (1.3 mmol), acetylene (1 mmol), GO/Pim/Cu (1.0 mol%), H₂O (2 ml).

^blsolated yield.

^cMeOH used as solvent to dissolve the substrates.

approximately 70%. In another experiment cross-linked poly(vinyl imidazole) (Pim) was prepared and used as a support for copper ions (entry 23). The result shows that in the absence of GO in the catalyst structure, the loading amount of copper is dramatically reduced to 0.61 mmol g⁻¹ which clearly shows the effect of GO on adsorption of copper ion. Therefore, with lower copper loading, higher mass of Pim/Cu is used compare to usage of GO/Pim/Cu. Moreover, GO/Pim/Cu shows higher activity than Pim/Cu which can be attributed to the porous structure of GO/Pim/Cu as a result of the presence of GO. For further investigation of catalyst activity, a very small amount of catalyst was used in large-scale production of triazole. The reaction was performed at a 10 mmol scale of reactants in the presence of 0.002 mol% of catalyst which gives a 93% yield for longer reaction time (20 h).

Encouraged by these results, several alkynes and halides were used for the synthesis of 1,2,3-triazole under the optimized conditions (Table 2). Both aliphatic and aromatic terminal alkynes readily produce the corresponding 1,2,3-triazole in good to excellent yields. Aliphatic alkynes in comparison to aromatic ones require longer reaction times. Surprisingly, electron-withdrawing alkynes which are difficult substrates for 1,2,3 triazole synthesis, give high yield of products with acceptable reaction time. It is found that chlorides have slower reaction rates than bromides (Table 2, entries 1, 3, 7 and 10). Hence, longer reaction times are required to achieve equivalent transformations. Moreover, electron-donating benzyl halides give lower yields in longer reaction times. These results reveal the efficiency of GO/Pim/Cu for the synthesis of 1,4disubstituted 1,2,3-triazoles.





Figure 6. Reusability experiments

Figure 5. Leaching experiment: reaction with catalyst (blue line) and reaction after catalyst removal (red line)

Table 3. Comparison of GO/Pim/Cu with reported catalysts in the synthesis of triazoles ^a								
Catalyst	Copper loading on catalyst (mmol g^{-1})	Catalyst loading (mol%)	Time (h)	T (℃)	Yield (%)	Ref.		
Cell-Cul NPs	0.37	3.7	2	70	96	[39]		
PS-C22-Cul (Cul cryptand 22)	0.15	0.6	10	r.t	99	[40]		
Cu/C	0.47	1	0.6–1	100	91	[41]		
MNP@BiimM (Cu)	1.7	0.85	0.5	r.t	99	[42]		
Cu NPs/Magsilica	1.07	4.3	1	70	98	[43]		
Functionalized chitosan/Cu	0.6	0.1	12	70	99	[44]		
Cross-linked poly(IL)/Cu	1.0	1.0	48	r.t	98	[45]		
lonic polymer/Cu	0.25	5	2.5	r.t	99	[46]		
Poly(4-vinyl pyridine)/Cu	1.32	13	0.4	100	89	[47]		
Nano ferrite/glutathione/copper	0.25	2.5	0.17	120, mw	99	[48]		
Poly(NIPAM/Im)/Cu	0.46	0.25	1.5	50	99	[49]		
Poly(NIPAM/Im)/Cu	0.46	0.00045	31	50	94	[49]		
MNP-CuBr	0.44	1.46	0.3	80, mw	96	[50]		
Cu/Al ₂ O ₃	0.29	10	1	r.t	92	[51]		
Cu(II)/clay	1.5	2	0.25	Sonic., r.t.	98	[52]		
Cu/SiO ₂	2.59	10	0.17	70, 50, mw	92	[53]		
CuNPs/MagSilica	1.07	4.3	1	70	98	[53]		
Cu NP/activated carbon	0.25	0.5	3	70	98	[54]		
MNP@PIL/Cu	1.87	0.7	0.4	50	95	[38]		
GO/Pim/Cu	2.1	1.0	0.5	50	99	This work		
GO/Pim/Cu	2.1	0.002	20	50	93	This work		
^a Reaction conditions: phenylacetylene, benzyl bromide, sodium ascorbate, sodium azide.								

Metal contamination of products is a serious issue while working with metal-supported heterogeneous catalysts. Metal leaching would imply a time-consuming and costly clean-up step which makes the synthesis procedure more expensive, and also leaching of active species could decrease turnover frequency (TOF). In order to investigate whether the observed catalytic activity is derived from the solid-supported heterogeneous catalyst or leached metal species, the following experiment was performed. The model reaction was carried out under the optimized condition (Table 1, entry 13), and the catalyst was removed from the reaction mixture after 10 min by centrifugation. Then, the reaction was allowed to continue for more than 45 min while monitoring with GC. The result shows that no further amount of product (1,2,3-triazole) is obtained after catalyst separation (Fig. 5). After catalyst removal, the reaction mixture was also analyzed using inductively coupled plasma optical emission spectrometry, and no significant leached copper is detected. These results verify the heterogeneous feature of the catalyst.

Along with the high activity of GO/Pim/Cu in the 1,2,3-triazole synthesis, other important advantages of the catalyst are its reusability and stability under the reaction conditions. To investigate the recyclability of the catalyst, reaction between benzyl bromide, phenylacetylene and sodium azide under the optimized conditions was selected as a model. After completion of the reaction, the catalyst was easily recovered by centrifugation and reused in another vessel under the same conditions. As depicted in Fig. 6, the catalyst can be reused eight times in subsequent runs with almost 92% yield and without significant loss of activity. According to the leaching experiment, a slight decrease in yield can be ascribed to the loss of catalyst mass during washing and recovery procedures.

To establish the merit of the current procedure for the synthesis of 1,2,3-triazole, a brief comparison of activity between GO/Pim/Cu and some other supported copper catalysts is presented at Table 3. Among the heterogeneous catalysts in Table 3, the present method gives high yield as well as requiring a low applied amount of

catalyst in the reaction. The presence of GO along with imidazole groups strongly adsorbs copper ions which results in high copper loading on the GO/Pim/Cu catalyst.

Conclusions

We have demonstrated a facile route for the one-pot synthesis of 1,4-disubstittued 1,2,3-triazole via a novel, environmentally benign entrapped graphene oxide/cross-linked poly(vinyl imidazole)-supported copper(II) catalyst. The multilayered structure of the catalyst provides a convenient support for high loading of active metal to reduce the amount of the catalyst in each reaction. The resulting catalyst was shown to be applicable to a wide substrate scope (aromatic/aliphatic alkynes and alkyl/benzyl halides) giving excellent yields under mild reaction conditions. The operational simplicity, purity of products, absence of hazardous organic solvents and high recyclability of the catalyst (up to eight runs) make it an attractive proposition for large-scale applications.

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References

- S. Mohammed, A. K. Padala, B. A. Dar, B. Singh, B. Sreedhar, R. A. Vishwakarma, S. B. Bharate, *Tetrahedron* **2012**, *68*, 8156–8162.
- [2] C. W. Tornøe, C. Christensen, M. Meldal, J. Org. Chem. 2002, 67, 3057–3064.
- [3] H. C. Kolb, M. G. Finn, K. B. Sharpless, Angew. Chem. Int. Ed. 2001, 40, 2004–2021.
- [4] V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, Angew. Chem. 2002, 41, 2596–2599.
- [5] Y. B. Zhao, Z. Y. Yan, Y. M. Liang, Tetrahedron Lett. 2006, 47, 1545–1549.

- [6] B. Y. Lee, S. R. Park, H. B. Jeon, K. S. Kim, *Tetrahedron Lett.* 2006, 47, 5105–5109.
- [7] D. R. Buckle, C. J. M. Rockell, J. Chem. Soc. Perkin Trans. 1982, 1, 627–630.
- [8] M. Whiting, J. Muldoon, Y. C. Lin, S. M. Silverman, W. Lindstrom, A. J. Olson, H. C. Kolb, M. G. Finn, K. B. Sharpless, J. H. Elder, V. V. Fokin, *Angew. Chem. Int. Ed.* **2006**, *45*, 1435–1439.
- [9] H. Nandivada, X. W. Jiang, J. Lahann, Adv. Mater. 2007, 19, 2197–2208.
 [10] V. D. Bock, H. Hiemstra, J. H. van Maarseveen, Eur. J. Org. Chem. 2006, 1,
- [10] V. D. BOCK, H. Hiemstra, J. H. van Maarseveen, Eur. J. Org. Chem. 2006, 1, 51–68.
- [11] D. Wang, N. Li, M. M. Zhao, W. L. Shi, C. W. Ma, B. H. Chen, Green Chem. 2010, 12, 2120–2123.
- [12] P. Appukkuttan, W. Dehaen, V. V. Fokin, E. V. Dereycken, Org. Lett. 2004, 6, 4223–4225.
- [13] G. Molteni, C. L. Bianchi, G. Marinoni, N. Santo, A. Ponti, New J. Chem. 2006, 30, 1137–1139.
- [14] J. Y. Kim, J. C. Park, H. Kang, H. Song, K. H. Park, Chem. Commun. 2010, 46, 439–444.
- [15] A. Alix, S. Chassaing, P. Pale, J. Sommer, *Tetrahedron* 2008, 64, 8922–8929.
- [16] P. Diz, A. Coelho, A. El Maatougui, J. Azuaje, O. Caamaño, E. Sotelo, J. Org. Chem. 2013, 78, 6540–6549.
- [17] P. Li, L. Wang, Y. Zhang, Tetrahedron 2008, 64, 10825–10830.
- [18] G. Chouhan, D. Wang, H. Alper, Chem. Commun. 2007, 45, 4809-4811.
- [19] B. H. Lipshutz, B. R. Taft, Angew. Chem. Int. Ed. 2006, 45, 8235–8238.
- [20] A. K. Geim, K. S. Novoselov, Nat. Mater. 2007, 6, 183–191.
- [21] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, A. K. Geim, *Rev. Mod. Phys.* **2009**, *81*, 109–162.
- [22] J. L. Li, B. Tang, B. Yuan, L. Sun, X. G. Wang, Biomaterials 2013, 34, 9519–9534.
- [23] J. Liu, L. Cui, D. Losic, Acta Biomater. **2013**, *9*, 9243–9257.
- [24] M. Terrones, A. R. Botello-Méndez, J. Campos-Delgado, F. López-Urías, Y. I. Vega-Cantú, F. J. Rodríguez-Macías, A. L. Elías, E. Muñoz-Sandoval, A. G. Cano-Márquez, J. C. Charlier, H. Terrones, *Nano Today* **2010**, *5*, 351–372.
- [25] V. Singh, D. Joung, L. Zhai, S. Das, S. I. Khondaker, S. Seal, Prog. Mater. Sci. 2011, 56, 1178–1271.
- [26] M. Pumera, Energy Environ. Sci. 2011, 4, 668–674.
- [27] X. Wang, L. Zhi, K. Müllen, Nano Lett. 2008, 8, 323-327.
- [28] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, R. S. Ruoff, *Nature* **2006**, *442*, 282–286.
- [29] Z. S. Wu, G. Zhou, L. C. Yin, W. Ren, F. Li, H. M. Cheng, *Nano Energy* 2012, 1, 107–131.
- [30] C. Zhang, R. Hao, H. Yin, F. Liu, Y. Hou, Nanoscale 2012, 4, 7326–7329.
- [31] L. S. Zhang, X. Q. Liang, W. G. Song, Z. Y. Wu, Phys. Chem. Chem. Phys. 2010, 12, 12055–12059.

- [32] D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, Chem. Soc. Rev. 2010, 39, 228–240.
- [33] C. Xu, X. Wang, J. Zhu, J. Phys. Chem. C 2008, 112, 19841–19845.
- [34] L. Dong, R. R. S. Gari, Z. Li, M. M. Craig, S. Hou, Carbon 2010, 48, 781–787.
- [35] G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, R. Mülhaupt, J. Am. Chem. Soc. 2009, 131, 8262–8270.
- [36] J. Pyun, Angew. Chem. Int. Ed. 2011, 50, 46-48.
- [37] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour, ACS Nano 2010, 4, 4806–4814.
- [38] A. Pourjavadi, S. H. Hosseini, N. Zohreh, C. Bennett, RSC Adv. 2014, 4, 46418–46426.
- [39] P. V. Chavan, K. S. Pandit, U. V. Desai, M. A. Kulkarni, P. P. Wadgaonkar, RSC Adv. 2014, 4, 42137–42146.
- [40] B. Movassagh, N. Rezaei, Tetrahedron 2014, 70, 8885-8892.
- [41] H. Sharghi, R. Khalifeh, M. M. Doroodmand, Adv. Synth. Catal. 2009, 351, 207–218.
- [42] M. Tajbakhsh, M. Farhang, S. M. Baghbanian, R. Hosseinzadeh, M. Tajbakhsh, New J. Chem. 2015, 39, 1827–1839.
- [43] F. Nador, M. A. Volpe, F. Alonso, A. Kirschning, G. Radivoy, *Appl. Catal. A* 2013, 455, 39–45.
- [44] M. Chtchigrovsky, A. Primo, P. Gonzalez, K. Molvinger, M. Robitzer, F. Quignard, F. Taran, Angew. Chem. 2009, 121, 6030–6034.
- [45] Y. Wang, J. Liu, C. Xia, Adv. Synth. Catal. 2011, 353, 1534–1542.
- [46] U. Sirion, Y. J. Bae, B. S. Lee, D. Y. Chi, Synlett 2008, 15, 2326–2330.
- [47] J. Albadi, M. Keshavarz, F. Shirini, M. Vafaie-nezhad, *Catal. Commun.* 2012, 27, 17–20.
- [48] R. B. Nasir Baig, R. S. Varma, Green Chem. 2012, 14, 625–632.
- [49] Y. M. A. Yamada, S. M. Sarkar, Y. Uozumi, J. Am. Chem. Soc. 2012, 134, 9285–9290.
- [50] X. Xiong, L. Cai, Catal. Sci. Technol. 2013, 3, 1301–1307.
- [51] N. Mukherjee, S. Ahammed, S. Bhadra, B. C. Ranu, Green Chem. 2013, 15, 389–397.
- [52] B. A. Dar, A. A. Bhowmik, A. Sharma, P. R. Sharma, A. Lazar, A. P. Singh, M. Sharma, B. Singh, *Appl. Clay Sci.* **2013**, 80–81, 351–357.
- [53] C. S. Radatz, L. A. Soares, E. R. Vieira, D. Alves, D. Russowsky, P. H. Schneider, *New J. Chem.* **2014**, *38*, 1410–1417.
- [54] F. Alonso, Y. Moglie, G. Radivoy, M. Yus, Adv. Synth. Catal. 2010, 352, 3208–3214.

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