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FULL PAPER

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A novel and highly efficient polyaniline-functionalized multiwall carbon nanotube-supported cu(I) complex for Sonogashira coupling reactions of aryl halides with phenylacetylene

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A polyaniline-functionalized multiwall carbon nanotube-supported Cu(I) complex was developed as an efficient catalyst for the Sonogashira reactions of aryl halides with phenylacetylene in the presence of potassium hydroxide in dimethylformamide at 135 °C under nitrogen atmosphere. The corresponding products were generated in good to excellent yields using this catalytic system. Moreover, the multiwall carbon nanotube-supported Cu(I) catalyst was simply recycled and reused for six consecutive runs.

KEYWORDS

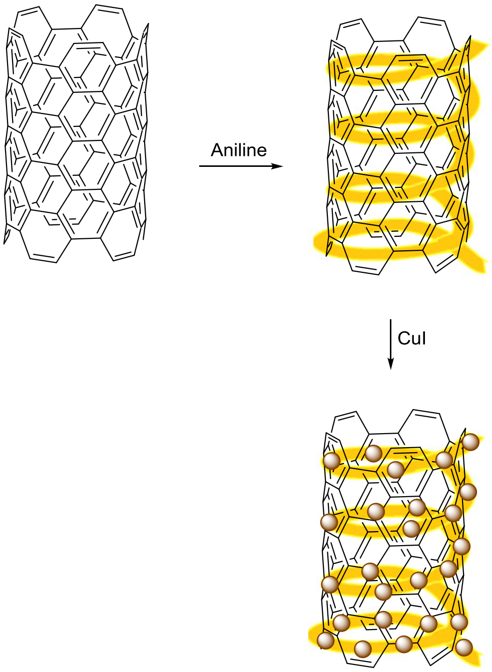
copper(I) nanocatalyst, heterogeneous catalyst, multiwall carbon nanotubes, polyaniline, Sonogashira coupling

1 | INTRODUCTION

The palladium/copper-catalyzed Sonogashira–Hagihara cross-coupling reaction is one of the most effective synthetic techniques for the preparation of carbon–carbon bonds.[1,2] It supplies simple and easy access to aryl alkynes and relevant conjugated enynes which are generally employed as precursors to pharmaceuticals, organic materials, natural products and industrial products.[3,4]

The original procedure for Sonogashira coupling reactions includes the use of a homogeneous palladium catalyst and a copper(I) salt as co-catalyst.[5,6] The role of the copper co-catalyst is to create a copper acetylide intermediate for transmetallation with palladium. However, palladium is expensive and toxic,[7] and a homogeneous palladium catalyst makes tedious the separation and recycling of the catalyst and might cause intolerable palladium pollution of products. Moreover, the need for a copper(I) salt as a co-catalyst restricts the employment of Sonogashira–Hagihara reactions in large-scale uses. Numerous significant studies have concentrated on the development of modern catalytic systems with impressive catalytic activity, including under phosphine (as a ligand)- and palladium-free conditions. Many metals have been advanced as active catalysts for Sonogashira cross-coupling reactions. Salts and nanoparticles of copper,[8] cobalt,[9] iron,[10] silver,[11] nickel[12] and ruthenium,[13] with various ligands have been identified as catalysts for Sonogashira-type cross-coupling reactions.

Recently, much effort has been devoted to the employment of copper complexes as catalysts for the Sonogashira coupling of aryl halides with terminal alkynes,[14] because copper salts are relatively economical and the system is mild and simple. In recent years numerous copper-based catalytic systems have been reported, including, Cu(I)/diamine,[15] the salt of [*N*-benzyl DABCO]$^+$[Cu_4Cl_5]$^-$,[8] choline chloride/CuCl,[16] monobenzylnicotinium chloride combined with copper(I) chloride,[17] Cu_2O/tetraethylammonium prolinate,[18] CuCl/Phen/Cs_2CO_3,[19] CuI/1,10-phenanthroline and CuI/2,2-bipyridine,[20] Cu_2Se nanoflakes[21] and DABCO-functionalized silica-supported copper(I) complex.[22] Hence, the development of a novel catalytic system that is efficient, readily available, inexpensive, eco-friendly and



SCHEME 1 Synthesis of heterogeneous cu(I)-PANI@MWCNT nanocatalyst

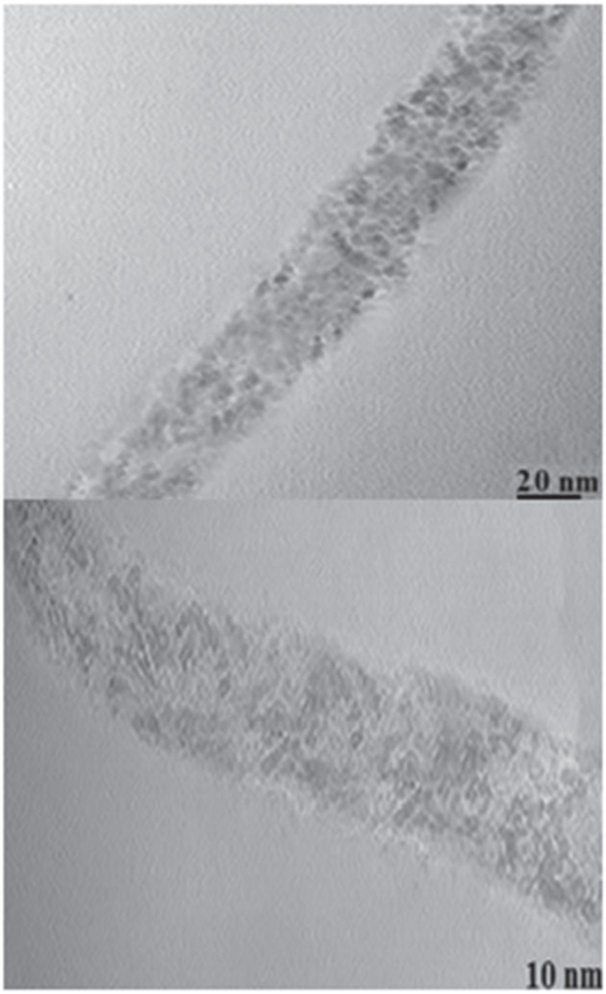


FIGURE 1 TEM image of cu(I)-PANI@MWCNT complex

operative under mild conditions would be useful in contemporary synthesis.

Herein, we report the Sonogashira coupling reactions of phenylacetylene with aryl halides catalyzed by a polyaniline-functionalized multiwall carbon nanotube-supported Cu(I) (Cu(I)-PANI@MWCNT) complex in the presence of potassium hydroxide in dimethylformamide (DMF), as shown in Scheme 1.

MWCNTs are some of the most up-to-date materials in organic chemistry and other fields of science which have been investigated widely due to their extraordinary mechanical, thermal and chemical properties and special potential for practical applications.[23,24] MWCNTs functionalized with polymers such as polyaniline show notable characteristics such as frequent heteroatom-containing sites, enormously high surface area amenable to metal conjugation and effective separation and allowing metal-free products. These features make them suitable as supports for immobilization of metal complexes which can then be employed as competent catalytic systems.[25–28]

In the work reported in this paper, we performed Sonogashira coupling reactions using the Cu(I) complex that can act as a new, effective, inexpensive and interesting catalyst. Also, we focused on removal of palladium

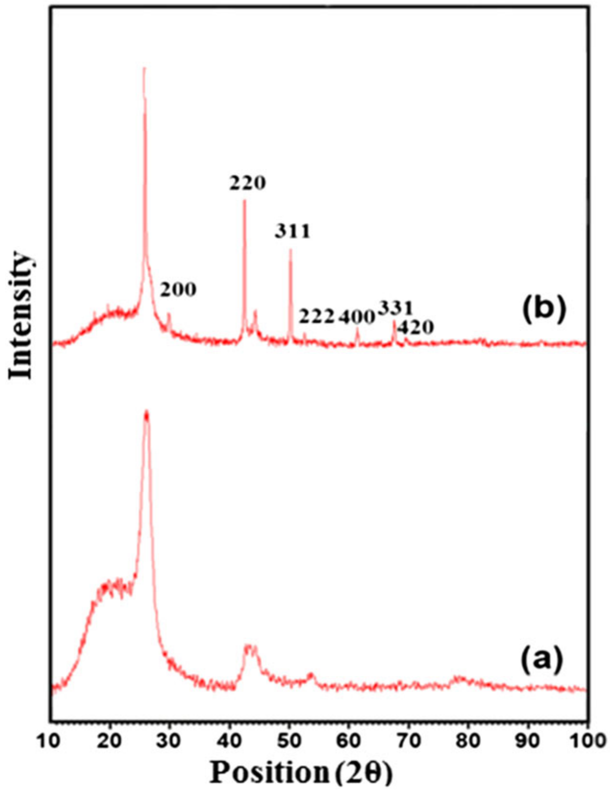


FIGURE 2 XRD patterns of (a) MWCNT and (b) cu(I)-PANI@MWCNT

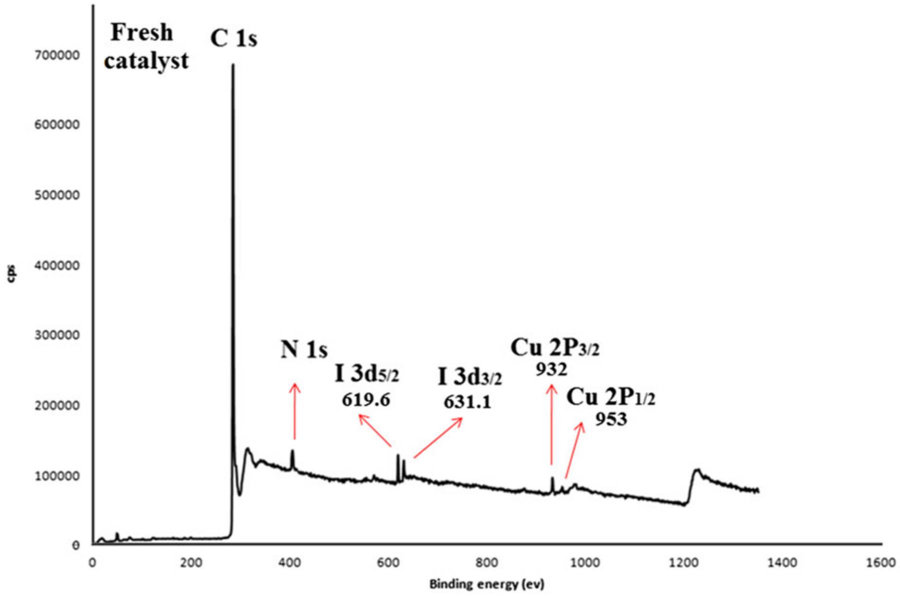
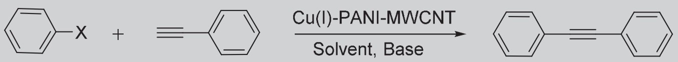


FIGURE 3 XPS spectrum of recycled cu(I)-PANI@MWCNT after sixth run

TABLE 1 Sonogashira coupling reaction of phenylacetylene with aryl halides in presence of various bases[a]



Entry	X	Base	Solvent	Time (h)	Catalyst (mol%)	Yield (%)[b]
1	I	Et_3N	DMF	2	10	93
2	I	Pyridine	DMF	2	10	82
3	I	Piperidine	DMF	2	10	93
4	I	Pyrrolidine	DMF	2	10	85
5	I	KOH	DMF	2	10	96
6	I	K_2CO_3	DMF	2	10	95
7	Br	Et_3N	DMF	4	10	57
8	Br	Pyridine	DMF	4	10	59
9	Br	Piperidine	DMF	4	10	52
10	Br	Pyrrolidine	DMF	4	10	54
11	Br	KOH	DMF	4	10	60
12	Br	K_2CO_3	DMF	4	10	54
13[c]	I	KOH	DMF	2	10	64
14	I	KOH	DMF	2	6	60
15	I	KOH	DMSO	2	10	89
16	I	KOH	CH_3CN	2	10	15
17	I	KOH	EtOH	2	10	5
18	I	KOH	Peg 200	2	10	15
19	I	KOH	H_2O	2	10	5

[a] Reaction conditions: phenylacetylene (1.2 mmol), halobenzene (1.0 mmol), base (2.0 mmol), solvent (4 ml), 135 °C, nitrogen atmosphere.

[b] GC yield.

[c] Reaction at 120 °C.

metal and replaced it with copper metal in our catalytic system. Compared to the frequently used costly palladium catalysts, copper-based catalysts have an economic advantage, and, therefore, remain noteworthy for industrial-scale preparations.

2 | RESULTS AND DISCUSSION

Polyaniline-functionalized MWCNTs (PANI@MWCNT) were synthesized by *in situ* oxidative polymerization.[29] Then, Cu(I)-PANI@MWCNT was prepared by reaction of CuI and PANI@MWCNT in a tetrahydrofuran (THF)–water mixture.

Successful synthesis of Cu(I)-PANI@MWCNT complex was confirmed using Fourier transform infrared (FT-IR) spectroscopy, transition electron microscopy (TEM), inductively coupled plasma (ICP) analysis, energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

The FT-IR spectrum of PANI@MWCNT in comparison with that of bare MWCNTs showed C═N and C═C stretching vibration bands at 1478 and 1574 cm^{-1} and C═N stretching vibration bands at 1243 and 1286 cm^{-1} (supporting information, Figure S1), confirming the formation of polyaniline in the emeraldine form. TEM observations confirmed the immobilization of copper nanoparticles on PANI@MWCNT (Figure 1). Also, a histogram of the size distribution of the catalyst indicated the size of Cu particles as between 1 and 6 nm and most particles were 3.2 nm (Figure S2). ICP analysis was used to determine the amount of copper loading of the Cu(I)-PANI@MWCNT complex as 6.1% (0.98 mmol g^{-1}). Also, the EDX analysis confirmed the presence of copper in the complex (Figure S3). As shown in Figure 2, the XRD pattern of Cu(I)-PANI@MWCNT composite indicated diffractions of CuI complexes, containing some peaks that are clearly visible and all of them can be indexed to crystalline CuI complexes. The peak positions are in agreement with those for CuI complexes reported previously.[22] Also, XPS analysis of recycled catalyst clearly indicated peaks corresponding to carbon, nitrogen, iodide and Cu^+ ion (Figure 3).

We investigated efficiency of Cu(I)-PANI@MWCNT in the Sonogashira reaction using iodobenzene with phenylacetylene as a model reaction, under various conditions with nitrogen atmosphere (Table 1). As is evident, among the screened bases, KOH showed the best result, and the corresponding coupling product was obtained in 96% yield (Table 1, entry 5). Effect of temperature on the activity of Cu(I)-PANI@MWCNT complex was also investigated. As the temperature decreased from 135 to 120 °C, the yield of product decreased from 96 to 64% (entry 13). A low copper concentration gave a decreased yield (entry 14). Thus for the optimum reaction conditions, Cu(I)-PANI@MWCNT complex (10 mol%) as the catalyst, KOH (2.0 equiv.) as the base and DMF (4 ml) as the solvent were used at 135 °C under nitrogen atmosphere. We examined the reaction of bromobenzene with phenylacetylene under these optimized conditions, and found that it was not efficient. However, by changing the reaction time to 4 h, bromobenzene could be smoothly coupled with phenylacetylene resulting in a yield of 60% of diphenylacetylene (Table 1, entry 11).

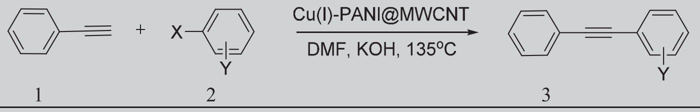
With the optimum conditions in hand, Cu(I)-PANI@MWCNT nanocatalyst was used for coupling of phenylacetylene with aryl iodides including those containing electron-donating or electron-withdrawing groups. Electron-rich, electron-poor or electron-neutral aryl iodides were reacted with phenylacetylene to produce the corresponding products in high yields under the optimized reaction conditions (Table 2, entries 1–10).

We next investigated the coupling of various aryl bromides with phenylacetylene. Unsurprisingly, aryl bromides were less reactive than aryl iodides, and the substituent effects in aryl bromides appeared to be more important than in aryl iodides. Nevertheless, as evident from Table 2, high catalytic activity was observed in the coupling of phenylacetylene with activated aryl bromides such as *p*-nitrobromobenzene, *m*-nitrobromobenzene, *p*-chlorobromobenzene, *o*-acetoxybromobenzene and *p*-methylbenzoate (entries 12, 13, 16, 19 and 20), whereas unactivated aryl bromides such as *p*-bromoanisole (entry 17) and *p*-bromotoluene (entry 18) indicated lower activity. It should be mentioned that the coupling reactions of aryl chlorides (entries 21–23) were not efficient.

A very important consideration of catalysts is their reusability. Hence, we investigated the recycling and reusability of this nanocatalyst utilizing the reaction of iodobenzene with phenylacetylene as a model reaction. After completion of the reaction, ethyl acetate was added to the reaction solution, and it was separated using centrifugation. The acquired solid materials were washed with water, ethanol and ethyl acetate and dried under vacuum for 10 h. Then we reused our recovered catalyst in six subsequent reactions under the same conditions. This heterogeneous nanocatalyst exhibited a good reusability (Table 3), which was confirmed from the XPS spectrum of the recycled nanocatalyst after the sixth run. Based on this analysis, the structure of CuI particles in the catalyst had not been destroyed after six consecutive runs (Figure 3).

To determine if metal is leached out into the solution during the reaction, the catalyst was collected from

TABLE 2 Sonogashira reaction of phenylacetylene with aryl halides[a]



Entry	X	Y	Time (h)	Product	Yield (%)[b]
1	I	H	2	**3a**	96
2	I	4-NO_2	2	**3b**	100
3	I	3-NO_2	2	**3c**	100
4	I	2-NO_2	2	**3d**	100
5	I	4-Br	2	**3e**	95
6	I	4-cl	2	**3f**	99
7	I	4-OCH_3	2	**3 g**	85
8	I	4-CH_3	2	**3 h**	78
9	I	2-$COCH_3$	2	**3i**	98
10	I	4-$COOCH_3$	2	**3j**	100
11	Br	H	4	**3a**	60
12	Br	4-NO_2	4	**3b**	75
13	Br	3-NO_2	4	**3c**	72
14	Br	2-NO_2	4	**3d**	65
15	Br	4-Br	4	**3e**	62
16	Br	4-cl	4	**3f**	70
17	Br	4-OCH_3	4	**3 g**	40
18	Br	4-CH_3	4	**3 h**	30
19	Br	2-$COCH_3$	4	**3i**	70
20	Br	4-$COOCH_3$	4	**3j**	72
21	Cl	H	4	**3a**	0
22	Cl	4-NO_2	4	**3b**	5
23	Cl	4-cl	4	**3f**	0

[a]Reaction conditions: phenylacetylene (1.2 mmol), aryl halide (1.0 mmol), Cu(I)-PANI@MWCNT (10 mol%), KOH (2 mmol), DMF (4 ml), 135 °C, nitrogen atmosphere

[b]GC yield.

TABLE 3 Sonogashira reaction of phenylacetylene with iodobenzene catalyzed by recycled catalyst[a]

Entry	Cycle	Yield (%)[b]
1	1	96
2	2	96
3	3	95
4	4	93
5	5	92
6	6	90

[a]Reaction conditions: phenylacetylene (1.2 mmol), iodobenzene (1.0 mmol), Cu(I)-PANI@MWCNT (10 mol%), KOH (2 mmol), DMF (4 ml), 135 °C, 2 h, nitrogen atmosphere.

[b]GC yield.

the solution after 1 h. The residual solution was then allowed to react, but no further progress in the conversion of the reactants was observed after 1 h. Additionally, ICP analysis of the solution only showed 0.01 ppm of Cu species was leached out from the supported heterogeneous catalyst during the course of the reaction, indicating the truly heterogeneous nature of the nanocatalyst.

3 | CONCLUSIONS

We developed a novel, inexpensive, efficient and safe catalytic system for the Sonogashira reaction by utilizing

Cu(I)-PANI@MWCNT as a heterogeneous nanocatalyst. The simplicity of synthesis, low cost and high activity make it a perfect complex for this reaction. The system acts very well for a broad diversity of aryl halides, and stands a variety of functional groups. In addition, the catalyst used is simply separated by centrifugation and can be reused for several consecutive cycles. The recyclability and high activity of the catalyst make it an alternative option among the large number of heterogeneous copper nanocatalysts reported to date for the Sonogashira coupling reaction. These advantages make the procedure very useful from the standpoint of synthesis.

4 | EXPERIMENTAL

4.1 | General

MWCNTs were purchased from Neutrino Co. (www.neunano.com; diameter 10–20 nm, length 30 μm, purity > 95%). All reagents and solvents were purchased from Merk or Aldrich and used without further purification.

4.2 | Preparation of PANI@MWCNT

PANI@MWCNT composites were prepared according to a previously reported procedure.[29] A round-bottom flask, containing HCl solution (2 M, 300 ml) and MWCNTs (1 g) was sonicated for half an hour at room temperature. In the following we added an aqueous solution of ammonium persulfate (2 g of $(NH_4)_2S_2O_8$ in 30 ml of deionized water). This reaction mixture was continuously stirred in an ice bath for 20 h. At the end of this time, the obtained PAN@MWCNT (in 97% yield) was separated by centrifugation and washed with distilled water and ethanol and dried at 50 °C.

4.3 | Preparation of cu(I)-PANI@MWCNT

To a round-bottom flask equipped with a magnetic stirrer bar and containing 100 ml of THF–H_2O (1:1) was added PANI@MWCNT (1 g) and the reaction mixture was suspended using ultrasound for 30 min. Following that, it was stirred for another 30 min. CuI (0.20 g) was added to the solution and the reaction mixture was stirred for 12 h at room temperature. Then the obtained black solid (in 96% yield) was separated by centrifugation and washed several times with distilled water, and dried in vacuum overnight at 50 °C.

4.4 | General procedure for Sonogashira coupling reaction

An aryl halide (1.0 mmol) and phenylacetylene (1.2 mmol) were added to a mixture of Cu(I)-PANI@MWCNT (10 mol%), KOH (2.0 mmol) and DMF (4 ml) in a glass flask under vigorous stirring. The reaction mixture was stirred at 135 °C for 2 h under nitrogen atmosphere. At the end of the reaction, the catalyst was separated by centrifugation, washed with ethyl acetate and water, vacuum dried and kept for the next reaction. Following GC analysis, the solvent was eliminated under vacuum, and the crude product was subjected to silica gel column chromatography using *n*-hexane–ethyl acetate as eluent to afford the pure product.

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SUPPORTING INFORMATION

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