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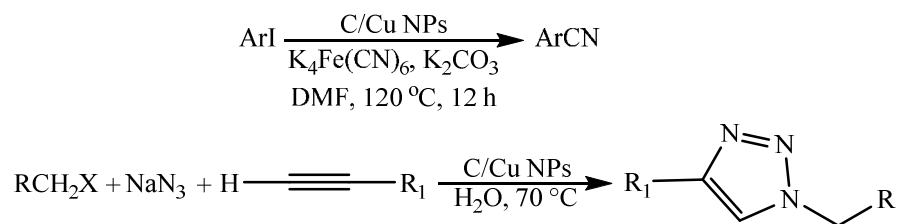
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Synthesis and catalytic activity of carbon supported copper nanoparticles for the synthesis of aryl nitriles and 1,2,3-triazoles

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Various substituted aryl nitrile and 1,2,3-triazole derivatives were prepared by using carbon supported copper nanoparticles (C/Cu NPs) as a heterogeneous catalyst under ligand-free conditions, which provided good to excellent yields. The nanocatalyst can be recycled and reused several times without significant loss of its catalytic activity.

Introduction

Nitriles have been used widely in synthetic organic chemistry and in industry for the manufacture of various pharmaceutical compounds, herbicides, agrochemicals and dyes.¹ They are also versatile intermediates in synthetic organic chemistry, since they can be easily transformed into various classes of compounds such as nitrogen-containing heterocycles, aldehydes, carboxylic acids and acid derivatives.²

The classical approaches to nitriles are based on the reaction of aryl halides with stoichiometric amounts of CuCN,³ Sandmeyer reaction via the diazotization of anilines⁴ or the transition metal-catalyzed cyanation of aryl halides using KCN, NaCN, Me₃SiCN and Zn(CN)₂ as cyanating agents.⁵ However, there are several factors in some of these methods which limited their applications. In many of these cases, the applicable reagents are toxic, hazardous, sensitive to moisture, expensive or out of accessible and cannot be stored. Among cyanation agents in the synthesis of nitriles, CuCN and Zn(CN)₂ lead to heavy metal waste. Also, most of the other methods for the synthesis of nitriles have disadvantages such as long reaction times, formation of side products, use of expensive catalyst, several-step methods and low yields. Therefore, it is desirable to develop a more efficient and convenient method for the synthesis of aryl nitriles without the application of expensive, moisture sensitive and toxic reagents.

Among cyanation agents in the synthesis of nitriles, K₄Fe(CN)₆ is commercially available on ton scale and cheaper than KCN and NaCN and even used in food industry for metal precipitation. Also, it is a nonexplosive, non-flammable, nonexpensive and non-toxic cyanide source and can be easily stored and is neither moisture sensitive and nor very volatile.⁶ Several syntheses of aryl nitriles have been reported using K₄Fe(CN)₆ in the presence of palladium or copper homogeneous catalysts,^{7,8} while less expensive copper heterogeneous catalysts have less received attention. The problem with homogeneous catalysis is the difficulty to separate the catalyst

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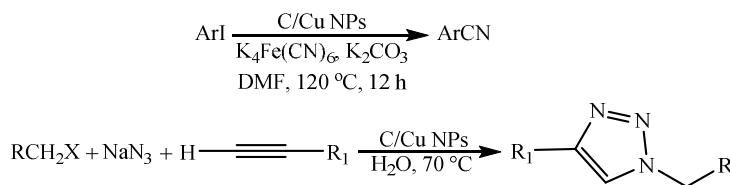
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from the reaction mixture and the impossibility to reuse it in consecutive reactions. Thus, the use of ligand-free heterogeneous copper catalysts is often desirable from the perspective of process development due to their easy handling, simple recovery, and recycling.

Since catalysis takes place on metal surface, nanoparticles (NPs) are much more reactive than the particulate metal counterpart due to their small sizes and large surface areas. So, heterogeneous catalysts are more and more used in the form of nanoparticles. Recently, considerable effort has also been devoted to the application of Cu(0)/Cu-oxide-nanoparticles as substitutes of bulk Cu metal in the title reaction in order to reduce the catalyst loading, reaction time and also to minimize the undesired products.⁹ Immobilization of catalysts on solid supports is one of the best methods to improve the efficiency and recovery of catalysts; many solid supported catalysts have been successfully utilized for catalytic applications.¹⁰⁻¹⁸ Most commonly used solid supports involve TiO₂,¹⁰ zeolites,^{11,12} magnetic-materials,^{13,14} graphene,¹⁵ insoluble polymers^{16,17} and gums.¹⁸ To prevent the agglomeration of metal nanoparticles (MNPs) and the over-stoichiometric use of Cu reagents, several inorganic materials such as alumina and silica have been used as a support for MNPs.¹⁹ It has been shown that embedding copper nanoparticles in supports such as silica improves both the catalytic stability and activity.

Recently carbon (C) structures are widely studied as supports of depositing metal nanoparticles as heterogeneous catalysts due to their extraordinary structure, good electronic conductivity, and improved accessibility of reactants to the active sites.²⁰ On the other hand, C structures display high surface area, tuneable porosity, extraordinary stability in acid and basic media as well as at high pressures and temperatures.²¹ Transition MNPs supported on C-catalyzed reactions provide the advantages of high atom efficiency, simplified isolation of product, and easy recovery and recyclability of the catalyst.²² Moreover, the decoration of transition MNPs onto the C support has shown a more versatility in carrying out the highly selective catalytic processes.²³ These outstanding catalytic activities of C-supported MNPs are mainly due to the effective dispersion in various solvents, very less aggregation of MNPs and larger surface area of the nanocatalyst.²⁴

In continuation of our efforts to develop environmentally friendly synthetic methodologies,²⁵ we report the synthesis of carbon supported copper nanoparticles (C/Cu NPs) in a single step by using the spark method and their application for one-pot synthesis of 1,2,3-triazoles and aryl nitriles under ligand-free conditions (Scheme 1). This heterogeneous catalyst system exhibits an excellent catalytic performance for these transformations and can be repeatedly used and subsequently recovered after the reaction.



Scheme 1. Preparation of aryl nitriles and 1,2,3-triazoles using C/Cu NPs.

Results and discussion

Characterization of catalyst

The stable C/Cu NPs obtained were fully characterized by BET, FT-IR, SEM, EDS, Raman and XRD and their behavior as catalyst was tested for the synthesis of 1,2,3-triazoles and aryl nitriles under ligand-free conditions.

The morphology of the C and C/Cu NPs are shown in the SEM image displayed Figure 1a and b. Figure 1a shows that the obtained carbon powder has a porous structure and nonuniform morphology, comprising differently shaped structures. Figure 1b indicated that produced copper nanoparticles were homogeneously supported on the carbon particles, also morphology of carbon structures altered. EDS analysis (Figure 1c) evidently shows the presence of copper and carbon in the sample. Also atomic and weight ratio are listed.

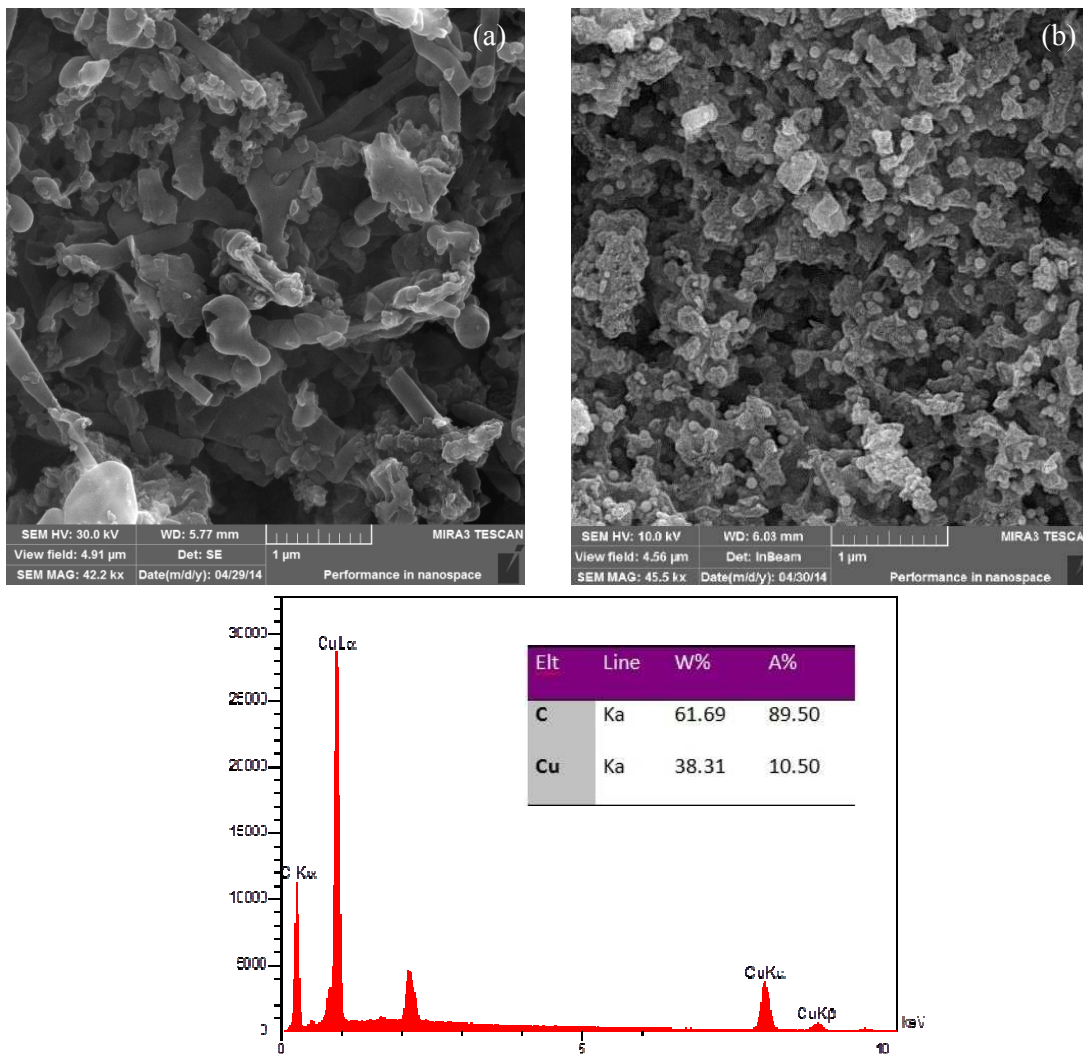


Figure 1. a) SEM image of carbon, b) SEM image of C/Cu NPs and c) EDS analysis of C/Cu NPs.

Figure 2a and b shows X-ray diffraction of C and C/Cu NPs respectively. In Figure 2a, the diffraction peaks at 26.4° and 43.5° can be attributed to the graphite structures (002) and (100). The broad band near (002) peak is also observed, implying presence of amorphous carbon in the sample.²⁶ By combining SEM and XRD results, it can be therefore inferred that this sample is contained of a highly disordered materials in the form of amorphous

carbon that accompanied with a mount of crystalline structures in graphite form. Therefore, the crystallites in the C samples have intermediate structures between graphite and amorphous state.

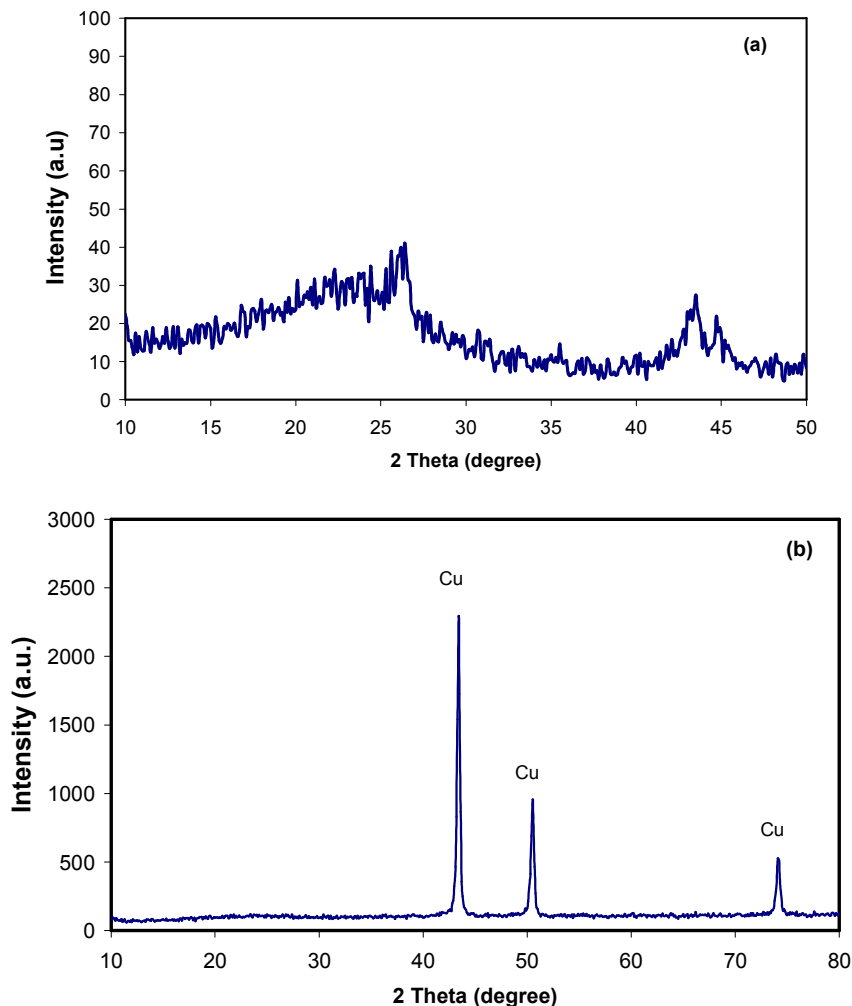


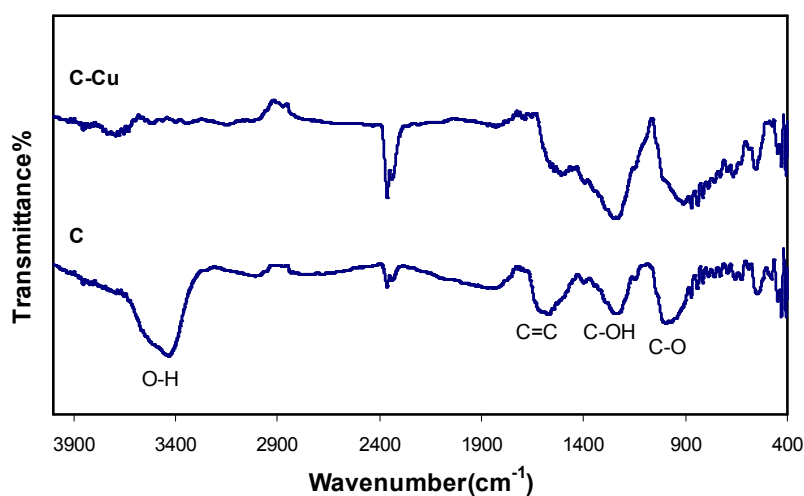
Figure 2. XRD pattern of a) C and b) C/Cu NPs.

In Figure 2b, three diffraction peaks at 2θ values of 43.4° , 50.5° and 74.1° corresponding to (111), (200) and (220) planes of copper were observed that can be indexed to standard XRD data for copper (JCPDS 04-0836). The corresponding d-spacing values of these peaks were calculated and were listed in Table 1. It is obvious that the positions of diffraction peaks and d-spacing values matched well with standard copper. The XRD study confirms that the resultant particles are fcc copper nanopowder. Also, in the XRD pattern of C/Cu NPs, copper nanoparticle diffraction peaks are so intense that those peaks related to carbon structures are not observable. Moreover, no diffraction peaks were observed for copper oxide indicating the formation of pure copper nanoparticles. EDS result (Figure 1c) was proved this result.

Table 1.Experimental and standard 2θ and d -value of copper.

Experimental data		JCPDS (04-0836)		hkl
2θ ($^\circ$)	d -spacing (\AA)	2θ ($^\circ$)	d -spacing (\AA)	
43.4	2.087	43.3	2.088	111
50.5	1.805	50.4	1.808	200
74.1	1.278	74.1	1.278	220

Figure 3 presents the IR spectrum of the C and C/Cu NPs and the three major absorption modes are detected: 3450 cm^{-1} assigned to the O-H groups, 1585 cm^{-1} attributed to the C=C band and 1250 cm^{-1} from C-O.²⁷

**Figure 3.** FT-IR spectra of C and C/Cu NPs.

Raman spectroscopy is known as a powerful technique in characterization of carbon carbonaceous materials. The structural features of C/Cu NPs have also been identified using Raman spectroscopy displayed in Figure 4. Two characteristic bands were observed in the Raman spectrum. The peak at about 1570 cm^{-1} (G band) is corresponded to an E_{2g} mode of graphite,²⁸ while another peak at about 1274 cm^{-1} (D band) is related to the defects and disorder.²⁹

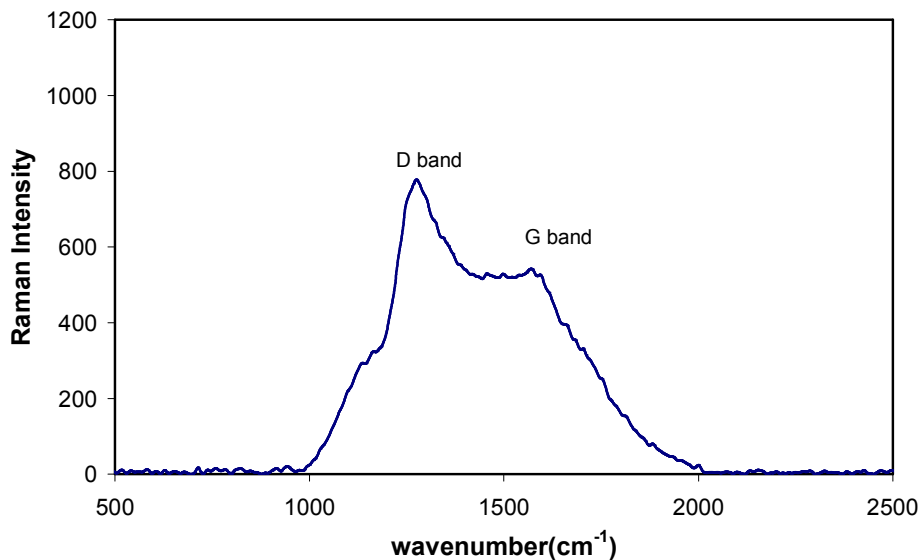
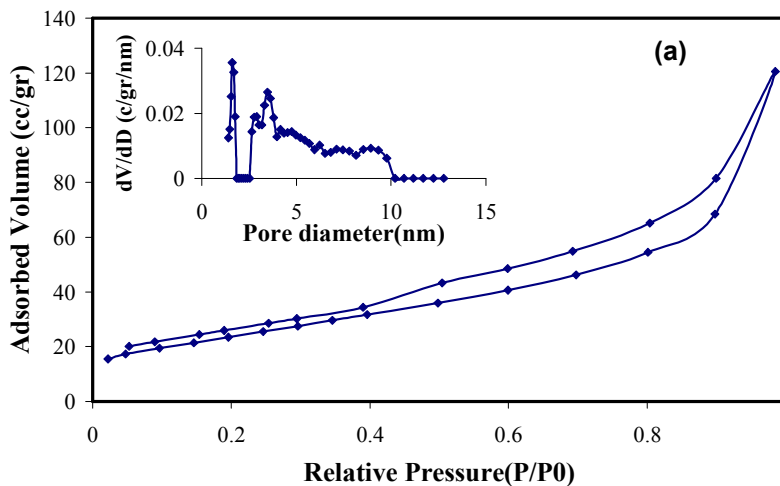


Figure 4. Raman spectra of C/Cu NPs.

N₂ adsorption-desorption isotherms of C and C/Cu NPs was shown in Figure 5a and b. The BET surface area of C and Cu/C are 86.52 m²/g and 45.56 m²/g respectively.

The pore size distributions plots, obtained from DFT method, are also shown in inner charts in Figure 5a and b. Main pore size is 8.6 nm for C and 12.64 nm for C/Cu NPs sample.



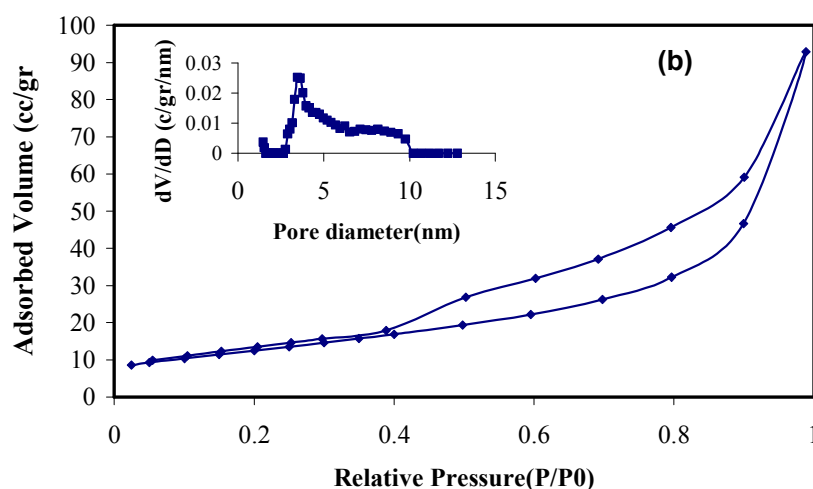


Figure 5. The N_2 adsorption-desorption isotherm and DFT pore size distribution plot of a) C and b) C/Cu NPs.

Evaluation of the catalytic activity of C/Cu NPs through the cyanation of aryl iodides

Usually the ligands play an important role for a successful copper-catalyzed cyanation of aryl halides. For optimization of the reaction conditions, we chose the reaction of phenyl iodide with $K_4Fe(CN)_6$ in the presence of C/Cu NPs as the model reaction, and the effects of the base and solvents were examined. Various ligands such as phosphine and nonphosphine for palladium catalyzed coupling reactions are described in the literature. Most of these ligands are air and moisture sensitive, difficult to prepare, and expensive. Thus, catalysis under ligand-free conditions is an area of high importance. In this work, the prepared C/Cu NPs were used as heterogeneous catalyst in the ligand-free cyanation reaction. First, several solvents were screened for the reaction. According to data given in Table 2, DMF was the most efficient solvent for this reaction (Table 2, entry 5). After choosing DMF as the solvent, we examined several bases. Our experiments showed that the base was necessary for the cyanation reaction (Table 2, entry 12). Among the selected bases, K_2CO_3 acted as the most effective one (Table 2, entry 5). A decrease in the catalyst loading from 0.5 to 0.3 mol% afforded the product in lower yield (Table 2, entry 13). No significant improvement on the yield was observed using higher amounts of the catalyst (Table 2, entry 14) and 0.5 mol% of the catalyst was found to be optimum. We then used the optimal reaction conditions (aryl halide (1.0 mmol), $K_4Fe(CN)_6$ (0.66 mmol), K_2CO_3 (1.0 mmol) and DMF as solvent) for cyanation of different aryl halides at 120 °C. No surfactant or ligand was required.

Table 2.Ligand-free cyanation reaction of $K_4Fe(CN)_6$ with phenyl iodide in the presence of different solvents and bases.^a

Entry	C/Cu NPs (mol%)	Base	Solvent	Temperature (°C)	Time (h)	Yield ^b (%)
1	0.5	K ₂ CO ₃	Toluene	Reflux	20	0
2	0.5	K ₂ CO ₃	CH ₃ CN	Reflux	20	0
3	0.5	K ₂ CO ₃	MeOH	Reflux	20	0
4	0.5	K ₂ CO ₃	NMP	120	12	87
5	0.5	K ₂ CO ₃	DMF	120	12	96
6	0.5	Cs ₂ CO ₃	DMF	120	12	94
7	0.5	Et ₃ N	DMF	120	12	25
8	0.5	NaF	DMF	120	12	45
9	0.5	KF	DMF	120	12	51
10	0.5	KOAc	DMF	120	12	83
11	0.5	Na ₂ CO ₃	DMF	120	12	63
12	0.5	-	DMF	120	20	0
13	0.3	K ₂ CO ₃	DMF	120	12	77
14	0.8	K ₂ CO ₃	DMF	120	12	96

^a Reaction conditions: phenyl iodide (1.0 mmol), $K_4Fe(CN)_6$ (0.66 mmol), base (1.0 mmol), solvent (5.0 mL).^b Yields after work-up.

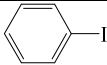
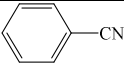
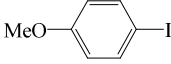
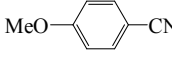
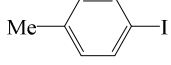
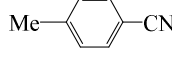
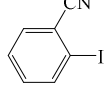
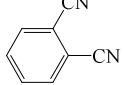
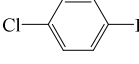
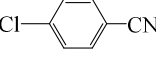
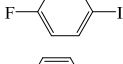
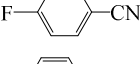

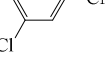
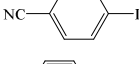
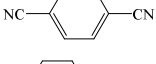
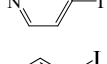
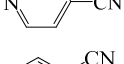

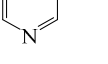
Having optimized the conditions, we explored the general applicability of C/Cu NPs as a catalyst for ligand-free reaction of $K_4Fe(CN)_6$ with aryl iodides containing electron-withdrawing or donating substituents. As indicated in Table 3, it is evident that our method is reasonably general and can be applied to several types of aryl iodides. The reactions were able to tolerate a wide range of functional groups. In all cases the reaction gave the corresponding products in good to excellent yields. In addition, the reactions appeared to be insensitive to the steric hindrance around the reaction site (Table 3, entry 4). As an example for electron-poor nitrogen heterocycles, 4-iodopyridine and 3-iodopyridine were cyanated in good yield (Table 3, entries 9 and 10).

Compared with the other literature works on the cyanation of aryl halides,⁴⁻⁸ the notable features of our method are:

- Elimination of toxic reagents and palladium or copper homogeneous catalysts;
- Toxic and expensive ligands are not needed;
- The yields of the products are high;
- Ease of handling and cost efficiency of the catalyst;
- The catalyst can be easily recovered and reused;
- Toxic, hazardous, sensitive to moisture and expensive cyanide sources are avoided;
- The use of $K_4Fe(CN)_6$ as a nonexplosive, non-flammable, nonexpensive and non-toxic cyanide source;
- The methodology is applicable to both the small and large scale.

Table 3.Cyanation reaction of different aryl iodides with $K_4Fe(CN)_6$ in the presence of C/Cu NPs.^a

$$\text{ArI} \xrightarrow[\text{K}_4\text{Fe(CN)}_6, \text{K}_2\text{CO}_3, \text{DMF}, 120^\circ\text{C}, 12 \text{ h}]{\text{C/Cu NPs}} \text{ArCN}$$

Entry	Aryl iodide	Product	Yield ^b (%)
1			96 (93) ^c
2			94
3			93
4			90
5			92
6			92
7			94
8			93
9			90
10			90

^a Reaction conditions: Aryl iodide (1.0 mmol), $K_4Fe(CN)_6$ (0.66 mmol), C/Cu NPs (0.5 mol%), K_2CO_3 (1.0 mmol), DMF (5.0 mL), 120 °C.^b Yields after work-up.^c Yields after the 5th cycle.**Evaluation of the catalytic activity of C/Cu NPs through the 1,3-dipolar cycloaddition reactions between sodium azide, terminal alkyne and organic halides**

1,2,3-Triazoles have a wide range of applications in the synthesis of pharmaceuticals.³⁰ Most common method for the preparation of 1,2,3-triazoles is the 1,3-dipolar cycloaddition reactions between substituted alkynes and azide derivatives.³⁰ Recently, three component coupling reactions were reported for the preparation of triazoles using catalysts such as microwave assisted Cu(0)-Cu(II), Cu(II)-sodium ascorbate-l-proline, monometallic palladium and bimetallic Pd(0)-Cu(I).³⁰

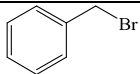
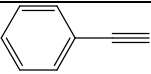
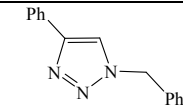
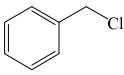
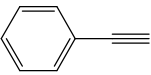
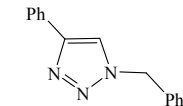
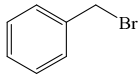
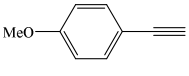
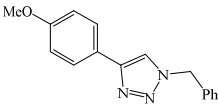
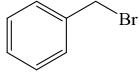
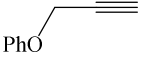
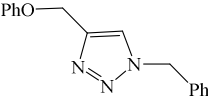
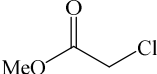
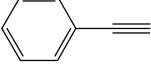
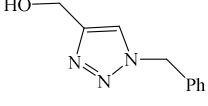
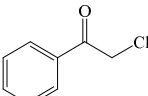
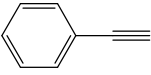
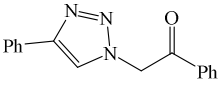
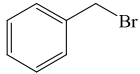
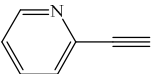
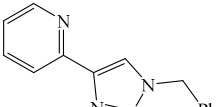

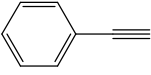
One of the main limitations of the copper catalyzed 1,3-dipolar cycloaddition is the presence of a significant amount of toxic, coloured, and expensive copper complexes in the end products. One strategy to circumvent the problems related with copper contamination, which became quite popular during the last 5 years, is to immobilize the catalyst on a heterogeneous support. In this way, it is economically and environmentally more interesting to use the coupling reaction on a large scale since the heterogeneous supports can both facilitate the isolation and the recycling of the catalytic system. Furthermore, supported catalysis possibly also provides a way to improve the reaction rate. The efficiency and stability of C/Cu NPs prompted us to use the catalyst for the commercially important 1,3-dipolar cycloaddition.

For optimization of the reaction conditions, we chose the reaction of sodium azide with phenylacetylene and benzyl bromide in the presence of C/Cu NPs at 70 °C in H₂O as the model reaction. In the absence of catalyst, the reactions did not proceed after a long reaction time. The best result was obtained with sodium azide (1.0 mmol), phenylacetylene (1.0 mmol), benzyl bromide (1.0 mmol), catalyst (0.5 mol%) and H₂O (2.0 mL) which gave the product in a good yield (97%).

Further we have tested the catalytic activity of C/Cu NPs for 1,3-dipolar cycloaddition reactions with variety of substrates and the results are summarized in Table 4. All the substrates produce the expected triazoles with very good to excellent yields. The substituents (electron-withdrawing, electron-releasing and heterocycle) do not have any peculiar effect, as most of the reactions were completed within 4-7 h. The catalyst was not effective for iodobenzene (Table 4, entry 10).

Table 4.Synthesis of triazoles using C/Cu NPs.^a

$$\text{R}-\text{CH}_2-\text{X} + \text{NaN}_3 + \text{H}-\text{C}\equiv\text{C}-\text{R}_1 \xrightarrow[\text{H}_2\text{O}, 70^\circ\text{C}]{\text{C/Cu NPs}} \text{R}_1-\text{C}_4\text{H}_3\text{N}_3-\text{CH}_2-\text{R}$$

Entry	Halide derivative	Terminal alkyne	Product	Time (h)	Yield ^b (%)
1				4	97, 94 ^c
2				6	98
3				6	91
4				7	78
5				7	80
6				7	80
7				6	90
8			No reaction	10	0

^a Reaction conditions: Organic halide (1.0 mmol), terminal alkyne (1.0 mmol), NaN₃ (1.0 mmol), C/Cu NPs (0.5 mol%), H₂O (2.0 mL), 70 °C.^b Yields after work-up.^c Yields after the fifth cycle.

The following items are observed in most of the procedures in the literature for the preparation of triazoles³¹:

- The use of toxic organic solvents;
- Relatively low yields;

- The difficulties in preparation of the catalyst and availability of reagents;
- The use of harsh reaction conditions (high temperature, hazards,);
- Tedious work-up;
- The over-stoichiometric use of Cu reagents;
- The use of expensive ligands and homogeneous catalysts; and
- The difficulties to recover and reuse for successive reaction cycles and the possibility of metal contamination with the end product.

All above items are wasting money and time consuming, so our proposed method can be considered as a green protocol which the reaction will take place in water under heterogeneous conditions. None of the above mentioned disadvantages are observed in our method. The methodology is applicable to both the small and large scale. On the other hand, one pot procedure for the synthesis of 1,2,3-triazoles through the reaction between in-situ generated azides from its corresponding organic halides is highly desirable and economical as this avoids the isolation step of azides. Also, the catalyst is easy to prepare, very versatile and reusable at a low copper loading.

Catalyst recyclability

The reusability of the catalyst is a very important theme, especially for commercial applications. Therefore, the recovery and reusability studies of the catalyst were done by conducting the reaction of iodobenzene with $K_4Fe(CN)_6$ (cyanation). Not much decrease in the activity of catalyst was observed even after 5 cycles (Table 3 and Figure 6). Thus, the catalyst is stable during the cyanation reaction. The reusability of the catalyst was also studied for the 1,3-dipolar cycloaddition reactions under the present reaction conditions (Table 4, entry 1).

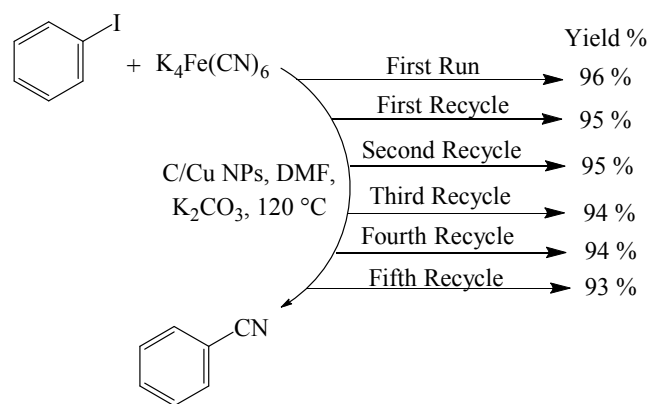


Figure 6. Reusability of C/Cu NPs for cyanation of phenyl iodide.

Heterogeneity test

We carried out a hot filtration test, when the cyanation reaction was half done, catalyst were removed at the reaction temperature, and the reactants were allowed to undergo further reaction in the solution. We confirmed that there was no further conversion of the reactants in the absence of the catalyst (monitored by thin layer chromatography). This shows that the reaction was caused by the heterogeneous catalyst only. These results further confirmed the high recyclability of the catalyst.

The scale-up synthesis of aryl nitriles and 1,2,3-triazoles

Finally, the scale-up synthesis of aryl nitriles and 1,2,3-triazoles were also investigated in the reaction of aniline with formic acid. The amount of the halide derivative increased to 15.0 mmol and the reaction was took place with the same procedure and same conditions which it was successful and the product obtained in high yield. After completion of the reaction, the insoluble catalyst was separated from the reaction mixture and reused.

Conclusions

Copper NPs immobilized on carbon, C/Cu NPs catalyst, has been utilized for the synthesis of aryl nitriles and 1,2,3-triazoles. The catalyst can be recycled and reused many times without losing its activity. In addition to easy recovery and reusability of the catalyst for a number of runs, simple operation, use of benign cyanating agent, requirement of no ligand and additive, elimination of homogeneous catalysts, good yields of products and tolerance for a wide variety of functionality make this procedure an attractive one for the synthesis of aryl nitriles and 1,2,3-triazoles. This procedure can be exploited in the synthesis of various drug intermediates. Further investigations using this catalyst system are underway.

Experimental section

All reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. Products were characterized by comparison of their physical and spectral data with authentic samples. The NMR (Nuclear Magnetic Resonance) spectra were recorded in DMSO. ^1H NMR spectra were recorded on a Bruker Avance DRX 400 MHz instruments. The chemical shifts (δ) are reported in ppm relative to the TMS as an internal standard and J values are given in Hz. ^{13}C NMR spectra were recorded at 100 Hz. FT-IR (Fourier transform infrared) spectra were recorded on a Perkin-Elmer 781 spectrophotometer. Melting points were taken in open capillary tubes with a BUCHI 510 melting point apparatus and were uncorrected. TLC was performed on silica gel polygram SIL G/UV 254 plates. Morphology of samples was investigated by scanning electron microscopy (SEM) (Cam scan MV2300). The chemical composition of the prepared nanostructures was measured by Energy Dispersive X-ray Spectroscopy (EDX) performed in SEM. X-ray powder diffraction (XRD) measurements were performed with a Philips powder diffractometer type PW 1373 goniometer. The Brunauer-Emmett-Teller (BET) specific surface areas (SBET) and the porosity of the samples were evaluated on the basis of nitrogen adsorption isotherms measured at 77 K using a BELSORP-max nitrogen adsorption apparatus (Japan Inc.). Raman spectra were performed on a Senterra model of Bruker Company (Germany) and the used Raman spectrometer was a 785 nm laser source.

Preparation of amorphous Carbon from tar

Carbon (C) has been synthesized by pyrolysis of tar. The tar was put in a tubular furnace at room temperature. A flow of N_2 was continuously passed over the furnace and the temperature was raised until 800 °C at a rate of 15 °C min^{-1} . The sample remained at 800 °C by 2 h. Then sample cooled slowly until room temperature. The resulting sample becomes black and will be referred to as C.

Preparation of C/Cu NPs

Carbon-Copper (C/Cu) composite powder was prepared by arc discharge method.³² The schematic of the experimental setup is shown in Figure 7. Ar as carrier gas with a low flow rate was passed through the vessel containing carbon powder and directed carbon particles toward the discharge chamber. In this chamber, two Cu rods (diameter: 1.5 cm and length: 1 cm) were used as electrodes. The position of the bottom electrode was fixed, whereas the top electrode was adjustable. The electrode gap was set to 2-3 mm at the beginning of the experiment and a high current (90 A) and a low voltage (20 V) was established between the electrodes. Then, the electrode gap was decreased until electrical discharge occurred between the electrodes resulting in evaporation of the electrode material and formation of Cu nanoparticles. Therefore, when carbon powder was transmitted through the electrodes, Cu nanoparticles were supported on carbon powder particles. Then, final products were collected in powder form on a surface filter element by a vacuum pump.

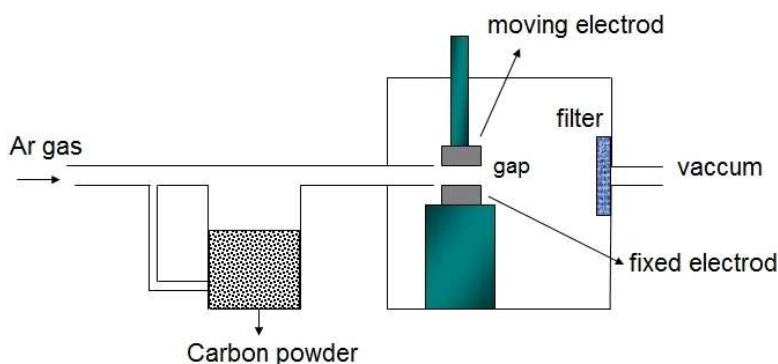


Figure 7. Schematic of the experimental setup.

General procedure for the synthesis of aryl nitriles

To a mixture of aryl iodide (1.0 mmol), $K_4Fe(CN)_6$ (0.66 mmol), K_2CO_3 (1.0 mmol), C/Cu NPs (0.5 mol% Cu) and 5 mL of solvent (DMF) was placed in a Schlenk tube (25 mL), and the mixture was vigorously stirred under for 15 h at 120 °C (Table 1 and 2). Upon completion, the mixture was cooled to room temperature, and diluted with ether and water. Organic layer was washed with brine, dried over $MgSO_4$, filtered and evaporated under reduced pressure using rotary evaporator to give the crude product. The residue was purified by recrystallization using ethanol and water. The purity of the compounds was checked by 1H NMR and yields are based on aryl iodide. All the products are known and the spectroscopic data (FT-IR and NMR) and melting points were consistent with those reported in the literature.^{4,33}

General procedure for the synthesis of 1,2,3-triazoles

In a typical procedure, C/Cu NPs (0.5 mol%) were added to a mixture of phenylacetylene (1.0 mmol), organic halide (1.0 mmol) and NaN_3 (1.0 mmol) in water (2.0 mL) and the mixture was stirred 70 °C. After completion of the reaction (as monitored by TLC), the catalyst and the solid reaction product were centrifuged and the reaction product was extracted with EtOAc. Organic layer was washed with water, dried over $MgSO_4$, filtered and evaporated under reduced pressure using rotary evaporator to give the crude product. Column chromatography was performed using silica gel with ethyl acetate and *n*-hexane (2:8) as eluent to get pure

product. All the products are known compounds and the spectral data (FT-IR and NMR) and melting points were identical to those reported in the literature.³¹

Acknowledgments

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