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# Novel Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel as an Efficient and Sustainable Magnetic Catalyst for the Synthesis of 1,4-Disubstituted-1,2,3-triazoles and 2-Substituted-Benzothiazoles via One-Pot Strategy in Aqueous Media

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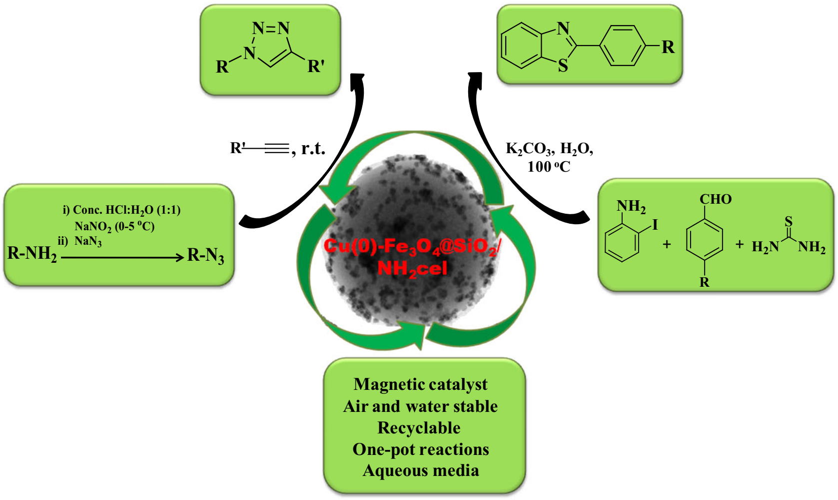
**Abstract** A novel, air stable, water dispersible and efficient magnetic catalyst based on copper nanoparticles onto ethylene diamine functionalized inorganic/organic composite [Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel] has been prepared. Functionalization of inorganic/organic composite by ethylene diamine imparts desirable chemical functionality and enables the generation of active sites for the immobilization of Cu(0) nanoparticles. The novel catalyst system has been well characterized by various techniques like FTIR, TGA, XRD, SEM, HRTEM, EDX, ICP-AES, UV–Vis and VSM. Further, Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel opens up a new avenue to introduce a very useful and efficient catalytic system for the one-pot synthesis of 1,4-disubstituted-1,2,3-triazoles via 1,3-dipolar cycloaddition of terminal acetylenes to azides, generated in situ from anilines in water at room temperature, and one-pot three component reaction of 2-iodoaniline, aldehyde and thiourea as sulphur source for the synthesis of 2-substituted-benzothiazole derivatives in water. The novel heterogeneous magnetic catalyst offers recyclability without significant deterioration in catalytic activity and can be easily recovered using an external magnet, thus making it eco-friendly and economical to perform the desired transformations.

## Graphical Abstract



**Keywords** Cu(0) NPs · Inorganic/organic composite · Amine functionalization · 1,4-Disubstituted-1,2,3-triazoles · 2-Substituted benzothiazole · Magnetic heterogeneous catalyst · Recyclability

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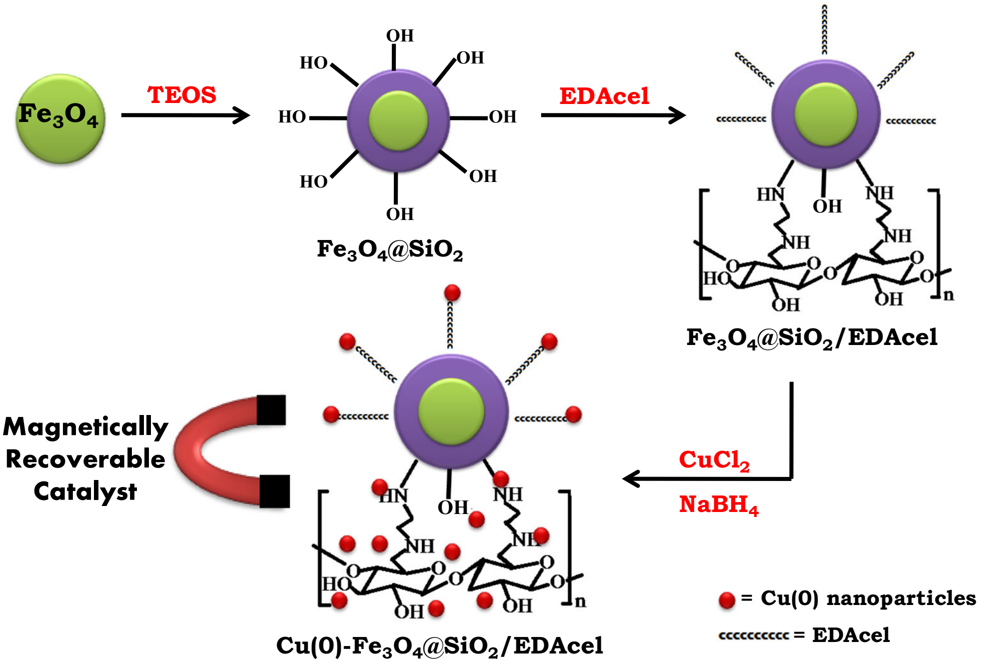
## 1 Introduction

Nanotechnology in the recent years has enabled revolutionary developments in various fields including environmental science, medicine and importantly, catalysis. Nanoparticles, being small, present close to a homogeneous experience, thus bridging the gap between homogeneous and heterogeneous catalysis [1, 2]. Hence, synthetic protocols can be made economic, greener and more sustainable by designing nanoparticle based heterogeneous catalytic systems. Recently, Cu(0) nanoparticles have drawn attention of chemists owing to their inexpensive nature, easy preparation and the ability to replace other noble metal nanoparticles, such as Ag, Au and Pt nanoparticles [3–5]. However, the use of Cu(0) nanoparticles is often complicated by issues associated with their oxidation and agglomeration in the absence of stabilizers, thereby diminishing their activity [6, 7]. Therefore, efforts have been made to stabilize nanoparticles by immobilization on different solid supports such as polymers, silica, and zeolites [8–10]. One of the most attractive alternatives to stabilize nanoparticles is the magnetic support, and their paramagnetic and insoluble properties enable the catalyst to be easily separated with an external magnetic field [11–13]. Further, the coating of magnetic nanoparticles or in general inorganic cores with functional outer shells of silica, zeolites and biocompatible polymeric materials like cellulose is a facile way to improve the solution stability for such hybrid core shell structures and prevents agglomeration, leading to stable and finely dispersed active species [14, 15]. Recently, much attention has been focused on amine functionalization of the core shell based magnetic substrates, since amines are well known to stabilise the nanoparticles against aggregation without disturbing the desired properties, and also recognised to increase their catalytic activity [16, 17].

1,2,3-Triazoles are an important class of organic compounds which have risen to prominence in recent years as superbly versatile five membered nitrogen heterocycles. The Cu(I)-catalysed (CuAAC) synthesis of 1,2,3-triazoles via 1,3-dipolar Azide–Alkyne cycloaddition click reaction introduced independently by Sharpless [18] and Meldal [19] in 2002, finds utility in many disciplines beyond synthetic organic chemistry [20–22]. Furthermore, 1,2,3-triazole moieties are emerging as powerful pharmacophores in their own right. As a result, a plethora of methods have been developed for this powerful conjugation tool with the aim to increase efficiency. Both homogenous and heterogeneous copper mediated methods have been developed for the synthesis of 1,4-disubstituted-1,2,3-triazoles [23–27]. Among them, special attention is needed to be given to those which combine the following three important aspects in current synthetic chemistry, (a) one-pot procedures: the in situ generation of organic azides from anilines by diazotization followed by the addition of sodium azide to acetylenes, which minimizes hazards derived from the isolation and handling of azides because of their toxic nature [28]; (b) magnetic heterogeneous catalysis, especially involving copper nanoparticles supported on magnetic supports, which offers several advantages compared to their solution counterparts, such as reusability, efficiency, enhanced stability and magnetic retrieval of the catalyst [29]; and (c) reactions in water, which offers key advantages, such as rate enhancement and insolubility of the final products, thus making synthetic processes cheaper, safer, and greener [30, 31]. Recently, copper nanoparticles (Cu NPs) due to their small sizes and large surface areas are being explored as click catalysts in the hope of improving reusability and efficiency for the synthesis of triazoles [32–34].

Further, benzothiazoles and their derivatives are present in many pharmaceuticals and exhibit remarkable biological and therapeutic activities [35–38]. Thus, the attractive biological profiles of this group of compounds stimulate chemists to explore efficient methods for the synthesis of benzothiazoles and their structural analogues. Synthesis of derivatives with a benzothiazole framework, involves commonly used approaches comprises of the condensations of 2-aminothiophenol with carboxylic acids, acid chlorides, nitriles and aldehydes [39–42]. But, these conventional reactions often suffers from drawbacks such as the use of strongly oxidizing or toxic reagents, multistep synthetic methodology, tedious workup procedures, and the instability of starting materials including 2-aminothiophenol [43–45]. Subsequently, the development of a simple, convenient and an eco-friendly method for the synthesis of benzothiazoles would be highly enviable. Despite the spectacular success in the field of triazole and benzothiazole synthesis, there is always much scope available for the improvement at several levels.

In this paper, we developed a facile and novel methodology for the synthesis of copper nanoparticles onto ethylene diamine functionalized inorganic/organic magnetic composite [Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel] which represent an excellent example of synergism of the properties of both inorganic and organic components (Scheme 1). Further, Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel was efficiently employed for the one-pot synthesis of 1,4-disubstituted-1,2,3-triazoles and 2-substituted benzothiazoles. Because of the magnetic nature of the catalyst, it can be retrieved using an external magnet, which eliminates the obligation of catalyst filtration after completion of the reaction and could be reused up to six times with high efficiency. To the best of our knowledge, the use of copper nanoparticles onto



**Scheme 1** Synthesis of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel

ethylene diamine functionalized inorganic/organic composite [Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel] as a catalyst for the one-pot synthesis of 1,4,-disubstituted-1,2,3-triazoles and 2-substituted benzothiazoles has not been previously reported in the literature.

## 2 Experimental

### 2.1 General Remarks

All the chemicals and solvents used were purchased from Aldrich Chemical Company or Merck. The $^1H$ and $^{13}C$ NMR data were recorded in $CDCl_3$ on Bruker Avance III (400 and 100 MHz) and mass spectral data on Bruker Esquires 3000 (ESI). The FTIR spectra were recorded on Perkin-Elmer FTIR spectrophotometer. TGA was recorded on Perkin Elmer, Diamond TG/DTA. X-ray diffratograms (XRD) were recorded in 2 theta range of 10°–80° on a Bruker AXSDB X-ray diffractometer using Cu Kα radiations. SEM images were recorded using JEOL Model JSM-6390LV Scanning Electron Microscope, High Resolution Transmission Electron Micrographs (HRTEM) were recorded on JEOL, JEM-2100F. EDX analysis was carried out using JEOL Model JED-2300 and the amount of metal in catalyst was determined by ICP-AES analysis using ARCOS from M/s. Spectro, Germany. The UV–visible spectra was recorded on Model Varian, Cary 5000. The magnetic properties of the prepared materials were measured using a vibrating sample magnetometer (VSM) using Model: 7410 series, Lakeshore at room temperature from −10,000 to +15,000 Oe. X-ray crystallographic study of novel compounds was carried on *X'calibur* CCD area-detector diffractometer.

### 2.2 Synthesis of Magnetite Nanoparticles ($Fe_3O_4$ NPs)

$FeCl_3$ (5.0 g) and $FeCl_2$ (2.0 g) were successively dissolved in distilled water (30 mL). The resulting solution was then added dropwise into aqueous NaOH solution (1 M, 200 mL) under vigorous stirring for 30 min. The precipitation and formation of nanoferrites took place by a conversion of the metal salts into hydroxides and that, in turn, immediately transformed into ferrites. After 15 min, the precipitated ferrites were separated with a magnet and washed to pH $<7.5$ by distilled water which were then dried under vacuum at 60 °C over night.

### 2.3 Synthesis of Silica Coated Magnetic Nanoparticles ($Fe_3O_4$@$SiO_2$)

$Fe_3O_4$ (2 g) was dispersed in water (30 mL) followed by the addition of ethanol (120 mL), ammonia (6 mL) and TEOS i.e., tetraethyl orthosilicate (6 mL). The mixture was then refluxed for 6 h under vigorous stirring. The resulting $Fe_3O_4$@$SiO_2$ colloid was separated with magnet and washed repeatedly with distilled water (3 × 10 mL) and ethanol (3 × 10 mL). Then, the final product, $Fe_3O_4$@$SiO_2$ was dried in vacuum at 60 °C over night.

## 2.4 Synthesis of Ethylene Diamine Functionalized Cellulose ($NH_2$cel)

Cellulose (5 g) previously activated at 80 °C for 12 h was suspended in *N*,*N*-dimethylformamide (100 mL), followed by the slow addition of thionyl chloride (16 mL) at 80 °C, under mechanical stirring. After the addition was complete, stirring was continued for another 4 h. The cellulose chloride (CelCl) obtained was washed with several aliquots of dilute ammonium hydroxide solution (0.5 mol/L $NH_4OH$) and the supernatant after each treatment was removed to bring the pH to neutral. To complete the washing, the suspension was exhaustively treated with distilled water (2 × 100 mL). The solid was then separated by filtration and dried in vacuum at room temperature.

A mixture of CelCl (2 g) and ethylene-1,2-diamine (12 mL) was stirred at 116 °C for 3 h. The reaction mixture was filtered through a sintered glass crucible and the solid was dried in vacuum at room temperature to afford EDAcel as yellow powder.

## 2.5 Synthesis of Ethylene Diamine Functionalized $Fe_3O_4$@silica/Cellulose ($Fe_3O_4$@$SiO_2$/$NH_2$cel)

To a solution of $Fe_3O_4$@$SiO_2$ (1 g) in $CHCl_3$ (15 mL), EDAcel (1 g), triethyl amine (0.3 mL) were added and stirred at 60 °C for 12 h under magnetic stirring. $Fe_3O_4$@$SiO_2$/$NH_2$cel was seperated with magnet and washed with chloroform (3 × 10 mL) followed by water (3 × 10 mL, and dried under vacuum at 60 °C over night.

## 2.6 Synthesis of Copper Nanoparticles onto Ethylene Diamine Functionalized $Fe_3O_4$@silica/cellulose [Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel]

To a dispersed solution of $Fe_3O_4$@$SiO_2$/EDAcel (1 g) in ethanol (6 mL), aqueous solution of $CuCl_2$ (0.134 g, 1.0 mmol, 3 mL) was added, and the reaction mixture was stirred at room temperature for 6 h. Then, aqueous solution of $NaBH_4$ (1.2 mmol, 5 mL) was added slowly during 8 h. Finally, Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel was seperated with magnet and washed successively with water (3 × 10 mL) and Ethanol (3 × 10 mL). Finally, it was dried under vacuum at room temperature to give the dark polymeric Cu(0) nanoparticles (Scheme 1).

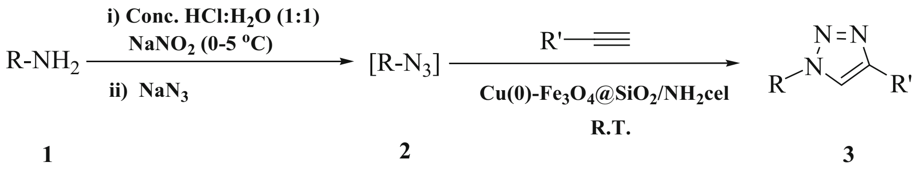
## 2.7 General Procedure for the Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel Catalyzed One-Pot Synthesis of 1,4-Disubstituted-1,2,3-triazoles

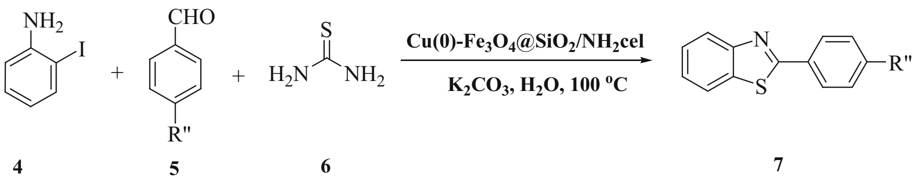
To a round bottomed flask maintained at 0–5 °C, aryl amine (2 mmol), and conc. HCl: $H_2O$ (1.5 mL, 1:1) were added, and the reaction mixture was stirred for 5 min. Then, solution of $NaNO_2$ (2.5 mmol in 1 mL water) was added dropwise to the reaction mixture over a period of 5 min while maintaining the temperature of round bottomed flask at 0–5 °C. After stirring for another 5 min, sodium azide (3 mmol) was added, and the reaction mixture was further stirred for 10 min. Finally, aryl alkyne (1.5 mmol) and Cu(0)–$Fe_3O_4$–$SiO_2$/EDAcel (0.05 g, 0.25 mol% Cu) were added to the reaction mixture followed by stirring at room temperature for the appropriate time (Scheme 2). After completion of the reaction (monitored by TLC), the catalyst was separated using an external magnet and the reaction mixture was diluted with ethyl acetate and filtered. The organic layer was washed with water and dried over anhyd. $Na_2SO_4$. Finally, the solvent was removed under pressure and the residue was crystallized from EtOAc-pet. ether to get the product. The recovered catalyst was washed with EtOAc (2 × 10 mL) followed by double distilled water (2 × 10 mL). It was dried and then reused for subsequent reactions.

## 2.8 General Procedure for the Synthesis of Cu (0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel Catalyzed One-Pot Three Component Synthesis of 2-Substituted Benzothiazoles

To a mixture of 2-iodoaniline (1 mmol), aryl aldehyde (1.2 mmol), thiourea (3 mmol), $K_2CO_3$ (3 mmol) and Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel (0.05 g, 0.25 mol% Cu) in a round-bottom flask (25 mL), water (5 mL) was added, and the reaction mixture was stirred at 100 °C for an appropriate time (Scheme 3). After completion of the reaction (monitored by TLC), the catalyst was separated using an external magnet and the reaction mixture was diluted with ethyl acetate. The organic layer was washed with water

**Scheme 2** Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel catalyzed one-pot synthesis of 1,4-disubstituted-1,2,3-triazoles in water at room temperature





**Scheme 3** Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel catalysed one-pot three component reaction of 2-iodoaniline, aldehyde and thiourea for the synthesis of benzothiazoles in water at 100 °C

(3 × 10 mL) followed by brine solution (2 × 10 mL) and dried over anhyd. $Na_2SO_4$. Finally the product was obtained after removal of the solvent under reduced pressure followed by crystallization with EtOAc-pet. ether. The recovered catalyst was washed with EtOAc (3 × 10 mL) followed by double distilled water (3 × 10 mL) which was dried and reused for subsequent reactions.

## 3 Results and Discussion

### 3.1 Synthesis and Characterization of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel

As part of our efforts to explore the use of novel catalysts based on inorganic/organic composites for organic reactions [46], we have designed, prepared, and characterized a novel catalyst system, Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel and its catalytic activity was studied in the one-pot synthesis of 1,4-disubstituted-1,2,3-triazoles and 2-substituted benzothiazoles .

The process of synthesis of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel is represented in Scheme 1. First, the $Fe_3O_4$ nanoparticles were prepared by co-precipitation of $Fe^{3+}$ and $Fe^{2+}$ salts, and then silica was coated onto the surface of the $Fe_3O_4$ nanoparticles by sol–gel process. Cellulose, an important biopolymer, characterized by hydrophilicity, chirality, biodegradability, and broad chemical-modifying capacity was modified by incorporating the ethylene-1,2-diamine moiety as a pendant chain covalently bonded to the main polymeric framework [47–49]. The inorganic/organic composite was prepared via formation of covalent bonds between ethylene diamine functionalized cellulose and hydroxyl groups of silica coated $Fe_3O_4$. Copper nanoparticles were then immobilized onto the surface of ethylene diamine functionalized $Fe_3O_4$@silica/cellulose substrate by in situ reduction of copper chloride using $NaBH_4$. The prepared novel magnetic catalyst, Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel was characterized by different techniques such as fourier transform infrared (FT-IR) spectroscopy, thermo gravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray (EDX) analysis, inductively coupled plasma atomic emission spectroscopy (ICP-AES,) ultra violet-visible absorption spectroscopy (UV–Vis) and vibrating sample magnetometery (VSM).

The surface chemical structure of the synthesized materials was characterized by FTIR spectroscopy. Figure 1 shows the FT-IR spectra of (a) $Fe_3O_4$@$SiO_2$, (b) $Fe_3O_4$@$SiO_2$/$NH_2$cel and (c) Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel. The characteristic peak at 578 $cm^{-1}$ due to the presence of Fe–O bond and the peaks around 1113, 798 and 475 $cm^{-1}$ due to the characteristic $SiO_2$ bands were observed in Fig. 1a, b, c. Further, the IR spectrum of $Fe_3O_4$@$SiO_2$/$NH_2$cel (Fig. 1b) characterized by the broad peak centred around 3400 $cm^{-1}$ was an envelope of stretching vibrations for O–H of the adsorbed water, silanol groups, and N–H of the ethylene diamine functionalized cellulose. Two additional characteristic bands around 2895 and 1628 $cm^{-1}$ were assigned to the stretching vibrations of the C–H of $CH_2$ groups and the bending vibrations of the −NH of the $NH_2$ groups respectively, both of which were associated with ethylene diamine modified $Fe_3O_4$@$SiO_2$/$NH_2$cel (Fig. 1b, c). These FT-IR spectra provided evidence of the formation of a silica shell onto the surface of $Fe_3O_4$ and also indicated that the ethylene diamine functionalized cellulose was successfully grafted onto $Fe_3O_4$@$SiO_2$.

To examine the thermal stability of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel, thermal gravimetric analysis was carried out in the temperature range of 39–700 °C at a heating rate of 10 °C/min under nitrogen atmosphere (Fig. 2). The TGA profile of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel indicated reasonable stability up to 210 °C, after which there was a sharp weight loss. The slight weight loss below 100 °C was attributed to the desorption of adsorbed water species from the catalyst surface, while the sharp decrease beyond 210 °C may be associated with the decomposition of cellulose and chemisorbed material i.e. ethylene diamine groups present in the modified $Fe_3O_4$@$SiO_2$/$NH_2$cel substrate. Thus, the catalyst is stable up to 210 °C and it is safe to carry out the reaction at room temperature under heterogeneous conditions.

The formation of Cu(0) nanoparticles was confirmed through X-ray powder diffraction studies. Figure 3 showed three reflection patterns at $2\theta = 43.4°$, 50.5°, and 74.2°

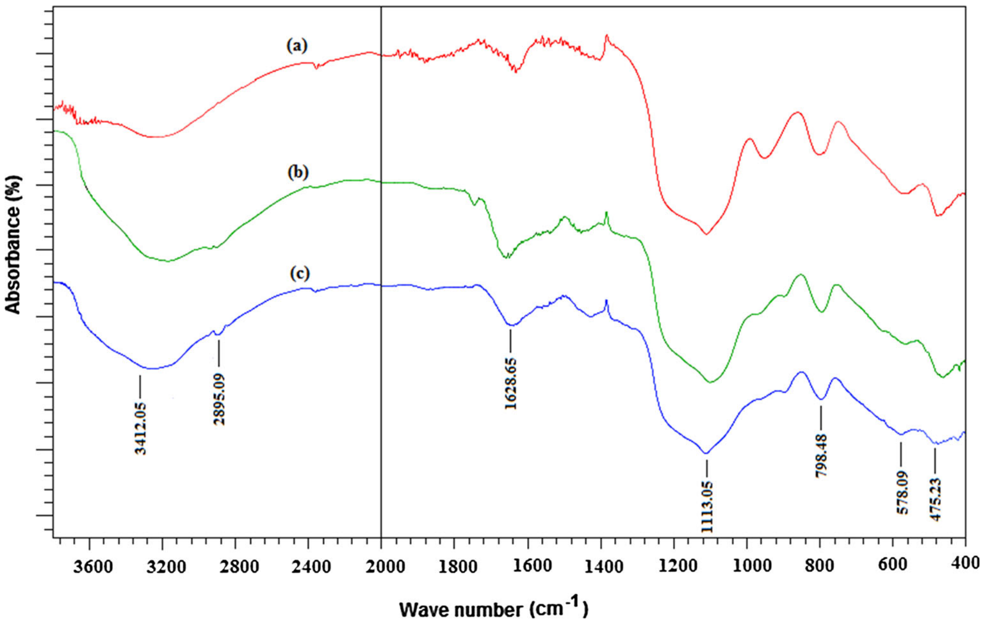


**Fig. 1** FT-IR spectras of **a** $Fe_3O_4@SiO_2$; **b** $Fe_3O_4@SiO_2/NH_2$cel; and **c** Cu(0)–$Fe_3O_4@SiO_2/NH_2$cel

corresponding to the [111], [200] and [220] crystalline planes of face-centered cubic (fcc) Cu [50]. These diffraction patterns clearly indicated that Cu nanoparticles were present in the zero oxidation state and no peaks of impurity were detected. Further, the diffraction peaks at $2\theta = 30.2°$, 35.6°, 42.3°, 57.1° and 62.3° corresponds to the [111], [220], [311], [440] and [511] planes of cubic phase of $Fe_3O_4$ lattice [51] and some enhanced peak intensity was caused by overlapping of peaks of Cu and $Fe_3O_4$ respectively. In addition to it, a broad diffraction peak at $2\theta = 20\text{-}29°$ was assigned to amorphous silica coated on the surface of $Fe_3O_4$ nanospheres.

In order to understand the surface morphology of Cu(0)–$Fe_3O_4@SiO_2/NH_2$cel, the systematic study on SEM analysis was carried (Fig. 4a, b). The SEM images showed that the catalyst was a homogeneous powder and Cu nanoparticles were uniformely distributed onto the surface of $Fe_3O_4@SiO_2/NH_2$cel, and most of the particles have quasi-spherical shape. The morphology and distribution of copper nanoparticles onto the surface of magnetic $Fe_3O_4@SiO_2/NH_2$cel substrate was examined by HRTEM analysis (Fig. 4c, d). The HRTEM images of the catalyst exhibited the presence of spherical particles as were observed in SEM micrographs also. Figure 4d of the Cu(0)–

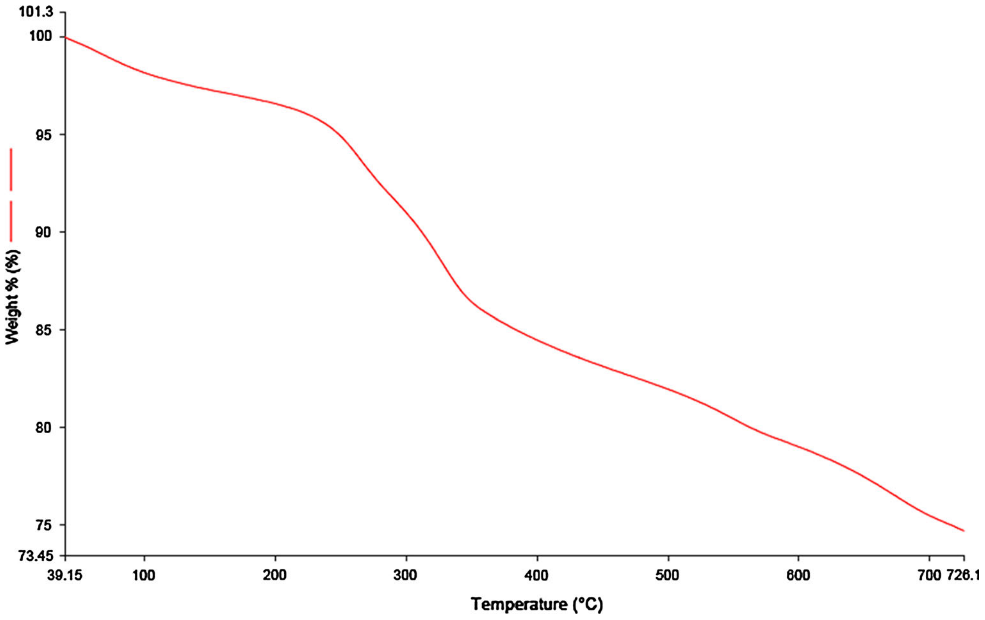


**Fig. 2** TGA of Cu(0)–$Fe_3O_4@SiO_2/NH_2$cel

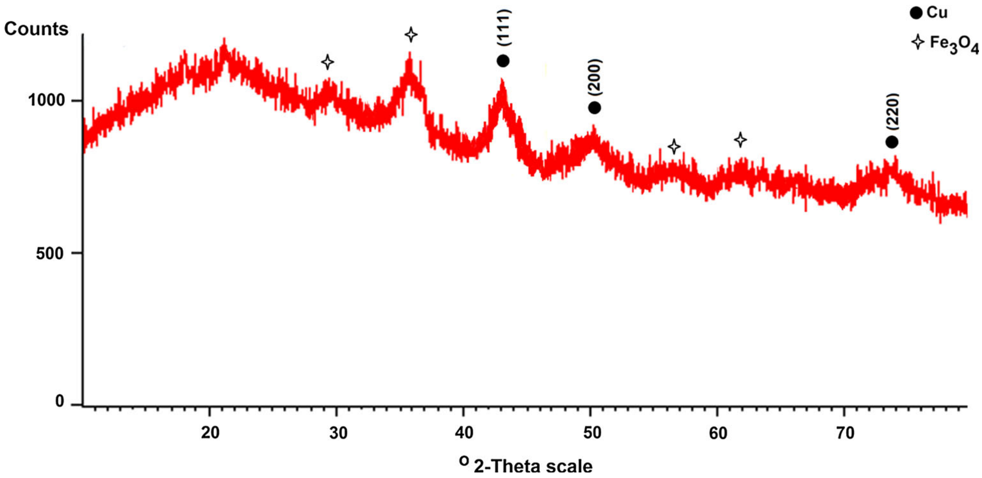


**Fig. 3** XRD of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel

$Fe_3O_4$@$SiO_2$/$NH_2$cel catalyst revealed that plenty of Cu nanoparticles with nearly spherical morphology and good dispersibility were distributed on the surface of the modified coreshell, $Fe_3O_4$@$SiO_2$/$NH_2$cel. Further, HRTEM image (Fig. 4e) of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel depict the lattice fringes with an interplanar spacing of approximately 0.21 nm corresponding to the characteristic metallic Cu [111] plane [52]. Furthermore, the size distribution of copper nanoparticles onto the surface of $Fe_3O_4$@$SiO_2$/$NH_2$cel was determined through the histogram which was proposed according to the data, obtained from the HRTEM (Fig. 4f). The average size of Cu(0) nanoparticles was 9 nm which showed a close agreement with the values calculated by XRD data.

The elemental composition of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel was analyzed by energy dispersive X-ray (EDX) spectroscopy and the outcome was acceptable with expected elements: iron, silicon, oxygen, carbon and copper (Fig. 5). Further, the weight percentage of Cu in Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results indicated that Cu content loaded onto $Fe_3O_4$@$SiO_2$/$NH_2$cel was 6.51 wt%.

UV–Vis spectroscopy of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel was done to determine the formation and stability of copper nanoparticles (Fig. 6). The results showed that the maximum absorbance appeared at 582 nm which was due to Cu(0) nanoparticles. Moreover, there is a weak band near 800 nm due to $Cu^{2+}$ ions [53] which may be attributed to the trace amounts of unreduced Cu(II) salt. Further, a peak at 263 nm was observed due to the absorbance of $Fe_3O_4$ nanoparticles.

The magnetic properties of $Fe_3O_4$ and Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel were evaluated by vibrating sample magnetometery (VSM) at room temperature. The VSM magnetization curves illustrates zero coercivity for both samples which exhibited a superparamagnetic behaviour (Fig. 7). The magnetic saturation values were 42.0 emu/g and 36.4 emu/g for $Fe_3O_4$ and Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel respectively. The decrease in magnetic saturation value for Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel was probably due to the existence of the large amount of non-magnetic material surrounding the magnetic $Fe_3O_4$ nanoparticles. The inset image in the Fig. 7, indicate that the magnetic properties of the catalyst allow a facile separation from the reaction mixture and subsequent redispersion into solution without any appreciable aggregation in successive reaction runs.

## 3.2 Catalytic Activity of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel for the One-Pot Synthesis of 1,4-Disubstituted-1,2,3 Triazoles

In order to obtain the most appropriate conditions for the designed protocol, reaction between phenylacetylene and phenyl azide formed in situ from aniline using water as the reaction medium at room temperature was selected as the model reaction (Scheme 2). Then, we set out to evaluate various experiments to compare the catalytic activity of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel with other catalysts and to optimize the various reaction parameters such as catalyst amount, reaction temperature and time. At first, the model reaction was performed without using any catalyst at 60 °C in $H_2O$ (Table 1, entry 1). No reaction was observed under this condition. Then, the model reaction was performed using 0.1 g of different catalyst systems, while keeping other conditions unaltered. Unfortunately, the yields obtained with other catalysts were not satisfactory (Table 1, entries 2–9). Further, we examined the use of Cu-nanopowder and heterogeneous magnetic catalyst, Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel for the model reaction (Table 1, entries 10–11). As can be seen from the results, use of Cu-nanopowder led to appreciable increase in the yield of product in 7 h (Table 1, entry 10) but best results were

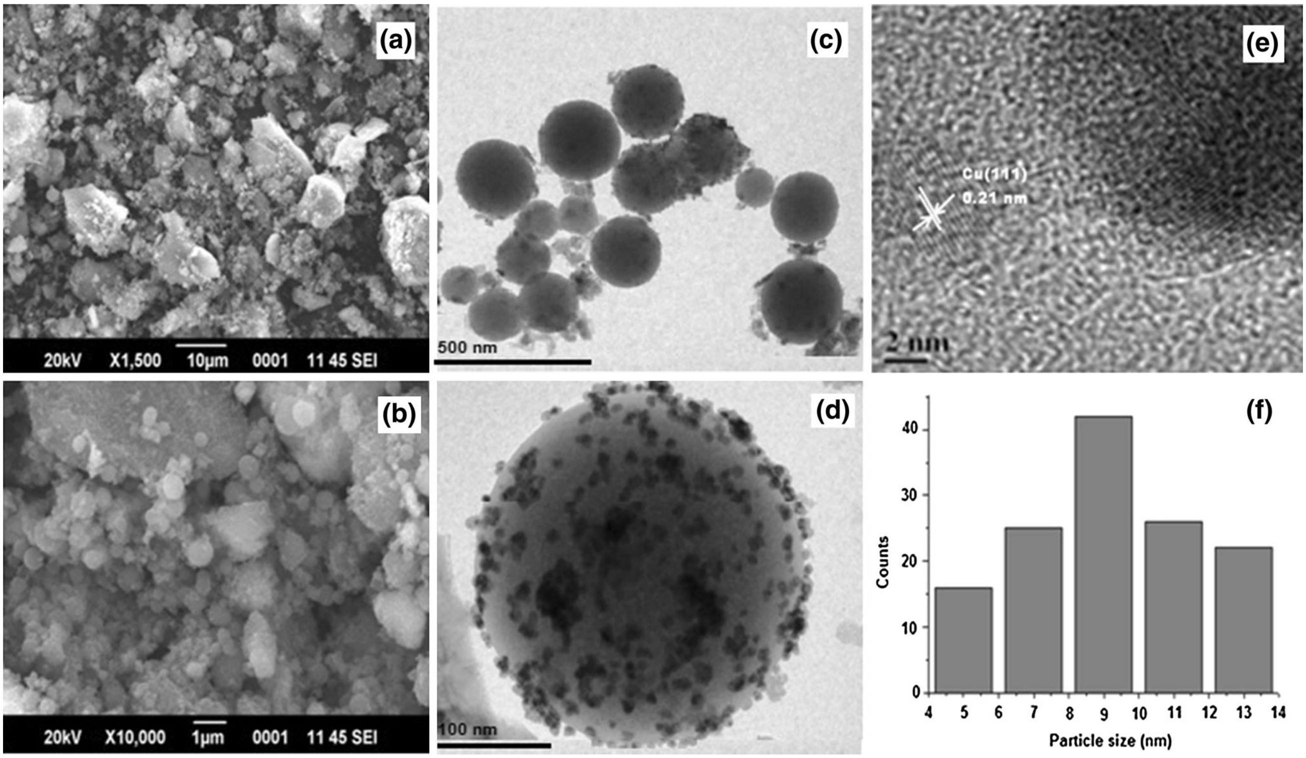


**Fig. 4** SEM (**a**, **b**), HRTEM (**c**, **d**, **e**) and particle size histogram (**f**) of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel

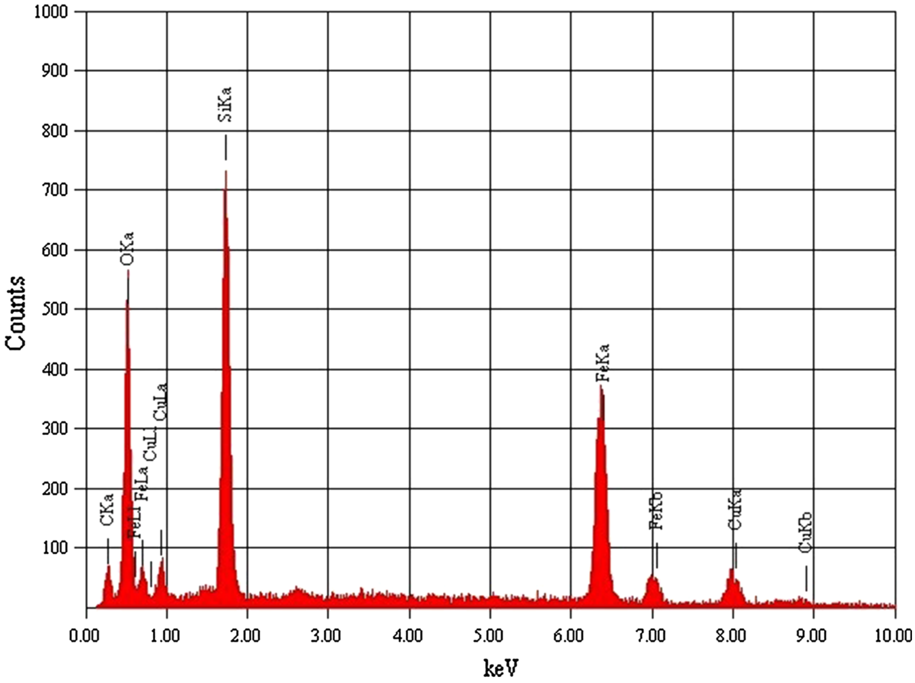


**Fig. 5** EDX of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel

obtained with 0.05 g (0.25 mol% Cu) of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel at 60 °C, and the desired product formation took place in 5 h with 97 % yield (Table 1, entry 11). Inspired by these results, we further tried the model reaction with Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel at room temperature. To our delight, no significant change in yield of product

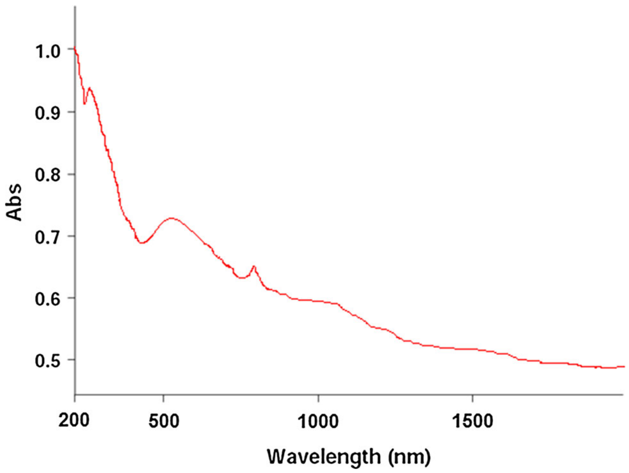


**Fig. 6** UV–Vis absorption spectra of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel

was observed at room temperature (Table 1, entry 12). Further decrease in the amount of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel from 0.05 to 0.025 g at room temperature led to the decrease in yield of the product (Table 1, entry 13). Thus, 0.05 g of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel was the effective amount required to carry out the desired reaction at room temperature. These results clearly indicates that the large surface-to-volume ratio of the nanoparticles together with their distribution on the magnetic support, played a significant role and could account for the excellent behaviour of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel in catalyzing the desired reaction.

After optimizing the reaction conditions, we further explored the scope and generality of the developed protocol for the synthesis of 1,4-disubstituted-1,2,3-triazoles in the presence of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel in water at room temperature. The results are summarized in Table 2. Initially, a range of diversely substituted amines were used for the in situ formation of azides which were reacted with phenylacetylene to get the corresponding 1,4-disubstituted-1,2,3-triazoles (Table 2, entries 1–9). These results showed that the reactions were equally facile with both electron-donating and electron-withdrawing substituents present in aniline and resulting in high yields of the corresponding triazoles. The structure of 1-(4-nitrophenyl)-4-phenyl-1*H*-1,2,3-triazole (Table 2, entry 8) was confirmed by single crystal X-ray crystallography (Fig. 8). For detailed crystal structure analysis, see ESI. Benzyl azide and 4-$NO_2$-benzyl azide formed in situ from benzyl amine and 4-$NO_2$-benzyl amine too undergo clean reactions with phenylacetylene to produce the corresponding triazoles in excellent yields (Table 2, entries 10 and 11). Further, we carried the one pot synthesis of triazoles using different phenylacetylenes (Table 2, entries 12-16). 1-Ethynyl-4-methoxybenzene smoothly reacted with 4-flourophenyl azide to form the 1-(4-flourophenyl)-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (Table 2, entry 12), the structure of which was also confirmed through X-ray crystallography [54] (Fig. S7, see ESI). 3-Ethynylthiophene also undergoes reaction smoothly with phenylazide prepared in situ from aniline to form 1-phenyl-4-(thiophen-3-yl)-1*H*-1,2,3-triazole in good yield (Table 2, entry 13). The reaction performed equally well with other substituted phenyl acetylenes to form the corresponding triazoles in high yields (Table 2, entries 14-16). In general, a clean and high yielding methodology was developed using Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel for the one-pot synthesis of wide variety of 1,4-disubstituted-1,2,3-triazoles under mild conditions.

To gather insights into the synthesis of 1,4-disubstituted-1,2,3-triazoles and to ascertain if the catalytic reaction involves the Cu(0) or Cu(I) intermediate, a plausible reaction mechanism has been proposed (Scheme 4), in which copper exhibited both zero as well as +1 oxidation state during the reaction because of its unsatisfied surface valencies [33, 55, 56]. As Cu(I) is considered to be the

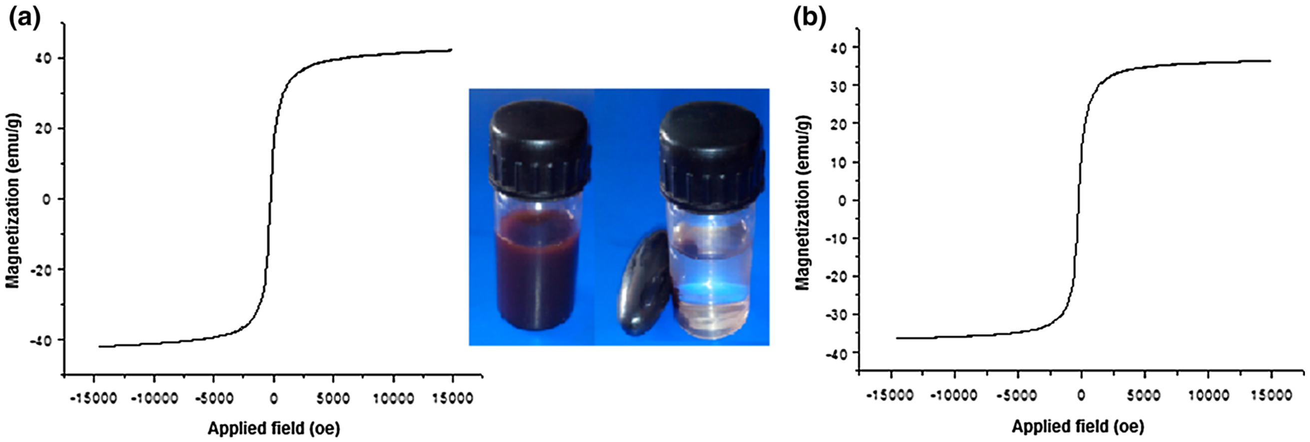


**Fig. 7** Room temperature magnetization curves of (**a**) $Fe_3O_4$ and (**b**) Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel

**Table 1** Optimization of reaction conditions for the one-pot synthesis of 1,4-diphenyl-1*H*-1,2,3 triazole from phenylacetylene and aniline

| Entry | Catalyst | Amount (g) | Temp (°C)[b] | Time (h) | Yield (%)[C] |
|---|---|---|---|---|---|
| 1. | – | – | 60 | 20 | – |
| 2. | $SiO_2$ | 0.1 | 60 | 15 | Traces |
| 3. | $Fe_3O_4$ | 0.1 | 60 | 15 | 30 |
| 4. | $Fe_3O_4@SiO_2$ | 0.1 | 60 | 15 | 35 |
| 5. | $Fe_3O_4@SiO_2/NH_2$cel | 0.1 | 60 | 15 | 42 |
| 6. | CuO | 0.1 | 60 | 15 | 55 |
| 7. | $Cu_2O$ | 0.1 | 60 | 15 | 60 |
| 8. | $Cu(OAc)_2$ | 0.1 | 60 | 15 | 62 |
| 9. | $CuCl_2$ | 0.1 | 60 | 12 | 70 |
| 10. | Cu-nanopowder | 0.1 | 60 | 7 | 83 |
| 11. | Cu(0)–$Fe_3O_4@SiO_2/NH_2$cel | 0.05 | 60 | 5 | 97 |
| 12. | Cu(0)–$Fe_3O_4@SiO_2/NH_2$cel | 0.05 | R.T. | 5 | 96 |
| 13. | Cu(0)–$Fe_3O_4@SiO_2/NH_2$cel | 0.025 | R.T. | 5 | 85 |

[a] Reaction conditions: aniline (0.186 g, 2 mmol), conc. HCl–$H_2O$ (1:1, 1.5 mL), $NaNO_2$ (0.17 g, 2.5 mmol), $NaN_3$ (0.19 g, 3 mmol), phenylacetylene (0.20 g, 2 mmol)

[b] Temperature refers to the second step

**Table 2** Cu(0)–$Fe_3O_4@SiO_2/NH_2$cel catalyzed one-pot synthesis of 1,4-disubstituted-1,2,3-triazoles in water at room temperature

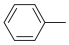
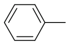
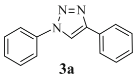
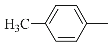
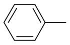
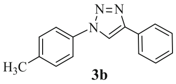
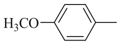
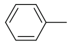
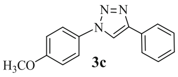
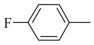
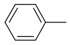
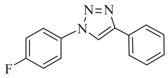
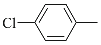
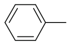
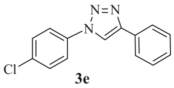
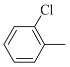
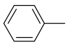
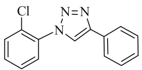
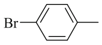
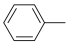
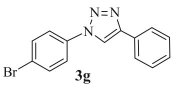
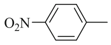
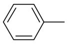
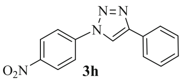
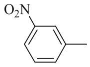
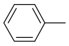
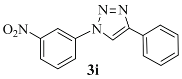
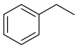
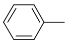
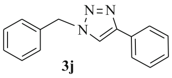
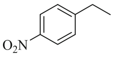
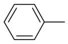
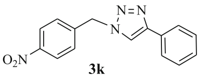
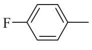
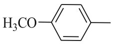
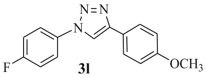
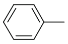
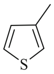
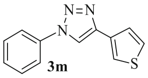
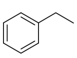
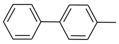
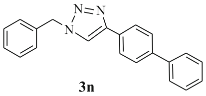
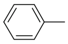
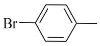
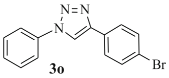
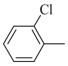
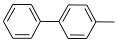
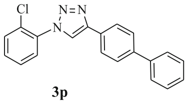
| Entry | R | R' | Product (3) | Time (h) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1. |  |  |  **3a** | 5 | 96 |
| 2. |  |  |  **3b** | 5 | 93 |
| 3. |  |  |  **3c** | 5 | 94 |
| 4. |  |  |  **3d** | 3.5 | 95 |
| 5. |  |  |  **3e** | 5 | 94 |
| 6. |  |  |  **3f** | 5 | 93 |
| 7. |  |  |  **3g** | 5 | 93 |

**Table 2** continued

| Entry | R | R' | Product (3) | Time (h) | Yield (%)$^b$ |
|---|---|---|---|---|---|
| 8. |  |  |  **3h** | 5 | 95 |
| 9. |  |  |  **3i** | 5 | 92 |
| 10. |  |  |  **3j** | 4 | 94 |
| 11. |  |  |  **3k** | 4 | 93 |
| 12. |  |  |  **3l** | 4 | 94 |
| 13. |  |  |  **3m** | 5 | 93 |
| 14. |  |  |  **3n** | 5 | 95 |
| 15. |  |  |  **3o** | 4 | 92 |
| 16. |  |  |  **3p** | 5 | 92 |

Reaction conditions: aryl amine (2 mmol), conc. HCl-$H_2O$ (1:1, 1.5 mL), $NaNO_2$ (2.5 mmol), $NaN_3$ (3 mmol) aryl alkyne (2.5 mmol), catalyst (0.05 g, 0.25 mol% Cu) at room temperature

[a] Isolated yields

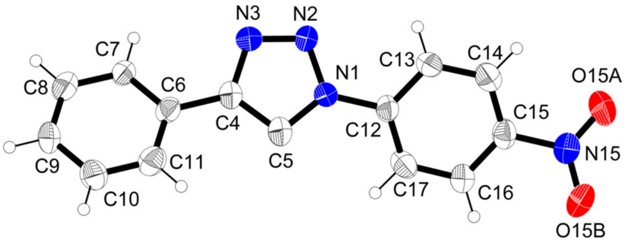


**Fig. 8** ORTEP of 1-(4-nitrophenyl)-4-phenyl-1*H*-1,2,3-triazole

most active species in the click reactions, so it is proposed that alkyne by initial coordination with Cu(0) NPs is converted to Cu(I)-acetylidine complex (**A**). Cu(I)-Acetylidine complex undergoes addition to azide group to give π-complex as an intermediate product, (**B**). Further, attack of the nitrogen of the azide to the C-2 carbon of the Cu-acetylidine takes place to give a six-membered transient copper metallacycle, (**C**) in which ring contraction occurs to afford a Cu(I)-triazolide complex, (**D**), which finally give triazole (**E**).

### 3.3 Catalytic Activity of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel for the One-Pot-Three Component Synthesis of 2-Substituted Benzothiazoles

In continuation of our efforts towards ‘one-pot’ reactions, the potential and efficiency of the designed catalyst, Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel was investigated for the synthesis of benzothiazole derivatives in water. In order to optimize the reaction conditions, one-pot three component reaction of 2-iodoaniline, benzaldehyde and thiourea as sulfur source in water at 100 °C was selected as the test reaction (Scheme 3). We, then began our experiment by comparing the catalytic activity of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel with other catalysts and by optimizing the various reaction parameters such as catalyst amount and reaction

**Scheme 4** Plausible mechanism of the Cu(0)–$Fe_3O_4@SiO_2/NH_2$cel catalysed synthesis of 1,4-disubstituted-1,2,3-triazoles

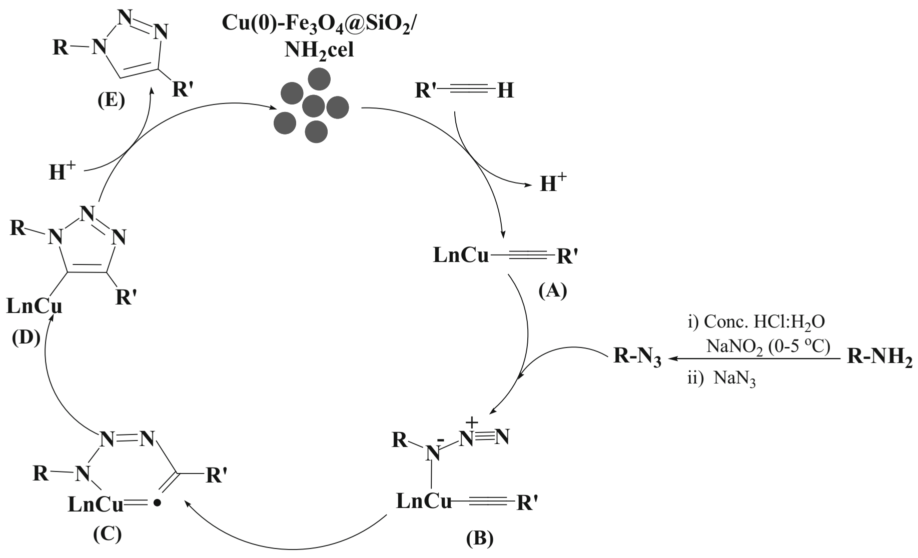


**Table 3** Optimization of reaction conditions for the one-pot three component reaction of 2-iodoaniline, benzaldehyde and thiourea for the synthesis of 2-substituted benzothiazoles in water at 100 °C

| Entry | Catalyst | Amount (g) | Temp (°C)[a] | Time (h) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1. | – | – | 60 | 10 | NR[c] |
| 2. | – | – | 80 | 10 | NR[c] |
| 3. | – | – | 100 | 10 | NR[c] |
| 4. | $SiO_2$ | 0.1 | 100 | 10 | Traces |
| 5. | $Fe_3O_4$ | 0.1 | 100 | 10 | 20 |
| 6. | $Fe_3O_4@SiO_2$ | 0.1 | 100 | 10 | 26 |
| 7. | $Fe_3O_4@SiO_2/NH_2$cel | 0.1 | 100 | 10 | 35 |
| 8. | CuO | 0.1 | 100 | 10 | 45 |
| 9. | $Cu_2O$ | 0.1 | 100 | 10 | 52 |
| 10. | $Cu(OAc)_2$ | 0.1 | 100 | 10 | 55 |
| 11. | $CuCl_2$ | 0.1 | 100 | 8 | 60 |
| 12. | Cu-nanopowder | 0.1 | 100 | 6.5 | 72 |
| 13. | Cu(0)–$Fe_3O_4@SiO_2/NH_2$cel | 0.1 | 100 | 6 | 83 |
| 14. | Cu(0)–$Fe_3O_4@SiO_2/NH_2$cel | 0.05 | 100 | 6 | 83 |
| 15. | Cu(0)–$Fe_3O_4@SiO_2/NH_2$cel | 0.025 | 100 | 6 | 74 |

Reaction conditions: 2-Iodoaniline (0.219 g, 1 mmol), benzaldehyde (0.127 g, 1.2 mmol), thiourea (0.228 g, 3 mmol), $K_2CO_3$ (0.414 g, 3 mmol), catalyst (0.05-0.1 g), $H_2O$ (5 mL)

[a] Isolated yield

temperature. The results are presented in Table 3. Initially, we carried out the test reaction without using any catalyst at 60, 80 and 100 °C in water, but no reaction was observed in all these cases and starting materials remained unreacted (Table 3, entries 1–3). Further, we carried out the reaction using 0.1 g each of $SiO_2$, $Fe_3O_4$, $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2/NH_2$cel (Table 3, entries 4–7). However, the results obtained with these catalysts were also not satisfactory. For the synthesis of benzothiazoles, copper as a catalyst has gained more attention [57, 58] because it is economical and has potential applications in large-scale reactions. So, further optimization with CuO, $Cu_2O$, $Cu(OAc)_2$, $CuCl_2$ and Cu-nanopowder had a pronounced effect on the yield of the product (Table 3, entries 8–11). Remarkably, the use of Cu-nanopowder increased the efficiency, and produced the good results (Table 3, entry 12). But, the best results were obtained by employing the present heterogeneous catalyst, Cu(0)–$Fe_3O_4@SiO_2/NH_2$cel for carrying out the test reaction which results in the drastic increase in the yield of the product to 83 % (Table 3, entry 13). Fascinated by these results, we carried out the test reaction using 0.05 g of Cu(0)–$Fe_3O_4@SiO_2/NH_2$cel, while keeping other conditions unaltered and the results indicated no significant change in the yield of product (Table 3, entry 14), although, further reduction in the amount of Cu(0)–$Fe_3O_4@SiO_2/NH_2$cel led to the decrease in the yield of product (Table 3, entry 15). Thus, 0.05 g (0.25 mol% Cu) of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel was the sufficient amount required to carry out the reaction at 100 °C. These results indicates that Cu(0) nanoparticles due to the large surface-to-volume ratio together with their distribution on the magnetic support, acts synergistically for the outstanding behaviour of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel in catalyzing the desired reaction.

With the optimum reaction conditions in hand, a wide range of substrates were examined to further explore the generality and scope of the designed protocol using Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel, and the representative results are summarized in Table 4. A variety of substituted aldehydes bearing either electron-withdrawing or electron-donating groups could proceed smoothly under the optimized reaction conditions, various functional groups such as methyl, methoxy, hydroxy, chloro, bromo, nitro at the *ortho*, *meta*, or *para* position of arene moiety all could be tolerated fairly well and afforded the desired products in moderate to high yields (Table 4, entries 1–12). Further, a range of heterocyclic aldehydes including furfural-2-aldehyde, thiophene-2-carbaldehyde and pyrrole-2-adehyde were successfully employed to get the corresponding products in good yields (Table 4, entries 13–15). Thus, a clean and efficient methodology was developed using Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel for the one-pot three component reaction of 2-iodoaniline, aldehyde and thiourea as sulphur source for the synthesis of benzothiazoles under the given reaction conditions.

## 3.4 Comparison of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel with Other Reported Catalyst Systems

In order to evaluate the merits of the current protocol for the synthesis of 1,4-disubstituted-1,2,3-triazoles and 2-substituted benzothiazoles, a comparison of the activity of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel with some of the reported catalytic systems in the literature was done. For the synthesis of 2-substituted benzothiazoles, majority of the reported protocols involves the condensations of 2-aminothiophenol with

**Table 4** Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel catalysed one-pot three component reaction of 2-iodoaniline, aldehyde and thiourea for the synthesis of benzothiazoles in water at 100°C

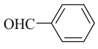
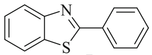
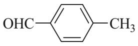
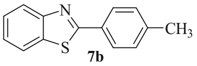
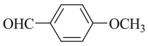
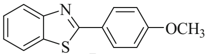
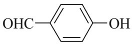
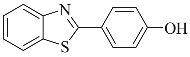
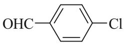
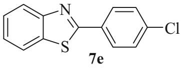
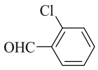
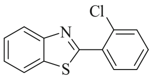
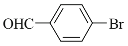
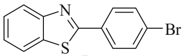
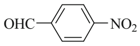
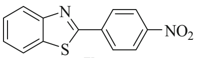
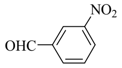
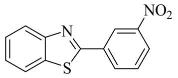
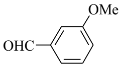
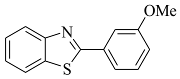
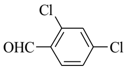
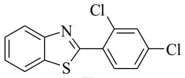
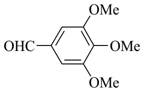
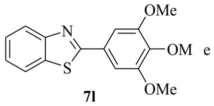
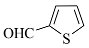
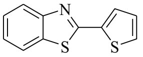
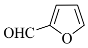
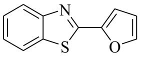
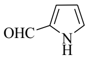
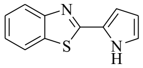
| Entry | Aldehyde | Product (7) | Time (h) | Yield (%)[b] |
|---|---|---|---|---|
| 1. |  |  **7a** | 6 | 83 |
| 2. |  |  **7b** | 6.5 | 81 |
| 3. |  |  **7c** | 6 | 82 |
| 4. |  |  **7d** | 7 | 82 |
| 5. |  |  **7e** | 5 | 83 |
| 6. |  |  **7f** | 5.5 | 82 |
| 7. |  |  **7g** | 5 | 82 |
| 8. |  |  **7h** | 5 | 84 |

**Table 4** continued

| Entry | Aldehyde | Product (7) | Time (h) | Yield (%)[b] |
|---|---|---|---|---|
| 9. |  | <br>**7i** | 6.5 | 81 |
| 10. |  | <br>**7j** | 6 | 80 |
| 11. |  | <br>**7k** | 5 | 82 |
| 12. |  | <br>**7l** | 5 | 84 |
| 13. |  | <br>**7m** | 6 | 81 |
| 14. |  | <br>**7n** | 6.5 | 81 |
| 15. |  | <br>**7o** | 6 | 80 |

Reaction conditions: 2-Iodoaniline (1 mmol), aldehyde (1.2 mmol), thiourea (3 mmol), $K_2CO_3$ (3 mmol), Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel (0.05 g, 0.25 mol% Cu), $H_2O$ (5 mL) at 100 °C

[a] Isolated yields

carboxylic acids, acid chlorides, nitriles and aldehydes [39–42], very less literature is available for the benzothiazole synthesis via the one-pot three component reaction of 2-iodoaniline, aldehyde and using thiourea as sulfur source [59]. The results obtained after comparing Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel with literature are compiled in Table 5, which clearly demonstrates the superiority of the present catalytic system by comparatively affording a truly green process using aqueous reaction media along with higher product yields in shorter reaction time.

## 4 Recyclability and Heterogeneity

To make the synthetic protocol more useful and economical, the recyclability of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel was studied in case of Table 2, entry 1 and Table 4, entry 1. For each of the repeated reactions, the catalyst was recovered by external magnet followed by washing with ethyl acetate (2 × 10 mL) and distilled water (2 × 10 mL). Then it was reused after drying in vacuum at 60 °C. The results indicated the high stability and activity of the catalyst after 6 subsequent reaction cycles (Table 6). Further, the heterogeneity of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel was tested by the hot filtration test to examine whether copper was being leached out from the catalyst surface to the solution. The reaction in case of Table 4, entry 1, has been carried out in the presence of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel, until the conversion was 48 % (2.5 h) after which the catalyst was filtered off at the reaction temperature and the filtrate was allowed to react further up to the completion of the reaction (6 h). In this case no significant conversion was observed, which suggests that the catalyst is heterogeneous in nature. Furthermore, the ICP-AES analysis of the used Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel after 6th run showed 6.46 wt% of Cu content, which indicated that a negligible amount of the Cu metal was removed from the surface of $Fe_3O_4$@$SiO_2$/$NH_2$cel (fresh catalyst contains 6.51 wt% Cu), thus resulting in insignificant leaching of copper. FTIR and TGA studies showed that the spent catalyst had no observable structural change relative to the fresh catalyst.

**Table 5** Comparison of the catalytic activity of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel with reported catalytic systems for the one-pot synthesis of 1,4-disubstituted-1,2,3-triazoles and 2-substituted-benzothiazoles

| Reaction | Catalyst | Reaction conditions | Time (h) | Yield (%) | Reference |
|---|---|---|---|---|---|
| 1,4-Disubstituted-1,2,3-triazoles | aq. $CuSO_4$ | Aniline, *t*-BuONO, $TMSN_3$, $CH_3CN$, Phenylacetylene, sodium ascorbate, r.t. | 16 | 88 | 60 |
| | $Cu(OAc)_2$ | Aniline, *N*-tosylhydrazone, PivOH, toluene, 100 °C | 12 | 73 | 61 |
| | CuNPs/C | Aniline, *t*-BuONO, $NaN_3$, Phenylacetylene, $H_2O$, 70 °C | 3 | 90 | 62 |
| | CuNPs@agarose | Aniline, *t*-BuONO, $NaN_3$, Phenylacetylene, $H_2O$ and *t*-BuOH (1:1), 40 °C | 12 | 82 | 63 |
| | Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel | Aniline, phenyl acetylene, $H_2O$, r.t. | 5 | 96 | This work |
| 2-Substituted benzothiazoles | Cu-Py-SBA-15 | 2-Iodoaniline, benzaldehyde, thiourea, $K_2CO_3$, $H_2O$, 100 °C | 12 | 75 | 59 |
| | Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel | 2-Iodoaniline, benzaldehyde, thiourea, $K_2CO_3$, $H_2O$, 100 °C | 6 | 83 | This work |

**Table 6** Recyclability of Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel for the one-pot synthesis of 1,4-disubstituted-1,2,3- triazoles and 2-substituted benzothiazoles

| Catalytic runs | 1,4-Disubstitited-1,2,3-triazoles yield (%)[a] | 2-Substituted benzothiazoles yield(%)[a] |
|---|---|---|
| 1 | 96 | 83 |
| 2 | 96 | 83 |
| 3 | 95 | 82 |
| 4 | 94 | 82 |
| 5 | 94 | 81 |
| 6 | 93 | 80 |

Reaction conditions [1,4-disubstituted-1,2,3- triazoles]: aniline (0.186 g, 2 mmol), conc. HCl–$H_2O$ (1:1, 1.5 mL), $NaNO_2$ (0.17 g, 2.5 mmol), $NaN_3$ (0.19 g, 3 mmol), phenylacetylene (0.20 g, 2 mmol), catalyst (0.05 g, 0.25 mol% Cu) at room temperature; [benzothiazoles]

[a] Isolated Yields. 2-Iodoaniline (0.219 g, 1 mmol), benzaldehyde (0.127 g, 1.2 mmol), thiourea (0.228 g, 3 mmol), $K_2CO_3$ (0.414 g, 3 mmol), catalyst (0.05–0.1 g), $H_2O$ (5 mL), 100 °C

## 5 Conclusion

In conclusion, we have developed Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel as a novel, highly efficient, and sustainable magnetic catalyst for the one-pot synthesis of 1,4-disubstituted-1,2,3-triazoles and 2-substituted benzothiazoles in water. In triazole synthesis, we have eliminated the use of toxic azides and these molecules were easily prepared from their corresponding anilines by diazotization followed by the addition of sodium azide. Futher, in the protocol for benzothiazole synthesis, we have ruled out the obligation of synthesizing the starting materials as well as the isolation of intermediates and thiourea has been used as sulphur source. Moreover, the heterogeneous magnetic catalyst, Cu(0)–$Fe_3O_4$@$SiO_2$/$NH_2$cel is stable showing negligible copper leaching and aggregation, easily separable using an external magnet and has shown an excellent recyclability up to six times without significant loss of catalytic activity. Thus, the magnetic catalyst due to its novelty, operational simplicity, recyclability and environmental friendliness, is highly desirable to address the environmental concerns and thus we believe that this protocol will find useful applications in green organic synthesis.

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