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Synthesis and Characterization of Copper(I)-Cysteine Complex Supported on Magnetic Layered Double Hydroxide as an Efficient and Recyclable Catalyst System for Click Chemistry Using Choline Azide as Reagent and Reaction Medium

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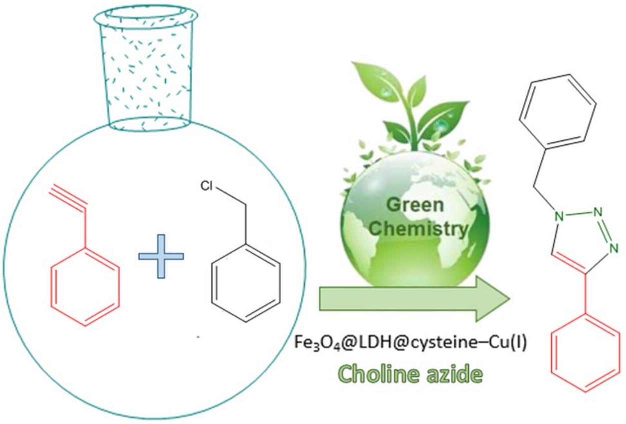
Abstract

In this study, Fe_3O_4@LDH@cysteine–Cu(I) nanoparticles as a novel and recyclable catalytic system was designed and successfully synthesized. These nanoparticles show high catalytic activity for preparation of the triazole family through reaction of the organic halides with alkynes in the presence of choline azide as reagent and reaction medium. In addition, Fe_3O_4@LDH@cysteine–Cu(I) could be easily recovered and reused for five times without any significant loss in catalytic activity.

Graphic Abstract



Keywords Layered double hydroxide · Choline azide · Click chemistry · Magnetic catalyst · Triazole

1 Introduction

Click chemistry is a powerful method for the synthesis of substituted triazoles that has attracted enormous attention in modern chemistry. The term click chemistry was proposed firstly by Sharpless and co-workers in 2001 [1] that has many attractive features including high yielding, simple to perform, excellent functional-group tolerance, wide in scope, fast and highly efficient reactions [2, 3]. Among click reactions, the Huisgen [3 + 2]-cycloaddition of organic azides and alkynes by using copper(I) catalyst

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is one of the most important click reaction due to its high regioselectivity and yield [4]. Also, 1,2,3-triazole derivatives have shown a wide range of biological activity, such as anticancer [5], anti-allergic [6], antiviral [7], antibacterial [8], antidiabetic [9], anti-HIV activity [10] and antimicrobial [11].

The copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) could be studied by new conditions for the synthesis of triazole. Various catalytic systems have been employed for synthesis of triazoles, such as hydroxyapatite [12] polysaccharide-supported nanoparticles [13], polydentate [14], CuO–HMSS [15], zeolite [16] [MNPs@FGly][Cl] [17], however there is still a requirement for the development of new efficient, widely applicable, usage of cheap and low toxicity reagent, feasible as well as eco-friendly method for synthesis of 1,2,3-triazoles.

Recent examples include the use of sodium azide as the source of azide in click reaction which this material is acutely toxic [18] and needs using solvent. The sources of azide can be choline azide that is used as an ionic liquid and azidation reagent. Ionic liquids have attracted significant attention due to the use as green solvent and catalyst for chemistry process. Choline azide is prepared by choline chloride and sodium azide, which can be used as a "green" solvent and safe azidation reagent for the synthesis of substituted triazoles in both laboratories and industrial applications [19].

Several heterogeneous and homogeneous copper-based catalytic systems were studied on CuAAC reactions [20–24], Among a new generation of heterogeneous catalysts, layered double hydroxides (LDHs) coated magnetite nanoparticles are indeed an effective surface of modified magnetic nanoparticle (MNP) which has low toxicity, facile synthesis, moisture, and air stability [25–29]. The resulting LDHs can be readily modified with cysteine through covalent bonding. LDHs are introduced by the general formula $[\mathrm{M\,II}_{1-x}\,\mathrm{M\,III}_x(\mathrm{OH})_2]^{x+}(\mathrm{A}^{n-})_{x/n}\cdot y\mathrm{H_2O}$, that M(II) and M(III) cations occupied octahedral holes in a brucite-like layer and A^{n-} anion is present in the hydrated interlayer. The molar ratio of $\mathrm{M}^{2+}/(\mathrm{M}^{2+}+\mathrm{M}^{3+})$ is equal to the amount of x [30].

In continuation of our efforts in the development of simple and efficient protocols for synthesis of triazoles [31], herein, we report copper(I)-cysteine complex immobilized on the surface of LDH coated magnetite nanoparticles, Fe_3O_4@LDH@cysteine–Cu(I), as an efficient and recoverable nanocatalyst for the synthesis of a number of 1,2,3-triazoles. The magnetic catalyst is easily separated by an external magnet and has several benefits such as thermal stability, recoverability and high surface. In this work, we observed remarkable catalytic activity of Fe_3O_4@LDH@cysteine–Cu(I) nanocatalyst in click Chemistry of organic halide derivatives, choline azide and alkynes. Therefore, this method is a green and effective rout because of employing choline azide instead of using sodium azide and solvent in this method.

2 Experimental

2.1 Materials and Instrumentation

All starting materials and solvents were purchased from Merck Company and Sigma–Aldrich and Merck Company. The monitoring of reaction progress was performed by analytical thin layer chromatography (TLC) on Merck 0.2 mm of silica gel 60F-254 Al-plates.

All structure of compounds were identified. ^{1}H NMR (500 MHz) spectra was determined on Bruker DRX-500 Advance spectrometers with $CDCl_3$ as solvent at ambient temperature by using TMS as the internal standard. Fourier transform infrared spectroscopy (FT-IR) was obtained on a Shimadzu FT-IR-8400S spectrometer by using the KBr plate technique.

Energy-Dispersive X-ray spectroscopy (EDX) spectra was performed by an Oxford Instrumental and also Field Emission Scanning Electron Microscopy (FE-SEM) image was obtained on Zeiss-Sigma VP 500. The magnetic measurements experiments were performed by using a vibrating magnetometer/alternating gradient force magnetometer (MD Co., Iran, www.mdk-magnetic.com). Transmission electron microscopy (TEM) was obtained at 120 kV (Philips, model CM120). X-ray diffraction pattern (XRD) was recorded by a Philips X-Pert 1710 diffractometer.

2.2 Preparation of Fe_3O_4

Generally, Fe_3O_4 was prepared by coprecipitation method. The $FeCl_3.6H_2O$ (10 mmol) and $FeCl_2.4H_2O$ (5 mmol) were dissolved in water (120 ml) under vigorous stirring (800 rpm). Then, NH_4OH (10 ml) was added dropwise to produce a black solid product (pH about 11) and then the mixture was refluxed for 1 h under argon. Finally, the black nanoparticles were separated by an external magnet from the aqueous solution, then washed with deionized water several times until the solution was neutral, and dried in an oven at 50 °C for 24 h.

2.3 Preparation of Fe_3O_4@LDH

The Fe_3O_4@LDH was prepared by dispersing about 1.0 g of Fe_3O_4 in 50 mL of water and 50 mL of methanol for 15 min. Then, 30 mL solution of NaOH (0.8 M) was added dropwise to reach pH 12. And then the mixture of $Mg(NO_3)_2.6H_2O$ (9 mmol) and $Al(NO_3)_3.9H_2O$ (3 mmol) in 100 mL H_2O ($Mg/Al = 3/1$) was added dropwise to the above suspension to reach $pH = 10$. After that, the temperature raised to

60 °C for 24 h. Then the resulting product was separated by an external magnet and thoroughly washed with deionized water and ethanol until the solution was neutral, and dried in an oven at 50 °C for 24 h.

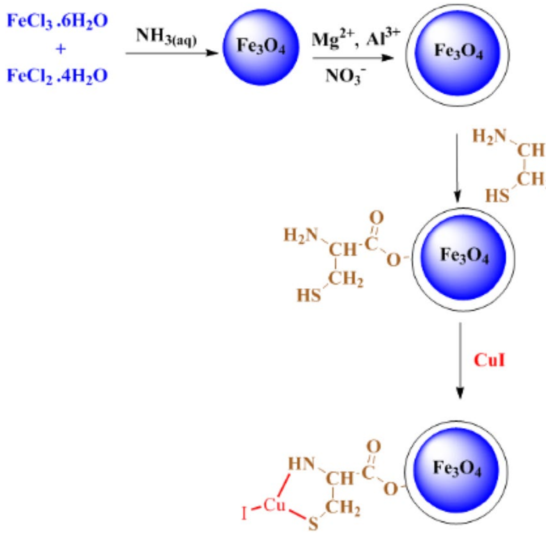
2.4 Preparation of Fe_3O_4@LDH@Cysteine–Cu(I)

The Fe_3O_4@LDH@cysteine was prepared by dispersing about 1.0 g of Fe_3O_4@LDH in 50 mL of water. Then, NaOH (0.8 M) was added dropwise to reach pH about 11. After that 1.5 mmol cysteine was added to this suspension. This solution was refluxed for 24 h. Next, the resulting product was separated by an external magnet and thoroughly washed with deionized water and ethanol until the solution was neutral, and dried in an oven at 50 °C.

1 g of Fe_3O_4@LDH@cysteine was dispersed in THF (50 mL) in an ultrasonic bath for 10 min, then CuI (0.5 mmol) was dispersed in dry THF (15 mL) after stirred at room temperature for 24 h. Finally, the product was separated by an external magnet and dried in an oven at 50 °C for 24 h (Scheme 1).

2.5 Preparation Choline Azide

A mixture of choline chloride (10 mmol), Sodium azide (10 mmol) and methanol (50 ml) was stirred at 65 °C for 6 h. After completion of the reaction, the product separated by filtered off and solvent of solution evaporate under reduced pressure and choline azide was separated as oily residue [19].



Scheme 1 Preparation of Fe_3O_4@LDH@Cysteine–Cu(I) nanocatalyst

2.6 Catalytic Click Reaction in Presence of Fe_3O_4@LDH@cysteine-Cu(I)

A mixture of alkyl halide (2 mmol), terminal alkyne (2 mmol) and choline azide (3 mmol) was stirred at 75 °C in the presence of 20 mg Fe_3O_4@LDH@cysteine-Cu(I) nanocatalyst. After completion of the reaction, the product was decanted by dilution of the residue with water and separated the magnetic catalyst by an external magnet and the solid product was purified by recrystallization from EtOH: H_2O (2:1 v/v). In some cases, products have to be isolated using chromatography on silica gel.

3 Results and Discussions

The method for the preparation of Fe_3O_4@LDH@Cysteine–Cu(I) is depicted in Scheme 1. Fe_3O_4 was synthesized by co-precipitation process. Next, Fe_3O_4@LDH prepared with $Mg(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ in presence NaOH. In the following, reaction of cysteine with magnetic layered double hydroxide led to produce Fe_3O_4@LDH@Cysteine. Finally, Copper(I)-cysteine complex supported on magnetic layered double hydroxide nanoparticles were synthesized by treatment of CuI with Fe_3O_4@LDH@Cysteine for 24 h. Characterization of the catalyst was performed by using different techniques for example FT-IR, FE-SEM, TEM, EDX, TGA, XRD and vibrating sample magnetometry (VSM). FT-IR of Fe_3O_4 (Blue curve), Fe_3O_4 coated with LDH (Orange curve), Fe_3O_4@LDH@cysteine (Grey curve) and Fe_3O_4@LDH@cysteine–Cu(I) before (Black curve) and after reaction (Green curve) were depicted in Fig. 1. The band Fe–O stretching vibration appeared at 578 cm^{-1}. The O–H stretch of Fe_3O_4@LDH (3440 cm^{-1}) was stronger than that of Fe_3O_4@LDH@cystein-Cu(I) due to cysteine interacts with the LDH and weakens the O–H vibration. As

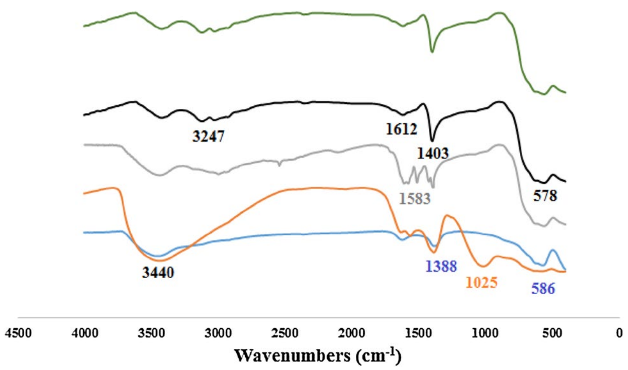


Fig. 1 The FT-IR spectra of the Fe_3O_4 (Blue curve), Fe_3O_4@LDH (Orange curve), Fe_3O_4@LDH@cysteine (Grey curve) and Fe_3O_4@LDH@cysteine-Cu(I) before (Black curve) and after reaction (Green curve)

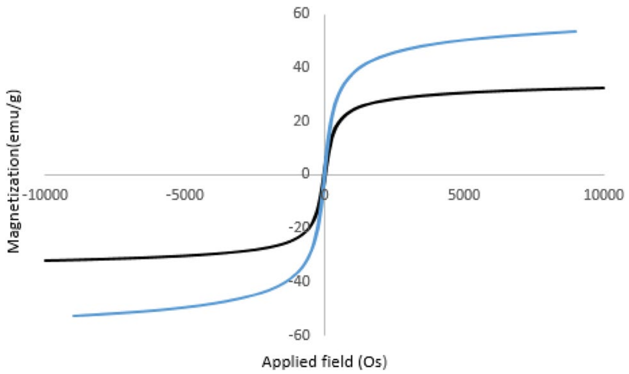


Fig. 2 Magnetization curves of Fe_3O_4 (Blue curve) and Fe_3O_4@LDH@ cysteine-Cu(I) (Black curve)

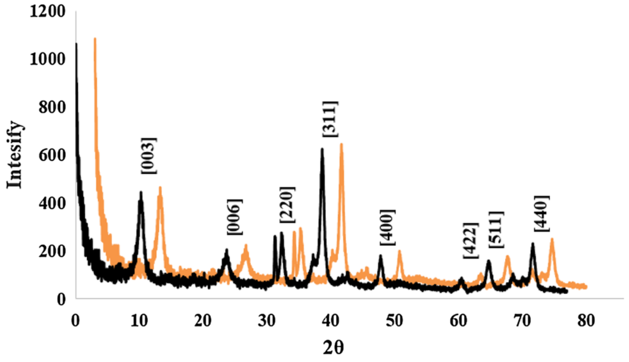


Fig. 3 The X-ray diffraction patterns of Fe_3O_4@LDH@cysteine-Cu(I) (Black) and Fe_3O_4@LDH (Orange)

can be seen in Fig. 1, the major peaks appeared at 3440-3471 cm^{-1} (hydroxyl O—H), 1388-1403 cm^{-1} (Fe–O stretching). Vibration in the FT-IR spectra of Fe_3O_4@LDH@cysteine at 1583 cm^{-1} with Fe_3O_4@LDH@cystein–Cu(I) at 1612 cm^{-1} prove formation of the complex. Also, it shows that the Fe_3O_4@LDH@cystein-Cu(I) nanoparticles have the same structure after 5 cycles (Green curve) and this the structure is stable.

The magnetic possession of the Fe_3O_4 (Blue curve) and Fe_3O_4@LDH@cysteine–Cu(I) (Black curve) was investigated by VSM (Fig. 2). Magnetic hysteresis measurements were done in an applied magnetic field with the the range of -10000 to $+10000$ Oe. Nanoparticles of Fe_3O_4 possessed high saturation magnetization 53 emu/g at 25 °C and decreased to 32.35 emu/g for Fe_3O_4@LDH@cysteine–Cu(I). The formation of Fe_3O_4@LDH@cysteine–Cu(I) takes place simultaneously due to Fe_3O_4@LDH@cysteine–Cu(I) had lower magnetization as compared with that of Fe_3O_4.

As can be seen in Fig. 3, these five peaks of the Fe_3O_4 could be seen for the synthesized Fe_3O_4@LDH@cysteine–Cu(I) ($2\theta = 35.12°$, 41.44°, 50.52°, 63°, 67°, and 74°). The five peaks correspond to the (220), (311), (400), (422), (511) and (440) lattice planes respectively. These XRD peaks confirm well to Fe_3O_4, which are in agreement with work done by Wei et al. [32]. This fact observes which the structure of Fe_3O_4 nanoparticles is kept after the surface modification with LDH@cysteine–Cu(I). Additional diffraction peaks at around 13.23°, 26.79°, and 40.73° are related to Mg–Al LDH [33]. These results indicate that Fe_3O_4@LDH@cysteine–Cu(I) have been successfully synthesized. The intercalated cysteine -LDH appeared a few shift of the (003), (006) and (440) reflections to lower angles, which agreed with intercalation cysteine into the inter-layer of the layered double hydroxide. The basal spacing's of the Layered double hydroxide could be calculated from the basal reflection by using Bragg's equation, $\lambda = 2d\sin\theta$. λ is the wavelength of Cu-Kα radiation, and θ is the half of the scattering angle of (0 0 3) peak. Results indicated that the interlayer spacing of Fe_3O_4@LDH@cysteine–Cu(I) (Å) is larger than that of Fe_3O_4@LDH (Å), demonstrating the intercalation of Fe_3O_4@LDH by a little of amount cysteine [34].

EDX analysis was used to give information about the elements present in Fe_3O_4@LDH@cysteine-Cu(I) (Fig. 4). EDX pattern clearly confirms the good dispersion of magnetic solid. Chemical characterization of the typical sample shows the presence of iron (34.36 wt%), magnesium (7.57 wt%), aluminium (1.07 wt%), nitrogen (1.17 wt%), sulphur (0.09 wt%), carbon (6.39 wt%), oxygen (47.46 wt%) and copper (1.88 wt%).

The size and the morphology of Fe_3O_4@LDH@cysteine-Cu(I) were investigated by using Fe-SEM and TEM that the Fe_3O_4@LDH@cysteine-Cu(I) nanoparticles were orderly decorated with spherical particles with particles size of about 27 to 30 nm (Fig. 5).

Quantitative determination of the cysteine loaded on the surface of Fe_3O_4@LDH was performed utilizing Thermogravimetric analysis (TGA) (Fig. 6). The TGA pattern of the nanocatalyst was recorded at a rate of 20 °C/min within the range of 20–800 °C under the N_2 atmosphere. The first weight loss appeared below 200 °C that is probably related to evaporation of adsorbed moisture. This is followed by a second peak at rang 170 °C and 428.93 °C, corresponding to the decomposition of the cysteine complex (weight loss of about 21.68%), Furthermore, according to thermal analysis, the nanoparticle was stable up to 170 °C.

Triazole compounds are widely used in the pharmaceutical industry. This method was chosen to evaluate the environmental effect of safe azidation reagent and catalytic activity. Choline azide is green reagent and safe solvent which developing a clean and cheap method for synthesis of triazole. Our preliminary experiments show that Fe_3O_4@LDH@cysteine-Cu(I) is a more efficient promoter for the rapid and convenient catalyst for click chemistry.

The yields of triazole from the click chemistry with benzyl bromide, propargyl alcohol and catalyst of Fe_3O_4@

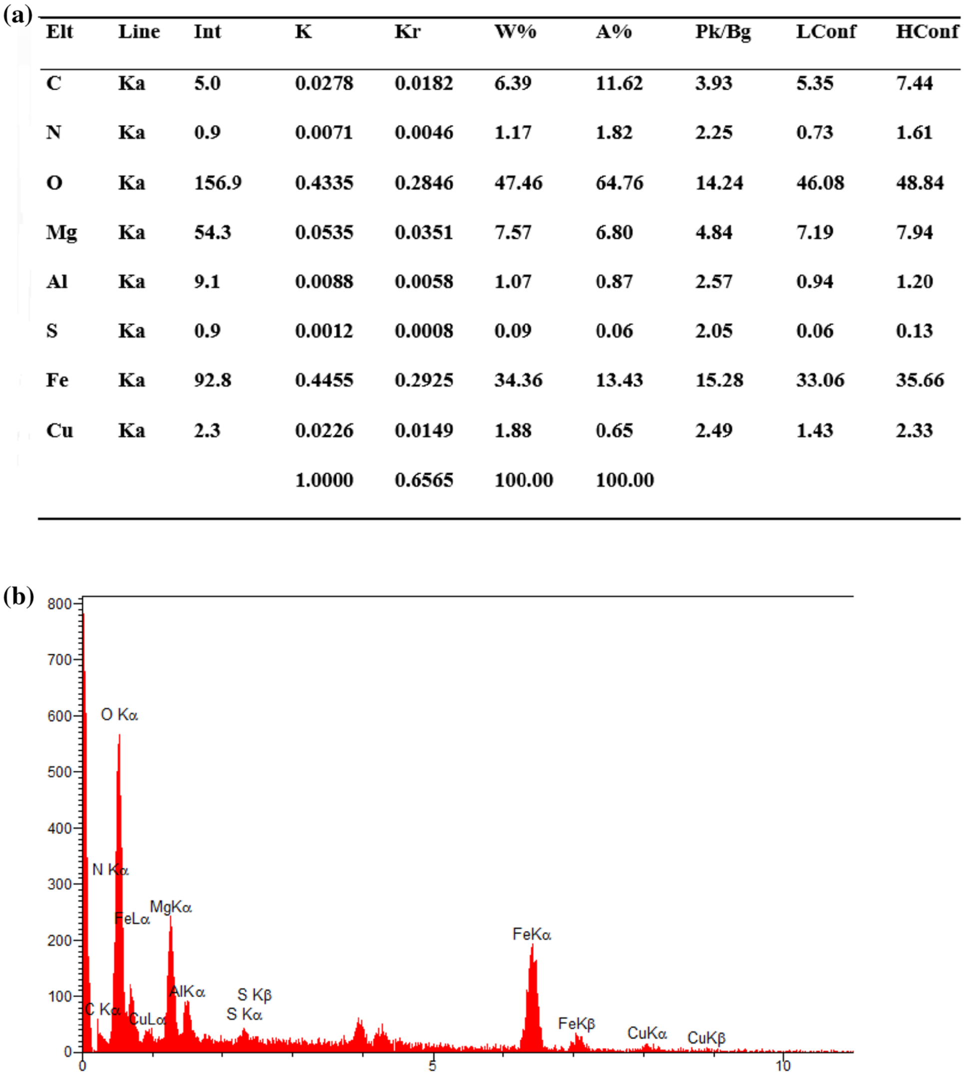


Fig. 4 **a** EDX analysis of the Fe_3O_4@LDH@cysteine-Cu(I) NPs; **b** Weight percent of various elements on the surface of Fe_3O_4@LDH@cysteine-Cu(I) NPs from EDX analysis

(a)

Elt	Line	Int	K	Kr	W%	A%	Pk/Bg	LConf	HConf
C	Ka	5.0	0.0278	0.0182	6.39	11.62	3.93	5.35	7.44
N	Ka	0.9	0.0071	0.0046	1.17	1.82	2.25	0.73	1.61
O	Ka	156.9	0.4335	0.2846	47.46	64.76	14.24	46.08	48.84
Mg	Ka	54.3	0.0535	0.0351	7.57	6.80	4.84	7.19	7.94
Al	Ka	9.1	0.0088	0.0058	1.07	0.87	2.57	0.94	1.20
S	Ka	0.9	0.0012	0.0008	0.09	0.06	2.05	0.06	0.13
Fe	Ka	92.8	0.4455	0.2925	34.36	13.43	15.28	33.06	35.66
Cu	Ka	2.3	0.0226	0.0149	1.88	0.65	2.49	1.43	2.33
			1.0000	0.6565	100.00	100.00			

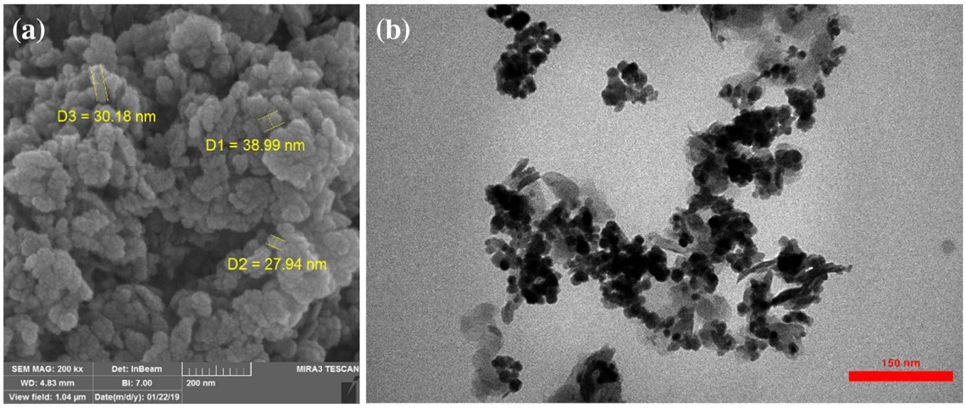


Fig. 5 **a** FE-SEM micrographs of Fe_3O_4@LDH@cystein_Cu(I) **b** TEM image

LDH@cysteine-Cu(I), (Scheme 2) with various solvent, amount catalyst and temperature are summarized in Table 1 (Entries 1–6).

The reaction proceeds slowly in acetonitrile and methanol (Table 1, Entry 2 and 3). As can be seen in this table, the reaction time is 35 min in water, higher than the reaction time when choline azide was used as a solvent (25 min) (Table 1, Entry 1 and 7). Finally, we used the 15, 20, 30, 40 and 50 mg of the catalyst in this reaction for indicating the best amount of catalyst. (Table 1, Entry 4, 5, 6, 7 and 8). The

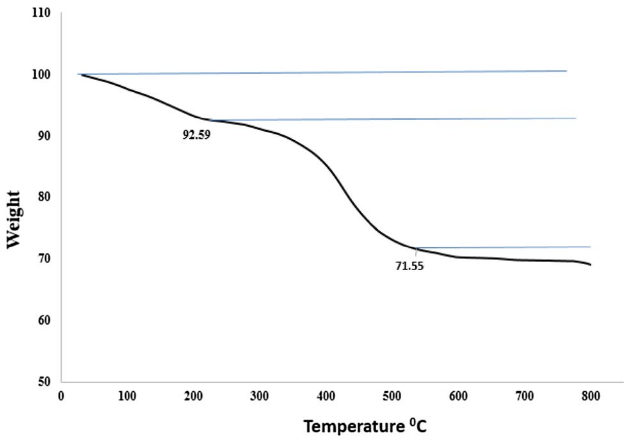
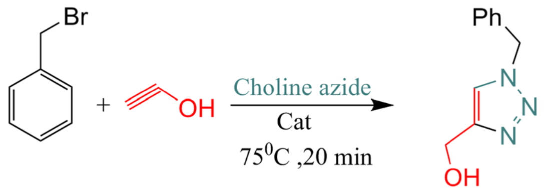


Fig. 6 TGA of Fe_3O_4@LDH@cystein_Cu(I)



Scheme 2 Fe_3O_4@LDH@cysteine–Cu(I) catalyzed click chemistry

Table 1 Optimization of the reaction conditions of click chemistry

Entry	Temperature (°C)	Amount catalyst (g)	Solvent	Time (minute)	Yield (%)^c
1	Reflux	0.02	Water^a	35	85
2	Reflux	0.02	CH_3CN^a	40	70
3	Reflux	0.02	CH_3OH^a	40	80
4	75	0.05	Choline azide^b	25	90
5	75	0.04	Choline azide^b	25	90
6	75	0.03	Choline azide^b	25	90
7	**75**	**0.02**	**Choline azide**^{b}	**25**	**90**
8	75	0.015	Choline azide^b	35	85

Reaction condition: ^{a}Benzyl halide (2 mmol), Alkyne (2 mmol), Sodium azide (3 mmol), Fe_3O_4@LDH@cysteine-Cu(I) (20 mg), 75 °C

^{b}Benzyl halide (2 mmol), Alkyne (2 mmol), Choline azide (3 mmol), different amount of Fe_3O_4@LDH@cysteine-Cu(I), 75 °C in different solvent

^{c}Isolated yields

best result was performed by using 20 mg Fe_3O_4@LDH@cysteine–Cu(I) at 75 °C in choline azide (Entry 7).

The efficiency of the Fe_3O_4@LDH@cysteine–Cu(I), Fe_3O_4@cysteine–Cu(I) and CuI (5 mol%) were compared under identical conditions (Table 2). When the mixture was heated to 75 °C without any catalyst no product was observed (Table 2 Entry 1). This reaction was performed by the homogeneous catalyst (CuI) that the resulting of this reaction is excellent (Table 2 Entry 2) but the separation of this catalyst from mixture reaction was difficult. Also, Fe_3O_4@LDH@cysteine–Cu(I) resulted in quantitative yield better than Fe_3O_4@cysteine–Cu(I) due to more active sites of LDH for linked to cysteine (Table 2, Entry 3 and 4).

The click reaction of choline azide with various alkynes and aryl halides performed by using the optimized conditions described above. Finally, the desired triazoles were generated in good to excellent yields. (Table 3).

When Phenylacetylene with *P*-methoxy benzyl bromide and benzyl bromide were used in the reaction, the corresponding product was obtained in the excellent yield (Table 3, Entry 1 and 2).

Allyl bromide or 2-bromo-4-nitroacetophenone with choline azide and phenylacetylene afforded the desired triazole in the good yield (Table 3, Entry 8 and 11).

The last generally proposed mechanism of this reaction is shown in Scheme 3 [35] Initially, formation of Cu(I) complex was followed by reaction of two Cu(I) ions and arylacetylene for some time, In the next step, alkyl azide preparation in situ from choline azide and alkyl halide then nitrogen of alkyl azide attack to Cu(I) complex. Finally, Triazole was formed in choline azide by protonolysis.

In addition, the reusability of the Fe_3O_4@LDH@cysteine–Cu(I) catalyst was evaluated using benzyl bromide, propargyl alcohol in choline azide as a model

Table 2 Screening of the catalysts

Entry	Catalyst	Yield (%)
1	None	<5%
2	CuI (5 mol %)	99%
3	Fe_3O_4@cysteine–Cu(I)	85%
4	**Fe_3O_4@LDH@cysteine–Cu(I)**	**90%**

Reaction condition: Benzyl halide (2 mmol), Alkyne (2 mmol), Choline azide (3 mmol), 75 °C, various catalyst

Table 3 Synthesis of 1,2,3-triazoles from organic halides, alkynes and choline azide using Fe_3O_4@LDH@cysteine–Cu(I)

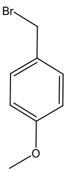
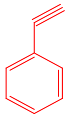
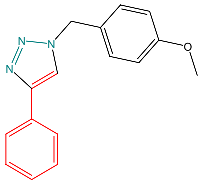
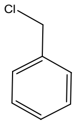
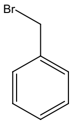
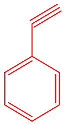
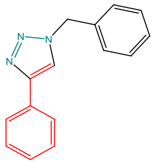
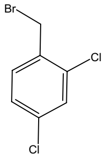
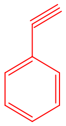
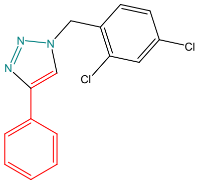
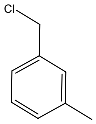
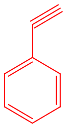
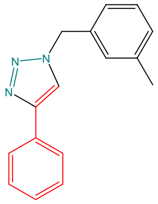
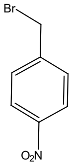
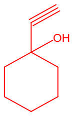
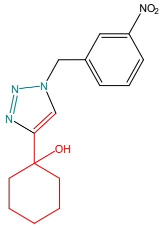
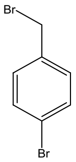
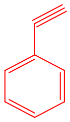
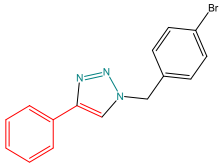
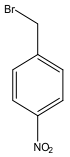
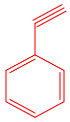
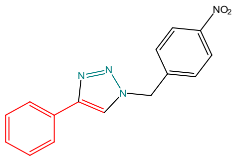
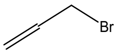
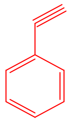
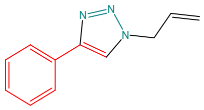
Entry	Halide	Alkyne	Product	Yield (%)[a]
1				97
2	 and 			95-97
3				90
4				95
5				90
6				96
7				88
8				80

Table 3 (continued)

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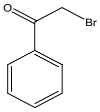
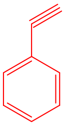
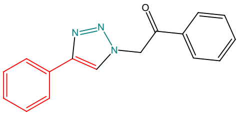
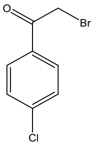
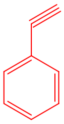
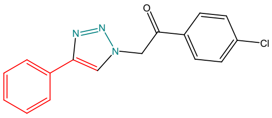
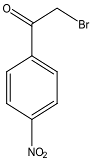
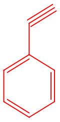
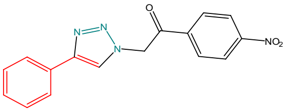
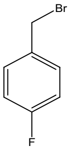
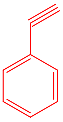
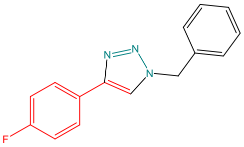
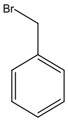
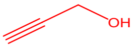
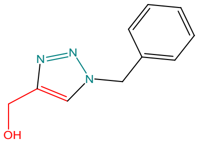
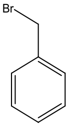
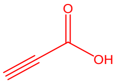
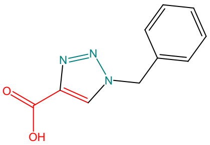
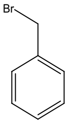
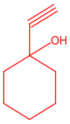
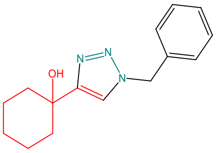
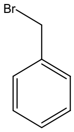
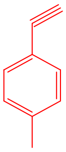
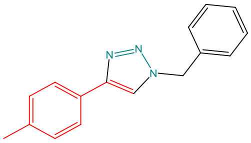
9				87
10				85
11				80
12				90
13				90
14				87
15				82
16				94

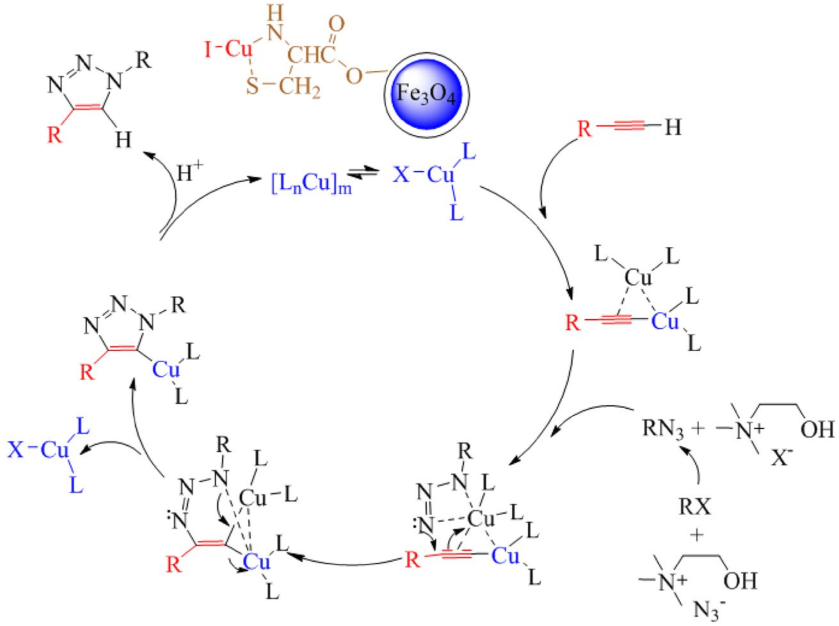
Reaction conditions: Benzyl/Alkyl halide (2 mmol), Alkyne (2 mmol), Choline azide (3 mmol), Fe_3O_4@LDH@cysteine-Cu(I) (20 mg), 75 °C

[a]Isolated yields

reaction. After each run the nanoparticles were separated by a permanent magnetic then washed with ethyl acetate, air-dried and applied in the next run (Fig. 7). Surprisingly, it is found that the magnetic nanoparticles were recovered and reused for 5 runs without any significant loss in the efficiency of the catalyst.

The results obtained for the click reaction under the optimized conditions were compared with previously reported catalysts in the literature. It can be seen in Table 4 that the

Scheme 3 Proposed mechanism of click reaction



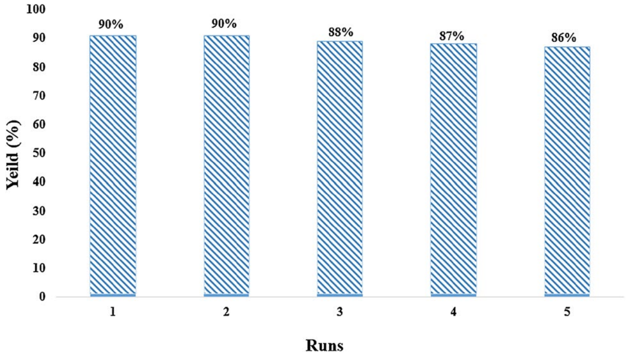


Fig. 7 Recyclability study of the catalyst in the preparation of 1,2,3-triazoles

present catalyst showed a good catalytic activity. Noticeably, this new catalyst is comparable in terms of price, eco-friendly, reusability, commercially available materials, easy preparation and facile separation.

4 Conclusions

We have demonstrated for the first time the use of cheap and magnetic LDH as support for immobilizing Cu(I). The catalytic activity of the Fe_3O_4@LDH@cysteine–Cu(I) nanoparticles were studied for the click chemistry reaction. The main advantage of this method employs safe and green

Table 4 Comparison of the catalytic efficiency of Fe_3O_4@LDH@cysteine–Cu(I) with the previously reported catalytic systems in the click reaction

Entries	Catalyst	Reaction conditions	Yield (%)
1	Cu NPs	Phenyl acetylene (0.5 mmol), benzyl chloride (0.6 mmol), NaN_3 (0.6 mmol), CH_3OH (2 mL), r.t., 10 h	86 [36]
2	Fe_3O_4-DOPA-CuNPs	Phenyl acetylene (1 mmol), benzyl bromide (1.2 mmol), NaN_3 (1.5 mmol), H_2O (5 ml), 120 °C, 10 min	96 [37]
3	HCP-NHC–Cu	Phenyl acetylene (1.0 mmol), benzyl chloride (1.0 mmol), NaN_3 (1.1 mmol), EtOH (2.0 mL),80 °C, 8 h	93 [38]
4	CFL	Benzyl chloride (1.0 mmol), Phenyl acetylene (1.0 mmol), NaN_3 (1.0 mmol) in EtOH: H_2O, r.t, 1.5 h	85 [39]
5	MNP@SPAAm/Cu	Phenyl acetylene (1.0 mmol), benzyl chloride (1.0 mmol), NaN_3 (1.3 mmol), H_2O (2.0 mL), Na-ascorbate (10 mol%), 50 °C, 3 h	97 [40]
6	Fe_3O_4@LDH@cysteine–Cu(I)	Benzyl halide (2 mmol), Alkyne (2 mmol), Choline azide (3 mmol), 75 °C, 25 min	95-97

azidation reagent and using the magnetically separable and recyclable catalyst. Also, The Fe_3O_4@LDH@cysteine–Cu(I) could be reused without a significant loss of its high catalytic performance.

Acknowledgements The financial support rendered by the University of Tarbiat Modares is gratefully acknowledged.

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