Peanut shell as a green biomolecule support for anchoring Cu$_2$O: a biocatalyst for green synthesis of 1,2,3-triazoles under ultrasonic irradiation

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Abstract
Cu$_2$O supported on peanut shell (Cu$_2$O@PS) was prepared by the reaction of copper acetate and peanut shell powder as a naturally available biopolymer support. The prepared catalyst was used as an efficient and reusable heterogeneous catalyst in the click reaction of benzyl halide or phenacyl bromides, acetylenes and sodium azide for the synthesis of potentially biologically active 1,2,3-triazoles under ultrasonic irradiation in EtOH-H$_2$O as green solvent.

Keywords: Bio-based support, Click reaction, Heterogeneous catalyst, Peanut shell, Triazoles, Ultrasonic irradiation

Introduction
Green chemistry is one of the most important research activities for chemists, both in the laboratory and industry. Therefore, many efficient, eco-friendly and clean synthetic strategies have been developed for the synthesis of biologically and industrially active molecules [1–5]. Meanwhile, metal-catalyzed multi-component reaction is one of the significant areas of green chemistry research. Transition metal-catalyzed click synthesis of triazoles is a powerful method for the synthesis of diverse complex molecules. Triazoles derivatives have developing application in medicinal chemistry and biological activities [6–10]. They also have numerous industrial applications as florescent whiteners, dyestuffs, photo-stabilizers of polymers, and optical brightening agents [11, 12]. Forasmuch as copper-catalyzed click reaction is one of the best methods for the synthesis of 1,2,3-triazoles [13, 14], numerous homogeneous copper catalysts have been reported [15, 16]. Most of these successful methods suffer from non-reusability of the catalysts, and the usage of toxic and/or expensive ligands [17–20]. To overcome these problems, many researchers have focused their efforts on copper-based heterogeneous systems [17, 21, 22].

Natural biopolymers are the attractive subjects for the design of bio-supported catalysts due to their eco-friendly, low cost and non-toxic properties [23–30]. Peanut shell as an agro-industrial waste containing considerable fraction of the biodegradable lignocellulosic waste [31] is discarded in the environment or burned about 13.7 million tons per year [32, 33]. This promising natural and renewable raw material consists of a combination of lignin, cellulose, proteins and hemicellulose biopolymers (Fig. 1) [34, 35]. There are many polar functional groups such as hydroxyl, methoxy and carboxyl groups on the surface of peanut shell. Therefore, peanut shell is an attractive candidate as a natural, renewable, non-toxic and very low, or no cost environmentally friendly support for metal nanoparticles.

Herein, in continuation of our research toward the development of nano bio-based catalytic systems...
[43–45], the synthesis of copper oxide supported on peanut shell (Cu₂O@PS) as a heterogeneous nano-biocatalyst and its catalytic activity for the click synthesis of triazoles in EtOH-H₂O as green solvent under ultrasonic irradiation is reported.

Results and discussion

Synthesis and characterizations of the catalyst

The preparation of the Cu₂O@PS nanocomposite is described schematically in Scheme 1. The Cu₂O@PS nanocomposite obtained by the reaction of peanut shell powder with copper acetate in water at 70 °C for 5 h. The catalyst was centrifuged and washed with water, ethanol, and acetone then dried in the oven at 70 °C.

![Scheme 1 Schematic diagram of catalyst preparation (The source of this diagram is taken from "http://nolinsteel.com/peanuts/" and the used softwares are Chemdraw and Paint. The Scheme was designed by authors)](image)

The Cu₂O@PS nanocomposite was characterized by FT-IR, thermogravimetric analysis (TGA), atomic absorption spectroscopy (AAS), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) analysis and X-ray diffraction (XRD) measurements. The FT-IR spectrum of peanut shell and Cu₂O@PS are shown in Fig. 2. The band around 3400 cm⁻¹ was ascribed to the mixed stretching vibration absorption band of amino and hydroxyl groups. The bands at 2950 cm⁻¹ were assigned to aliphatic C–H, mainly CH₂ stretching. The small band obtained at 1738 cm⁻¹ was assigned to the carbonyl groups stretching vibration [29, 46]. As can be seen in the FT-IR spectrum of Cu₂O@PS, the presence of characteristic bands of PS in the 1738 and
3500 cm$^{-1}$ regions clearly confirms the existence of PS in the final catalyst. Also, the band shift from 1738 cm$^{-1}$ (in PS) to 1727 cm$^{-1}$ (in Cu$_2$O@PS) reveals the coordination of copper to peanut shell [46].

Thermogravimetric analysis was further used to study the composition of the catalyst (Fig. 3). The TGA curve of the catalyst shows a weight loss at ~ 100 °C that is associated with the release of physically adsorbed water. The weight loss above ~ 230 °C (and continued to ~ 600 °C) is related to the decomposition of PS and organic groups on the Cu$_2$O@PS. Thermal analysis showed that the catalyst has good thermal stability up to 230 °C. Also, the copper content on the Cu$_2$O@PS nanocomposite was measured 0.28 mmol g$^{-1}$ by atomic absorption spectroscopy.

Morphologies of fresh peanut shell and the Cu$_2$O@PS nanocomposite were determined by SEM. The fresh PS is basically smooth (Fig. 4a). The SEM images of Cu$_2$O@PS show the formation of spherical particles in size around 30–40 nm on the surface of the peanut shell (Fig. 4b).

In addition, comparing the EDS analysis of Ps and Cu$_2$O@PS clearly shows the presence of Cu, C, O, and N elements in this composite and demonstrate that copper was anchored to the PS (Fig. 5a and b). In the XRD pattern of the Cu$_2$O@PS nanocomposite, the diffractions at 2$\theta$ = 36.4°, 42.5°, 61.4°, and 73.4° can be assigned to the (111), (200), (220) and (311) lattice planes of Cu$_2$O, in accordance with Cu$_2$O standard data (JCPDS card NO. 05–0667) (Fig. 6).

Catalytic studies
The catalytic activity of Cu$_2$O@PS nanocomposite was investigated in the click synthesis of 1,2,3-triazoles. The reaction of phenyl acetylene 1, 4-nitrobenzyl bromide 2...
and sodium azide (NaN₃) was chosen as a model reaction under different conditions. As the first experiment, K₂CO₃ was used as a base in the presence of 1 mol% of catalyst, and this reaction was tested by employing various solvents such as toluene, MeCN, MeOH, EtOH, H₂O, EtOH-H₂O, and MeOH-H₂O at 50 °C under ultrasonic irradiation for 45 min (Table 1, entries 1–7). A superior yield was obtained when EtOH-H₂O (1:1) was used as the solvent (Table 1, entry 6). Then, different base were screened in the model reaction. A moderate yields were obtained with Cs₂CO₃ and KOt-Bu (entries 8 and 9) and the reaction proceed in fairly good yields in the presence of NaOH and KOH (entries 10 and 11). Also, some experiments were carried out at different temperatures, and finally 50 °C was chose as optimum reaction temperature (entries 6, 12–14). Effect of the catalyst loading was also investigated under the optimum reaction conditions. It was found that, when the amount of catalyst increased from 0.5 and 1 to 2 mol%,
the yield of product changed from 65 and 91% to 92%, respectively. So, 1 mol% of catalyst is sufficient to promote this reaction (entries 6, 15–16). When this reaction was carried out without catalyst, the yield of the product was trace (entry 17). To delineate the role of ultrasound, the reaction was investigated without ultrasonic irradiation at 50 °C in various solvents. In all reactions, the result obtained by the use of ultrasound irradiation leads to a higher yield (entries 18–20).

Finally, when this reaction was carried out with PS or Cu₂O as catalyst, the yield of the product was trace and 78% yield, respectively (entries 21 and 22).

To explore the scope of the click reaction various benzyl bromides and aryl acetylenes, containing both electron donating and electron withdrawing functionalities were screened in optimized reaction conditions and high isolated yields were obtained (Table 2). Under the same reaction conditions benzyl chlorides provided target products in good yields (Table 2, entries 12–14).

Observation of great potential activity of Cu₂O@PS nano-biocatalyst in the Click reaction of benzyl bromides and aryl acetylenes encouraged us to investigate the Click reaction of aryl acetylenes 1 with phenacyl bromides 4 and sodium azide in the same reaction conditions. As can be seen from Table 3, the Click reaction of aryl acetylenes and phenacyl bromides contain electron withdrawing or donation groups provide 1H-1, 2, 3-triazol-ethan-1-one derivatives in good isolated yields in the presence of 1 mol% of catalyst in EtOH-H₂O under ultrasound irradiation at 50 °C.
Table 2  Click synthesis of 1H-1,2,3-triazoles

\[
R^1 \text{Me} + X^2 \text{R} + \text{NaN}_3 \xrightarrow{\text{Cu}_2\text{O@PS (1 mol%)}} (\text{EtOH-H}_2\text{O, K}_2\text{CO}_3) \xrightarrow{50 \degree C} R^2 \text{N} \text{N} \xrightarrow{R^1} \text{NaX} \]

| Entry | R¹ | R² | X   | Product | Yield (%) | M.P. (°C) | Refs. |
|-------|----|----|-----|---------|-----------|-----------|-------|
| 1     | ph | ph | Br  | 3a      | 90        | 131–133   | [47]  |
| 2     | ph | 4-NO₂-ph | Br | 3b      | 91        | 140–141   | [48]  |
| 3     | 4-OMe-ph | ph  | Br  | 3c      | 86        | 142–143   | [49]  |
| 4     | 4-OMe-ph | 4-Me-ph | Br | 3d      | 92        | 149–151   | [50]  |
| 5     | ph  | 4-Me-ph  | Br  | 3e      | 89        | 106–107   | [51]  |
| 6     | ph  | 4-Br-ph  | Br  | 3f      | 93        | 150–152   | [48]  |
| 7     | 4-Me-ph | 4-Br-ph  | Br  | 3g      | 92        | 202–203   | [48]  |
| 8     | 4-OMe-ph | 4-NO₂-ph | Br | 3h      | 97        | 167–168   | [47]  |
| 9     | 4-CF₃-ph | 4-NO₂-ph | Br | 3i      | 88        | 215–217   | [52]  |
| 10    | 4-Me-ph | ph    | Br  | 3j      | 90        | 153–154   | [53]  |
| 11    | 4-Me-ph | 4-NO₂-ph | Br | 3k      | 86        | 159–160   | [54]  |
| 12    | ph  | 4-OMe-ph | Cl  | 3l      | 88        | 136–138   | [49]  |
| 13    | 4-Me-ph | 4-OMe-ph | Cl  | 3m      | 89        | 133–136   | [51]  |
| 14    | 4-OMe-ph | ph    | Cl  | 3n      | 88        | 142–143   | [49]  |
| 15    | ph  | n-C₃H₇  | Br  | 3n      | 64        | 41–42     | [55]  |
| 16    | ph  | n-C₄H₉  | Br  | 3o      | 65        | 42        | [56]  |
| 17    | CO₂Me | ph   | Br  | 3p      | 63        | 104–105   | [57]  |
| 18    | CO₂Me | 4-NO₂-ph | Br | 3q      | 61        | 189–190   | [57]  |

Reaction conditions: benzyl halide (1 mmol), arylacetylene (1.2 mmol), K₂CO₃ (2 mmol), NaN₃ (1.2 mmol), Cu₂O@PS (1 mol%), 45 min

* Isolated yield

Table 3  Synthesis of 1H-1, 2, 3-triazol-ethan-1-one derivatives by Click reaction

\[
R^1 \text{Me} + \text{Br} \xrightarrow{\text{Cu}_2\text{O@PS (1 mol%)}} (\text{EtOH-H}_2\text{O, K}_2\text{CO}_3) \xrightarrow{50 \degree C} \text{N} \text{N} \xrightarrow{R^1} \text{R}^2 \]

| Entry | R¹ | R² | Product | Yield (%) | M.P. (°C) | Refs. |
|-------|----|----|---------|-----------|-----------|-------|
| 1     | H  | H  | 5a      | 93        | 166–167   | [58]  |
| 2     | OMe| H  | 5b      | 89        | 190–191   | [58]  |
| 3     | H  | Br | 5c      | 86        | 145–146   | [59]  |
| 4     | H  | NO₂| 5d      | 77        | 180–181   | [60]  |
| 5     | H  | Cl | 5e      | 89        | 150–152   | [59]  |
| 6     | H  | OMe| 5f      | 88        | 142–143   | [59]  |
| 7     | CF₃| H  | 5g      | 81        | 221–223   | [58]  |
| 8     | Me | H  | 5h      | 85        | 165–167   | [58]  |

Phenacyl bromides (1 mmol), arylacetylene (1.2 mmol), K₂CO₃ (2 mmol), NaN₃ (1.2 mmol), Cu₂O@PS (1 mol%), 90 min

* Isolated yield
Then, we examined the heterogeneous nature of the catalyst. Firstly, to assess the copper leaching of the catalyst, we performed hot filtration test for the click reaction of 4-nitro benzyl bromide 2, phenylacetylene 1 and NaN₃. The reaction was stopped after ~ 50% of the reaction time. Hot filtrate was transferred to another flask containing base and H₂O-EtOH at 50 °C. Upon further heating of the catalyst-free solution for 1.5 h, no considerable progress was observed by GC analysis (Fig. 7a). Moreover, atomic absorption spectroscopy (AAS) of the same reaction solution at the midpoint of completion indicated that no significant quantities of copper were lost to the reaction medium during the process. Furthermore, the reusability of catalyst was investigated in the reaction of 4-nitro benzyl bromide, phenylacetylene, and NaN₃. The catalyst could be reused successively five times without significant loss of activity (Fig. 7b). Moreover, atomic absorption spectroscopy revealed that the loading of copper was 0.27 mmol g⁻¹ after five runs and there was no significant change in the copper content of the recovered catalyst. All results confirm the reaction occurs mainly via a heterogeneous pathway. The SEM micrographs of reused catalyst after five times reveal that the reused catalyst has a similar texture with fresh catalyst (see Additional file 1).

Based on literature reports [61], a possible mechanism for click catalytic synthesis of triazole is proposed in Scheme 2. Synthesis of triazole proceeds through the formation of copper acetylide (A). The coordination of organic azide (B) (formed in situ by the reaction of organic bromide with NaN₃) to the copper acetylide, followed by the Huisgen 1, 3-dipolar cycloaddition reaction of (A) and (B) give the complex (C). Subsequently, the desired triazole was obtained by copper-acidic hydrogen exchange followed by regeneration of the catalyst for the next use in the catalytic cycle. It is notable; functional groups such as hydroxyl, amine, methoxy and carboxyl groups on the surface of peanut shell have good potential to coordinate with copper nanoparticles.

Reports in Table 4, compares the efficiency of Cu₂O@ PS nanocomposite with some other heterogeneous copper catalysts in literature in the Click reaction of phenylacetylene, phenacyl bromides and NaN₃. Table 4 shows that although all of methods have good efficiency, the present catalyst affords some advantages such as biodegradability using green nano bio-support for immobilization of copper, reasonable reaction time and low temperature which are all energy and time-consuming processes.

**Experimental**

**Material and measurements**

All chemicals were purchased from Merck, Aldrich or Fluka were used without further purification. IR spectra were recorded on a Shimadzu FT-IR-470 FT-IR spectrophotometer. EDS characterization was performed using...
an electron microscopy Oxford Instrument Company, Germany. Field emission scanning electron microscopy (FESEM) was performed using a ZEISS instrument, SIGMA VP model, Germany. The NMR spectra were recorded on a Brukerdrx-300Avance spectrometer. The concentration of Cu was estimated using a Shimadzu AA-680 flame atomic absorption spectrophotometer. Diffraction data were collected on a STOE STADI P with scintillation detector, secondary monochromator and Cu-Kα1 radiation (λ = 1.5406 Å). Gas chromatography was performed on a Trace GC ultra from the Thermo Company equipped with FID detector and Rtx®-1 capillary column. Melting points of products were measured with an Electrothermal 9100 apparatus and are uncorrected. Thermogravimetric analysis (TGA) was done by D-32609 Hullhorst. The peanut shell was obtained from Astaneh Ashrafiyeh Township located in 37° 16′ latitude and 49° 56′ longitude in north of Iran.

Preparation of Cu₂O@Peanut shell
Crushed peanut shells were ground in a ball mill to a fine powder. A mixture of peanut shell powder (1 g) and copper acetate (0.1 g) was stirred in de-ionized water (30 ml) at 70 °C for 5 h. The catalyst was then centrifuged and washed with water, ethanol, and acetone and dried in the oven at 70 °C to obtain Cu₂O@Peanut shell.

General procedure for Click reactions
A mixture of Cu₂O@PS (1 mol% of Cu, 40 mg), K₂CO₃ (2 mmol), aryl bromide (1.0 mmol), phenyl acetylene (1.2 mmol), and NaN₃ (1.2 mmol) in H₂O-EtOH (3 ml, 1:1) was sonicated at 50 °C for an appropriate time. After completion of the reaction monitored by TLC (EtOAc:n-hexane (1:3); the catalyst was separated and the filtrate was extracted with Chloroform (2 × 2 ml). The organic solvents were removed under vacuum and the pure product was obtained by recrystallization with CHCl₃:n-hexane (1:3). All of the Click products are known compound and were reported previously.

Conclusions
In summary, Cu₂O@Peanut shell nano-biocomposite was synthesized and used as an effective heterogeneous catalyst in a one-pot Huisgen 1,3-dipolar cycloaddition reaction under ultrasonic irradiation in EtOH-H₂O as a green solvent for the synthesis of 1,2,3-triazole derivatives. The reusability of the catalyst is high and the catalyst can be reused five times without a significant decrease in its catalytic activity. Notable features of this catalytic reaction are bio-degradable and bio-renewable polymeric support, compatibility with a wide range of substrate, mild reaction conditions, high atom economy, good-yields of the products, ligand-free, leaching-free and eco-friendlyness characteristics of the catalyst.

Additional file
Additional file 1. Supporting information including the FESEM images of PS, Cu₂O@PS, and reused Cu₂O@PS after 5 times, characterization of triazole products, and ¹H NMR spectrum of products.

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Authors’ contributions
ZD and AM performed the experiments, collected the data and drafted the manuscript; AB and SJ designed the study and edited the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials
All data generated or analysed during this study are included in this published article [and its Additional file 1].

Competing interests
The authors declare that they have no competing interests.

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Table 4 Comparison of efficiency of various heterogeneous catalysts for triazole synthesis

| Catalyst                  | Cu (mmol g⁻¹) | Catalyst (mol%) | Time (h) | T (°C) | Solvent      | Yield (%) | Refs. |
|---------------------------|---------------|-----------------|----------|--------|--------------|-----------|-------|
| GO/Pim/Cu                 | 2.1           | 1               | 1.5      | 50     | H₂O          | 90        | [62]  |
| Cell-CuI NPs             | 0.37          | 3.7             | 2        | 70     | H₂O          | 96        | [51]  |
| P[imCl/IL][Cu]           | 1.3           | 0.1             | 3.5      | 55     | H₂O/1BuOH    | 98        | [63]  |
| Mag-Cu                   | 0.46          | 2               | 6        | 55     | H₂O/1BuOH    | 93        | [64]  |
| PANi@CuI-NPs             | 0.94          | 5               | 0.5      | 100    | H₂O          | 85        | [65]  |
| Fe₃O₄@SiO₂-ABT/Cu(OAc)₂  | 3             | 0.02            | 2        | 70     | PEG/H₂O      | 85        | [66]  |
| Cu₂O-Ag NPs              | 2.8           | 3.5             | 2        | 25     | H₂O-EtOH     | 92        | [67]  |
| Cu₂O@PS                  | 0.28          | 1               | 1.5      | 50     | H₂O-EtOH     | 93        | This work |
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