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ORIGINAL PAPER

Polyvinyl alcohol-stabilized cuprous oxide particles: efficient and recyclable heterogeneous catalyst for azide–alkyne cycloaddition in water at room temperature

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Abstract The PVA-stabilized Cu_2O particles were prepared using a novel and simple rout in aqueous medium at room temperature under aerobic conditions. Initially, Cu(II) ions were fixed in PVA matrix via complex formation with OH groups, subsequently this PVA–Cu(II) macromolecular complex as a precursor reacted with ascorbic acid as a reducing agent at pH = 12 to obtain the PVA–Cu_2O composite. The products were characterized using XRD, FE-SEM, FTIR, and UV–Visible techniques. The as-prepared PVA–Cu_2O composite was applied as an effective and recyclable heterogeneous catalyst for 1,3-dipolar cycloaddition reactions between terminal alkynes and azides to prepare 1,2,3-triazoles under an environmentally friendly reaction conditions. The substituted triazoles were produced of various aryl and benzyl azides using a catalytic amount of this composite as efficient, stable, and air- and moisture-tolerant catalyst in excellent yields in water at room temperature. These PVA-stabilized Cu_2O particles could be recovered in a facile manner from the reaction mixture and reused several times without any loss of catalytic activity.

Keywords Polyvinyl alcohol · Cuprous oxide · Catalyst · Click reaction · 1,2,3-Triazoles

Introduction

An important goal in catalysis research is the development of an efficient catalytic system that may be new, eco-friendly, available, mild, and easily separable. Many efforts have been directed toward the development of new catalytic systems that increase activity and selectivity in chemical synthesis and also minimize contamination in the reaction conditions [1–5].

Cuprous oxide (Cu_2O) is a p-type semiconductor, and recently, much attention has been paid to this and related materials because of its potential applications in fields such as solar cells [6], pigments [7], catalysts, and photocatalysts [8]. Several successful methods have been reported for the production of Cu_2O [9, 10]. Chemical reduction is a method which is widely used for preparation of nanoparticles due to its convenience and low cost, in which the preparation of Cu_2O from Cu^{2+} salts involves the reduction of Cu^{2+} ions to Cu^+ with a reducing agent. Ram et al. [11] have reported a liquid-reduction method to make Cu_2O nanocrystals. They used $NaBH_4$ to reduce $CuCl_2$ at 80–100 °C via ion exchange reaction of $Cu^{2+} \rightarrow Cu \rightarrow Cu^+$. Also, the sequential reduction process $CuO \rightarrow Cu_2O \rightarrow Cu$ has been reported by Pike et al. [12] with CuO reducing completely to the intermediate Cu_2O phase before further reduction to metallic copper using temperature-programmed reduction of CuO nanoparticles. Gou et al. [13] have prepared crystals of Cu_2O (200–450 nm) via reduction of Cu(II) salt using ascorbic acid as reducing agent and cetyltrimethylammonium bromide (CTAB) as surfactant. It is known that Cu_2O is chemically unstable in air with respect to further oxidation to form CuO [14].

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Polyvinyl alcohol (–[CH_2–CHOH]–*n*/PVA) is recognized as a water-soluble and crystalline vinyl polymer with hydroxyl (–OH) groups bonded to carbon atoms in the back bone of long-chain molecule.

1,2,3-triazoles [15] are basically five-membered nitrogen heterocyclic compounds, which are commonly prepared through Copper (Cu) Catalyzed Alkyne–Azide Cycloaddition (CuAAC) reaction that is the most well-documented example of "Click" reactions. The 'Click Chemistry' concept was developed by Sharpless and co-workers [16] and CuAAC reaction is done via [3 + 2] cycloaddition of terminal alkynes with azides. 1,2,3-triazoles are associated with a wide range of biological properties such as antiallergic [17], anticancer [18], anti HIV [19], and antimicrobial activities [20].

Much efforts have been devoted to the synthesis of 1,2,3-triazoles through cycloaddition reaction between alkynes and azides using various Cu-based catalysts. Sarkar et al. [21] used PVP-stabilized copper nanoparticles as catalyst to synthesize 1,2,3-triazoles. Molteni et al. [22] have reported the use of mixture of Cu/Cu-oxide nanoparticles as catalyst for the "click" [3 + 2] cycloaddition between azides and terminal alkynes. Zhang et al. [23] have prepared polyvinylpyrrolidone (PVP)-coated Cu_2O nanoparticles as an efficient catalyst for azide–alkyne click chemistry in water at 37 °C. Wang and co-workers [24] have reported catalytic system of Cu_2O/H_2O. They found that Cu_2O as a catalyst in water could be quite robust for the azide–alkyne cycloaddition reaction.

In this work, we describe a facile, environmentally benign, and simple route for the synthesis of Cu_2O particles embedded in polyvinyl alcohol matrix using PVA–Cu(II) composite as precursor and ascorbic acid as reducing agent in aqueous medium at pH = 12 and room temperature. The as-prepared PVA–Cu_2O composite was used as an efficient and recyclable heterogeneous catalyst for azide–alkyne click reaction in water at room temperature.

Experimental

General procedure for the synthesis of PVA-stabilized Cu_2O particles

Preparation of PVA–Cu(II) complex

One gram of polyvinyl alcohol (crystalline powder, high molecular weight) was dissolved in 50 ml distilled water. In another beaker, a solution of NaOH (4.0 g) in 25 ml distilled water was prepared, and this solution was added to the PVA solution under stirring and then the mixture was heated at 70 °C for 3 h. After cooling, the solution of $CuSO_4{\cdot}5H_2O$ (1.25 g) in 20 ml distilled water was added dropwise to the above PVA solution under vigorous stirring. A green gel was produced when $CuSO_4$ solution was added and the mixture was heated at 90 °C overnight. Afterward, the reaction mixture was cooled down to room temperature and followed by reduction stage.

Reduction of PVA–Cu(II) complex by ascorbic acid

Ascorbic acid (0.89 g) was dissolved in 10 ml of distilled water and was added dropwise into the PVA–Cu(II) reaction mixture at room temperature, under very slow stirring [the mole ratio ascorbic acid:Cu(II) was 1:1]. After several seconds, the orange-red particles appeared in the reaction mixture. The resulting mixture was then aged in air at room temperature, overnight. A reddish product obtained which was then washed with distilled water and ethanol several times to remove impurities and dried in air.

General procedures for the PVA–Cu_2O-catalyzed [3 + 2] cycloaddition of azides and phenylacetylene

Aryl azide as azide-precursor

A solution of tetrabutylammonium bromide (0.016 g), aryl azide (0.1 mmol), phenylacetylene (0.12 mmol), and PVA–Cu_2O (0.005 g) in water (2 mL) was stirred at room temperature and monitored by TLC until conversion of the starting materials was complete. After completion, the reaction mixture was decanted and washed with water followed by dissolving in boiling ethanol and filtering to remove the PVA–Cu_2O catalyst. The ethanol was evaporated and the residue was crystallized by acetonitrile and water to give the corresponding pure triazole.

Multicomponent synthesis of 1,2,3-triazoles

Tetrabutylammonium bromide (0.016 g), benzyl bromide or chloride (0.1 mmol), NaN_3 (0.15 mmol), and phenylacetylene (0.12 mmol) were stirred in water (2 mL) in a 10-ml round-bottomed flask at room temperature. Sequentially, PVA–Cu_2O (0.005 g) was added and the reaction mixture was monitored by TLC until satisfactory conversion of the starting materials. Then the reaction mixture was decanted and washed with water followed by dissolving in boiling ethanol and filtering to remove the PVA/Cu_2O catalyst. The ethanol was evaporated, and the residue was purified by column chromatography (Hexane:EtOAc, 90:10) to give the corresponding pure triazole.

Results and discussion

The first objective of this work was the synthesis of the Cu_2O particles embedded in polyvinyl alcohol matrix. For this, initially, a complex of PVA–Cu(II) was prepared; subsequently, this product was used as a precursor reacting with ascorbic acid as a reductant to produce the PVA-stabilized Cu_2O crystals. During the reduction process the color of reaction mixture changed from deep green to a reddish appearance. Here the reduction stage takes place in PVA network, and the copper(II) ions which are chelating with OH groups of PVA are reduced and PVA–Cu_2O composite is formed.

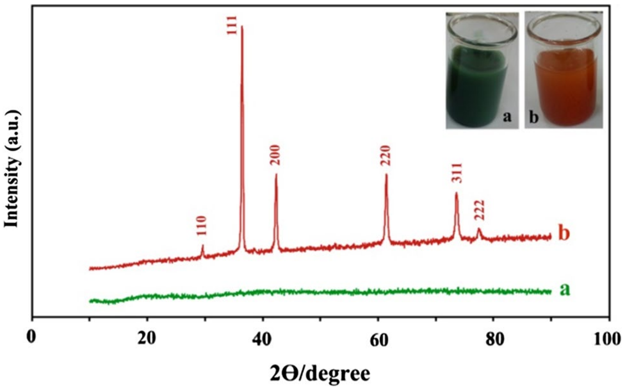


Fig. 1 X-ray diffraction patterns of PVA–Cu (II) complex (*a*) and PVA–Cu_2O composite (*b*). The color exchange of reaction mixture has been shown in the image

Chemical phase analysis was carried out by X-ray powder diffractogram, and Fig. 1 demonstrates XRD patterns of precursor PVA–Cu(II) complex and final product PVA–Cu_2O composite.

The pattern of PVA–Cu(II) complex is fully amorphous; therefore, it may be impossible to determine the constituent phases of this compound. However, XRD pattern of PVA–Cu_2O composite indicates diffractions of Cu_2O particles, containing six peaks that are clearly distinguishable and all of them can be perfectly indexed to crystalline Cu_2O particles. The peak positions are in good agreement with those for Cu_2O powder reported in references (JCPDS 5-667) [25]. These results confirm that cupric ions in precursor PVA–Cu(II) composite are reduced to crystalline Cu_2O particles embedded in PVA matrix. The color changes during reaction, provides substantial evidence for reduction of the precursor (green) to the reddish product PVA–Cu_2O.

The phase morphology of PVA–Cu(II) complex and PVA–Cu_2O composite was studied using field emission scanning electron microscopy (FE-SEM). As shown in Fig. 2, the FE-SEM micrograph of PVA–Cu(II) complex clearly shows particles have been well distributed in the PVA matrix. After the reduction stage, the surface morphology of prepared PVA–Cu_2O composite compared with the PVA–Cu(II) complex has changed.

Figure 3a and b shows FTIR spectra of the PVA–Cu(II) complex and the PVA–Cu_2O composite. The both spectra

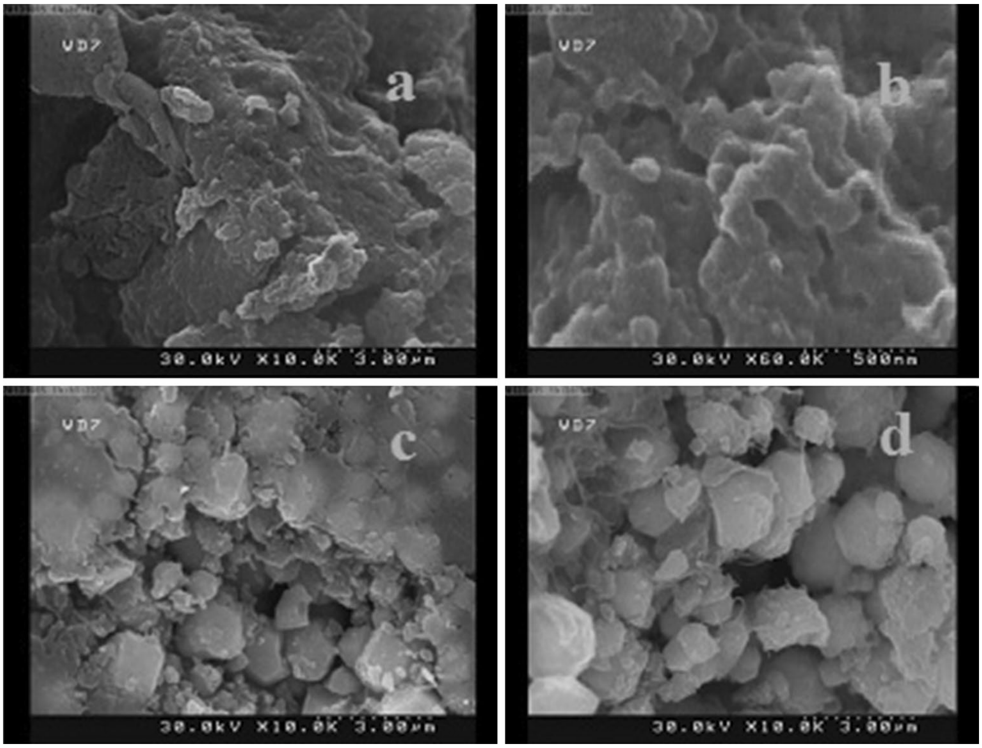


Fig. 2 FE-SEM images: PVA–Cu (II) complex (**a**, **b**), PVA–Cu_2O composite (**c**, **d**)

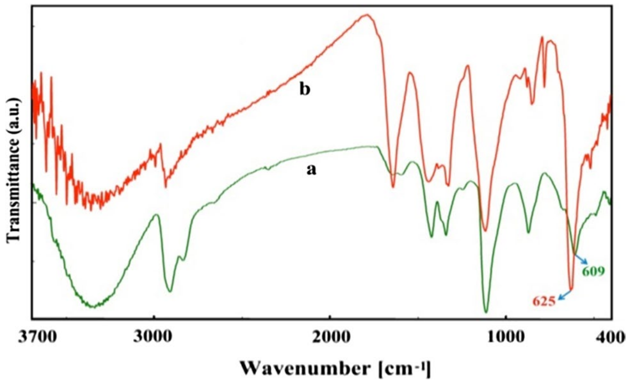


Fig. 3 FTIR spectra of PVA–Cu(II) complex (*a*) and PVA–Cu_2O composite (*b*)

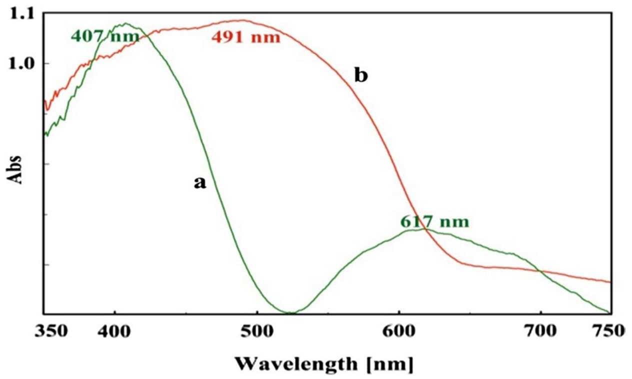


Fig. 4 Visible spectra of PVA–Cu(II) complex (*a*) and PVA–Cu_2O composite (*b*)

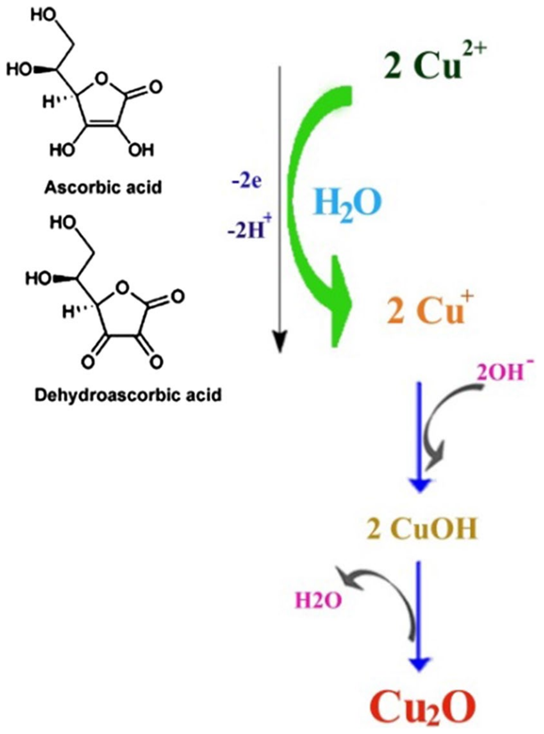


Fig. 5 Sequential reactions of the reduction stage to produce the Cu_2O particles

Table 1 Optimization of the catalyst loading

Entry	PVA–Cu_2O (g)	Yield (%)[a]
1	0.001	35
2	0.003	60
3	**0.005**	**95**
4	0.01	96

Reaction conditions 3-nitrophenyl azide (0.1 mmol), Phenylacetylene (0.12 mmol), TBAB (0.016 g), H_2O (2 mL), PVA–Cu_2O, r.t, 1 h

[a] Isolated yield

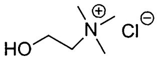
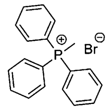
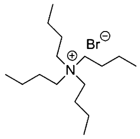
exhibit characteristic bands of stretching and bending vibrations of O–H, C–H, and C–O groups attributed to PVA. The peak at 3,350 cm^{-1} is the characteristic band of the O–H stretching vibration of PVA. The bands observed at 1,640–1,585 cm^{-1} have been assigned to stretching mode of C=O and C=C groups in polymer chain. Two strong bands observed at 1,422 and 1,347 cm^{-1} have been attributed to CH_2 and combination frequency of (CH + OH) groups, respectively [26]. The strong band at 1,114 cm^{-1} has been assigned to the stretching mode of C–O. In the spectrum of PVA–Cu(II) complex, the absorption peaks at about 677, 609 and 486 cm^{-1} indicate the vibrations of Cu(II)–O bond [27], and Fig. 3b represents Cu(I)–O vibration for PVA–Cu_2O composite at 625 cm^{-1} [28].

To investigate the optical properties, the visible spectra of PVA–Cu(II) complex and PVA–Cu_2O were examined and are shown in Fig. 4. For measurements, solid pellet samples of the isolated products were used in the 350–750 nm range. The spectrum of PVA–Cu(II) complex shows two broad absorption bands at 617 nm and 407 nm. However, the PVA–Cu_2O has an intense absorption in the visible range and the maximum absorption wavelength is observed at 491 nm. In the interpretation of the visible spectra it should be noted that the size, morphology, and crystallinity of particles would affect the optical absorption peaks [29].

Cu_2O is a *p*-type semiconductor with a direct band gap of 2.17 eV [30]. In this study, the calculated band gap for as-prepared PVA–Cu_2O composite obtained about 1.88 eV. The smaller band gap value of PVA–Cu_2O, as compared to that of Cu_2O, is attributed to the effects of PVA and particle size.

Since PVA is a hydrophilic and environmentally benign polymer, here we chose PVA as a stabilizing and dispersing matrix to make a stable Cu_2O-polymer system that can be well adapted to aqueous solutions and biological environments.

Table 2 Optimization of the phase-transfer additives

Entry	phase transfer additive	Time (h)	Conversion (%)[a]
1	Tween 40	4	95
2	 Choline chloride	4	40
3	 methyltriphenylphosphonium bromide	4	95
4	 tetrabutylammonium bromide (TBAB)	3	95
5[b]	–	4	80

Reaction conditions 4-azidoacetophenone (0.1 mmol), Phenylacetylene (0.12 mmol), phase-transfer additive (50 mol %), H_2O (2 mL), PVA–Cu_2O, r.t

[a] TLC conversion

[b] In the absence of phase-transfer additive

Embedding cupric ions in the PVA template makes diffusion and migration of ions in solution become more difficult. Many researches have studied the molecular structure of PVA–Cu(II) complexes, and various structures have been reported for these compounds [31]. Isolated Cu=O molecules and/or –(Cu–O)n– chains in PVA network are represented as possible structures.

Here the reduction process carried out at pH = 12, and in this system, the OH^- is a key factor for the production of Cu_2O particles. In the absence of OH^-, the XRD pattern of reduction stage product showed diffractions of metallic copper (Fig. S1).

For the Cu(I) ions, there are three possible reactions that are competing with each other [32]:

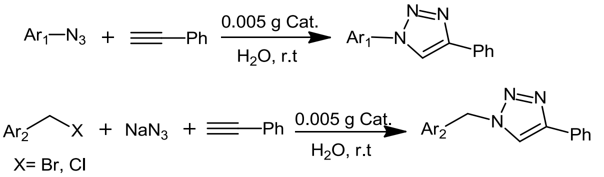
$$Cu^+ \rightarrow Cu^0 \tag{1}$$

$$2Cu^+ \rightarrow Cu^0 + Cu^{2+} \tag{2}$$

$$2Cu^+ + 2OH^- \rightarrow 2CuOH \rightarrow Cu_2O + H_2O \tag{3}$$

In the presence of OH–, the reaction corresponding to Eq. (3) probably occurs, and only the reaction (3) leads to the formation of cuprous oxide. Under our reduction

Table 3 Scope of aryl azides and benzyl halides in the PVA–Cu_2O-catalyzed click reactions

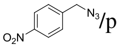
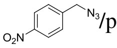
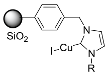
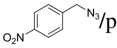
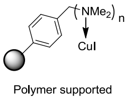


Entry[a, b]	Ar_1	Ar_2	Time (h)	Yield (%)
1	3-$NO_2C_6H_4$	-	1	95
	Run 2		1	95
	Run 3		1	95
	Run 4		1	94
2	4-$PhCOC_6H_4$	-	4	94
3	4-AcC_6H_4	-	3	85
4	4-$NO_2C_6H_4$	-	1.5	72
5	2-$NO_2C_6H_4$	-	8	90
6	4-CNC_6H_4	-	2.5	90
7	-	C_6H_5 (X=Br)	3	70
8	-	C_6H_5 (X=Cl)	3	68
9	-	4-$NO_2C_6H_4$ (X=Br)	4	85
10	-	2-$NO_2C_6H_4$ (X=Cl)	9	70
11	-	3-BrC_6H_4 (X=Br)	8	85

[a] Isolated yield after purification

[b] TBAB (0.016 g) was added as phase-transfer additive

Table 4 Comparison of results for the preparation of 1-(4-nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole (Table 2, entry 9) through the various procedures reported in the literatures

Entry	Catalyst	Reaction conditions	Yield (%) [Ref.]
1	Copper–aluminum hydrotalcite (3:1)	 /phenylacetylene/CH_3CN/r.t/12 h.	75 [33]
2	Copper(I) Zeolite [Cu(I)–USY]	 /phenylacetylene/toluene/r.t/15 h.	76 [34]
3		 /phenylacetylene/neat/r.t/0.5 h/N_2 atmosphere.	97 [35]
4	$CuFe_2O_4$	4-Nitrobenzyl bromide/NaN_3/phenylacetylene/H_2O/70 °C, 5 h.	86 [36]
5		4-Nitrobenzyl bromide/NaN_3/phenylacetylene/PEG 400-H_2O (1:1)/Et_3N (1 equv.)/r.t/8 h.	94 [37]
6	Present work	4-Nitrobenzyl bromide/NaN_3/phenylacetylene/H_2O/TBAB/r.t/4 h.	85

Supplementary data, XRD patterns and ^{1} HNMR spectra of triazole products have been prepared and provided as a separate file

conditions, at pH = 12, the cuprous oxide particles were obtained and no impurity of metallic copper was observed.

We also found that H_2O plays an important role in the process of reduction in this system. When reduction stage carried out in absolute ethanol as solvent in the presence of ascorbic acid, no color exchange of reaction mixture was observed; however, as soon as H_2O was added into the reaction mixture, the reddish particles appeared.

It can be understood that the formation process of Cu^+ ions and final Cu_2O particles composes the sequential reactions demonstrated in Fig. 5.

We next examined the catalytic activity of as-prepared PVA–Cu_2O in the model Huisgen reaction between terminal alkyne and organic azides, employing two protocols: (1) the use of aryl azides as azide-precursor and (2) in situ generation of aliphatic azides from the nucleophilic substitution reaction of organic halide with sodium azide (multicomponent synthesis).

Different amounts of PVA–Cu_2O were applied for the reaction mentioned in Table 1, to evaluate the catalyst loadings in this reaction system. A catalyst loading of 0.005 g was found to be optimal with respect to yield and short reaction times (Table 1, entry 3). The low catalyst concentration usually led to a long period of reaction as increasing the amount of catalyst shortened the reaction time.

In order to follow the majority of the principles of the Green Chemistry [16] framework and eliminate the organic solvents, we used H_2O as solvent in our reaction system. Since reactants are organic phase in aqueous medium, a phase-transfer additive was added to all reaction mixtures to facilitate the movement of reactants. Among the different phase-transfer additives tested such as choline chloride, tween 40, tetrabutylammonium bromide (TBAB), and methyltriphenylphosphonium bromide, TBAB gave the best result (Table 2).

In both protocols, phenylacetylene was used as alkyn-precursor and as shown in Table 3, both aromatic and aliphatic azides worked well in these reactions, and the corresponding 1,2,3-triazoles were isolated in good to excellent yields.

The PVA–Cu_2O composite was handled in air, and all the experiments were carried out under aerobic conditions. It is important to investigate the stability of as-prepared PVA-protected Cu_2O particles. This product was applied as a heterogeneous catalyst, and the reusability of catalyst is an important topic in the field of heterogeneous catalysis that is commonly attributed to its stability. We examined the possibility of recovery and reuse of PVA–Cu_2O catalyst using the CuAAC reaction between phenylacetylene and 3-nitrophenyl azide as the substrates under the same conditions reported in Table 3. After each run, the catalyst was separated by decantation, followed by washing with ethanol several times, and after drying, the catalyst was reused directly for the next run without further purification. The catalyst could be recovered and reused at least 3 times without any drop in the product yield.

The present catalytic method was compared with the some procedures reported for reaction of 4-Nitrobenzyl azide with phenylacetylene in the literatures, and the results have been shown in Table 4. The most important advantages of this method are mild and eco-friendly reaction conditions, availability, simplicity, short reaction times, and good yields.

Conclusions

In summary, PVA-stabilized Cu_2O particles were prepared using PVA–Cu(II) macromolecular complex as a precursor and ascorbic acid as a reducing agent in the aqueous medium at pH = 12 and room temperature. The as-prepared PVA–Cu_2O was tested as a heterogeneous catalyst in the copper(I)-catalyzed [3 + 2] cycloaddition reactions of terminal alkyne and organic azide. This catalyst showed a high catalytic activity in this system and could be easily recycled.

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