Highly Active Pandanus Nanocellulose-Supported Poly(amidoxime) Copper (II) Complex for Ullmann Cross-Coupling Reaction †

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Abstract: The transition metal-catalyzed chemical transformation of organic electrophiles, and organometallic reagents have turned up as an exceedingly robust synthetic tool. The evolution of transition metal catalysts has attained a stage of civilization that authorizes for an extensive scope of chemical bonds formation partners to be combined efficiently. The applications of Cu-based nanoparticles have received great attention owing to the earth-abundant, low toxicity and inexpensive. Due to these characteristics, copper nanoparticles have generated a great deal of interest especially in the field of catalysis. In this study, poly(acrylonitrile) was synthesized by undergoes free-radical initiation process and followed by Beckmann rearrangement with hydroxylamine solution converted into the poly(amidoxime) ligand and anchored the copper onto poly(amidoxime). Cu(II)@PAM was characterized using different techniques such as FTIR, FESEM, EDX, TEM, TGA, DSC, ICP-OES, and XPS analyses. The Cu(II)@PAM showed high stability and high catalytic activity in a wide variety of electrophilic substituted phenols with substituted aryl/benzyl halides. 0.15 mol%, ±3 mg of Cu(II)@PAM could efficiently promote Ullmann reaction to give the corresponding coupling product up to 99% yields. The complex was easy separated and recovered from the reaction mixture by simple filtration.

Keywords: pandanus nanocellulose; poly(amidoxime), copper (II) complex; Ullmann reaction; C-O bond formation

1. Introduction

The formation of a diaryl ether linkage/aryl-O bond is a vital reaction as it produces numerous chemical intermediates that have been proved to have significant importance in biology, pharmaceutical, life science, and material interest [1]. Owing to some disadvantages given by the conventional method of diaryl ether formation [2], researchers shifted their attention to the copper-catalyzed Ullmann coupling reaction. However, the classic Ullmann reaction requires a high temperature, excessive usage of copper catalyst, limitation of substrate scope and production of moderate yield [3]. Therefore, development of economical, environment friendly and recyclable is highly desirable for organic transformation. Despite the fact that the usage of heterogeneous copper catalysts is preferential over their homogenous counter partner owing to easy separation of product and reusability of catalyst, their use still faces some issues related to agglomeration due to the high surface energy in an aqueous environment [4]. To overcome this problem, copper particles are immobilized on a solid support such as cellulose [5]. Cellulose, the most abundant polysaccharides in nature, have been used as supports due to their biodegradability, environmentally friendly, cost-
effectiveness, water insolubility and reactivity of its hydroxyl groups [6]. Pure cellulose obtained from the food and agricultural industrial waste does not have high adsorption capacity, resulting in the removal of trace levels of metals become ineffective. Its adsorption ability can be improved by simple chemical modifications of its surface [6–8] and therefore, the newly formed surface will possess ionic or covalent interaction with heavy metals in the aqueous environment [6,9].

In this report, we anchored copper NPs onto pandanus nanocellulose-supported poly(amidoxime) as an efficient heterogeneous catalyst for C–O bond formation. The Cu(II)@PAM were found greatly effective in the C–O bond formation reactions. The catalyst was easy to recover and reused without any significant loss of their catalytic activity.

2. Methodology

2.1. Synthesis of Nanocellulose

Pandanus fruit was collected from Papar in Sabah, Malaysia (Figure 1). The cellulose pulp was extracted from waste pandanus fruit fiber according to the method described elsewhere [10]. The nanocellulose was prepared by stirring 5.0 g of pandanus cellulose pulp in 250 mL 40% of conc. sulphuric acid for 1.5 h with well shaking. After the reaction, the resultant product was directly poured into cold water to stop the reaction. Then the nanocellulose was washed with water until it became neutral. The product was dried in oven for 50 °C for one day to get a constant weight.

![Figure 1. Pandanus fruit.](image)

2.2. Graft Copolymerization; PAC

About 5.0 g of nanocellulose put in 500 mL of distilled water. Then 3 mL of the conc. H2SO4 was added to the mixture followed by 2.0 g of ceric ammonium nitrate. 15 mL of purified acrylonitrile solution was added into the mixture and stirred for 5 h under the inert condition at 60 °C (Scheme 1). At the end of reaction, the mixture was precipitated out by excess amount of methanol. The resultant product was then dried in an oven at 55 °C to obtain a constant weight.

2.3. Synthesis of Nanocellulose-Based Poly(amidoxime) Chelating Ligand; PAM

About 20.0 g of hydroxylamine hydrochloride was dissolved in 500 mL of methanolic solution. Then about 50% of NaOH solution was added in the cold condition, and the precipitate NaCl salt was filtered out. 10.0 g of PAC and 100 mL of hydroxylamine solution were added into a reagent bottle and the reaction was carried out at 80 °C for six hours. The resultant product was filtered out and washed using methanol. Then PAM was dried in an oven at 55 °C to obtain a constant weight.

2.4. Preparation of Cu(II)@PAM

10.0 g of PAM was added into 1M of copper (II) sulfate solution (9.33 g, 50 mL H2O) at room temperature. The yellow color of the PAM should be immediately turned into dark green color, and the mixture was filtered out and washed with methanol and dry at 60 °C for one day. The ICP-OES analysis was used to estimate the copper adsorbed by the amidoxime ligand (Scheme 1).
2.5. General Procedure for the Ullmann Etherification Cross-Coupling Reaction

±0.3 mg of Cu(II)@PAM was added into a mixture of aryl halide/benzyl halide (1.0 mmol), phenol (1.2 mmol) and K₂CO₃ (3 mmol) in acetonitrile (5 mL) at 50 °C. The corresponding product was monitored by TLC and GC analyses. The metal catalyst was separated by filtration after the reaction. The corresponding product was extracted with dichloromethane. The crude product was purified by silica gel column (ethyl acetate/hexane) to give the corresponding cross-coupling product [11].

3. Result and Discussion

The bio-waste pandanus nanocellulose-supported poly(acrylonitrile) and poly(amidoxime) ligand were prepared and characterized (FTIR) according to early report [10,12]. The amidoxime ligand was anchored with copper at room temperature to give dark green color Cu(II)@PAM (Scheme 1). The ICP-OES showed that 0.50 mmol/g of copper was coordinated with the PAM.

3.1. FE-SEM, TEM and EDX Analysis

After chemical treatment of fiber, pandanus cellulose pulp showed noticeably smooth wooden stick-like structure (Figure 2a). Followed by the nanocellulose (Figure 2b) showed the same morphology as cellulose pulp. The only difference between pandanus cellulose pulp and nanocellulose are the size of and shape. PAC presented with a rough surface with deformed spherical-like morphologies (Figure 2c). In PAM ligand, an unsmooth structural surface with a distinguishable small sphere shape was observed (Figure 2d). Continued, Cu(II)@PAM showed smaller spherical shapes with similar accumulation was observed, as shown in Figure 2e.

Figure 2. FE-SEM image of (a) pandanus cellulose, (b) nanocellulose, (c) poly(acrylonitrile), (d) poly(amidoxime), (e) Cu(II)@PAM; (f) TEM image of Cu(II)PAM, (g) TEM image of Cu(II)PAM with measurement; (h) EDX image of Cu(II)@PAM.
The TEM analysis of the Cu(II)@PAM was showed the presence of copper onto the PMA surface (Figure 2f) and the average nanoparticles size of copper $\varnothing = 27.51 \pm 2$ nm was measured (Figure 2g). The copper nanoparticles exhibited spherical morphology with no agglomeration occur. As shown in Figure 2f, a random distribution of copper nanoparticles was well distributed on the PAM surface.

Figure 2h represents the EDX spectra of Cu(II)@PAM after anchoring the copper. Upon the inspection of the result, it is evidence that the value of copper has been increased after evacuated of copper in the copper solution. It can seem that at 8.05 keV show around 35.4% of copper anchored on the PAM.

3.2. Thermogravimetry Analysis

The thermal behavior of the cellulose, poly(acrylonitrile), poly(amidoxime) ligand and Cu(II)@PAM were performed with heating rate 10 min$^{-1}$ in nitrogen condition and the obtained result was presented in Figure 3. In the complete analysis, there are several changes in four materials with the elevation of the sample temperature. A small weight loss was notified in four materials before 150 °C. These may have resulted from the remaining water molecules that are located in the external surface and internal cavities of the synthesize materials. The cellulose TA curve shows that there is a significant weight loss at around 315–390 °C due to the degradation of -OH and -CH$_2$OH function group (Figure 3d) [13]. The PAC was degraded in temperature range 285–550 °C. The first weight loss (~40%) at about 285–400 °C was due to the dehydrogenation reaction and degradation of the cyanide group. The second stage of the weight loss (~15%) was started at 400–550 °C and could belong to the degradation of the remaining of acrylonitrile chain (Figure 3c) [14]. The poly(amidoxime) ligand was degraded from 175–455 °C due to the degradation of the amidoxime functional group (Figure 3b).

The total weight loss of PAM is 50% while PAC is 60%. Overall, PAM and Cu(II)@PAM were more stable than their precursors, which has good nature in term of degradation behavior of final product.

3.3. X-ray Photoelectron Spectroscopy Analysis (XPS)

Amidoximes are the bidentate ligands which are efficiently bound with copper due to the strong chelating ability to transition metal ions. The X-ray photoelectron spectra are acquired to explain the binding mechanisms of copper on the PAM. The wide scan XPS spectra of Cu(II)@PAM and pure PAM are shown in Figure 4a. The binding energies (BEs) peaks in Figure 4a were found at 287.5, 402.0 and 534.0 eV corresponding to the C 1s, N 1s, and O 1s spectra, respectively. The binding of Cu(II) is confirmed by the presence of two new peaks with BEs of 935.5 and 952.0 eV for the signals of Cu2p3/2 and Cu2p1/2 as shown in Figure 4a(i). The O 1’s XPS spectra of the pure PAM showed two peaks at the BEs of 531.5 and 534.0 eV, which correspond to the oxygen atoms in the C-OH and C=N-OH species, respectively. After binding with copper, a new peak at a BE of 531.0 eV belonging to the peaks of O 1s of the oxygen atoms in C=N-OH was formed (Figure 4c).

In the core-level N 1s spectra for the PAM, the N 1s peak of polymer ligand showed two peaks at the BEs of 402.0 and 398.5 eV, which correspond to nitrogen atoms in C-NH$_2$ and C=N-OH species.
respectively. After PAM was bonded with copper, a new peak for the N 1s was found with a BE of 402.5 eV owing to the coordinated bond of the amidoxime group with copper (Figure 4d).

Figure 4. (a(i)) Survey scan XPS of Cu(II)@PAM, (a(ii)) Survey Scan XPS of PAM before encahed copper; (b) curve fitting XPS of Cu(II)@PAM; (c) curve fitting XPS of O 1s; (d) curve fitting XPS of N 1s.

3.4. Copper (II) Catalyzed Ullmann Etherification Coupling Reaction

The performance of Cu(II)@PAM was examined in the Ullmann reaction of phenol and benzyl halide. The initial reaction was performed using 15.0 mg of Cu(II)@PAM at 80 °C for 8 h in presence 3 mol of K₂CO₃ and 5 mL of acetonitrile. It was found that Cu(II)@PAM can afford to correspond product in 98% yield (Table 1, entry 1) smoothly. We also accomplish the reaction by changing the catalyst loading, time and temperature and eventually found that ±3.0 mg of Cu(II)@PAM, 2 h of reactions time and the reaction conduct at 50 °C shall be sufficient to bring forward the reaction efficiently.

Table 1. Screening of Ullmann cross-coupling reaction.

| Entry | Cu(II)@PAM (mg) | Temperature (°C) | Time (h) | Yield (%) |
|-------|----------------|-----------------|----------|-----------|
| 1     | 15             | 80              | 8        | 98        |
| 2     | 5              | 50              | 8        | 99        |
| 3     | 3              | 50              | 2        | 99        |
| 4     | 1.5            | 50              | 2        | 89        |

Conditions: 4-nitrobenzyl bromide (1 mmol), phenol (1.2 mmol), a catalytic amount of complex copper and 3 mol equiv. of K₂CO₃ in 5 mL of acetonitrile.

To prospect the extensive applicability of Cu(II)@PAM in the Ullmann etherification, plenty of structurally diverse of phenol-substituted compound and phenyl halide/benzyl halide compound were used under earlier settled optimized reaction conditions and the result are summarized in Table 2. As illustrated in Table 2, this Cu(II)@PAM could efficiently drive these reactions toward the desired product in good to excellent yield. Phenol derivatives with both electron-donating and electron-withdrawing groups proceed smoothly with very good efficiency to form the desired products in high yields (77–99%); (Table 2).
Table 2. Ullmann reaction of substituted benzyl halide and phenol derivatives compound.

| R1 | R2 | Conditions: Benzyl halide (1 mmol), phenol (1.2 mmol), ±3.0 mg of Cu(II)@PAM and 3 mol equiv. of K2CO3 in 5 mL of acetonitrile. All the compound was determined by GC-MS and NMR.

| R1 | R2 | Conditions: Benzyl halide (1 mmol), phenol (1.2 mmol), ±3.0 mg of Cu(II)@PAM and 3 mol equiv. of K2CO3 in 5 mL of acetonitrile. All the compound was determined by GC-MS and NMR.

The aryl halide compound also used to investigate the applicability of Cu(II)@PAM. This is because the halogen group is direct-attached to sp2 hybridized carbon of benzene ring and hence, more electronegative and more challenging to break [15]. Within this part of the study, the result suggested that the aryl halide substituted with electron-withdrawing groups achieved a better yield compare to the electron-donating group. The reactivity of the aryl halide was following the general reaction, which Ph-I > Ph-Br > Ph-Cl (Table 3). Besides, the aryl chloride was significantly affected by the substituent that attached to it. For example, neutral chlorobenzene provided only 20% of diphenyl ether product, whereas 4-cyanochlorobenzene afforded the respective product with 65% yield. In the study, the aryl-bromide substituted with bromo and nitro together give a reasonable result (65–75%); (Table 3).

Table 3. Ullmann reaction of substituted aryl halide and phenol compound.

| X | Conditions: Aryl halide (1 mmol), phenol (1.2 mmol), ±3.0 mg of Cu(II)@PAM and 3 mol equiv. of K2CO3 in 5 mL of acetonitrile. All the compound was determined by using GC-MS and NMR.

4. Conclusions

In summary, we have synthesized pandanus fruit fiber nanocellulose-supported-poly(amidoxime) copper (II) complex which it was successfully applied in the Ullmann Etherification cross-coupling reaction with different substituted compounds. The catalyst efficiency (±3.0 mg/0.15 mol%) promoted Ullmann cross-coupling reaction to produce corresponding products with satisfying yields. Moreover, the catalyst can be easily filtered out after the reaction is done.
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