HIGHLY ACTIVE PANDANUS NANOCELLULOSE-SUPPORTED POLY(AMIDOXIME) COPPER (II) COMPLEX FOR ULLMANN CROSS-COUPLING REACTION

BY:

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BACKGROUND

- Synthesis process is necessary due to the **molecular complexity** and various type of **bond formation** through the organic transformations is being grown in parallel fashion.

- C-C or C-N bonds formation (cross-coupling) reactions are **important** for the synthesis of essential chemicals such as:

  1. Fine chemicals,
  2. Drug and intermediate products,
  3. Natural products etc.

- Transition metal catalysts (Pd, Cu, Ni) are normally used for cross-coupling reactions (suzuki, heck, sonogashira, click etc.).

Catalyst

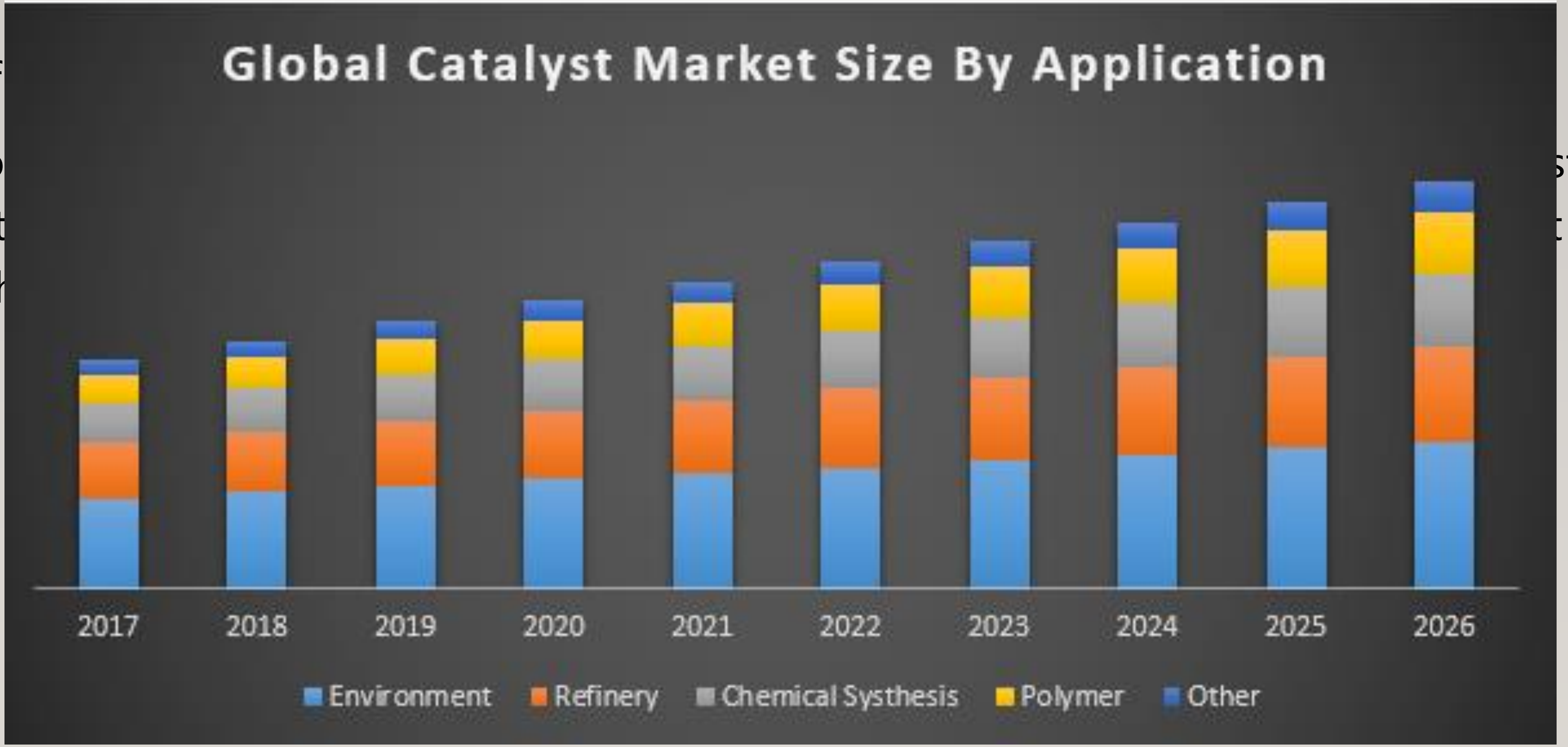
Homogeneous

Heterogeneous

Homogeneous catalyst	Heterogeneous catalyst
❑ Expensive	❑ Less expensive
❑ Purification of product is difficult	❑ Easy to purify the product
❑ Can not be reused	❑ Reusable
❑ Environmental pollution	❑ Environmental-friendly
❑ Not stable in the reaction media	❑ Stable under harsh conditions

- Price of

- Therefo stainable chemist t of the research



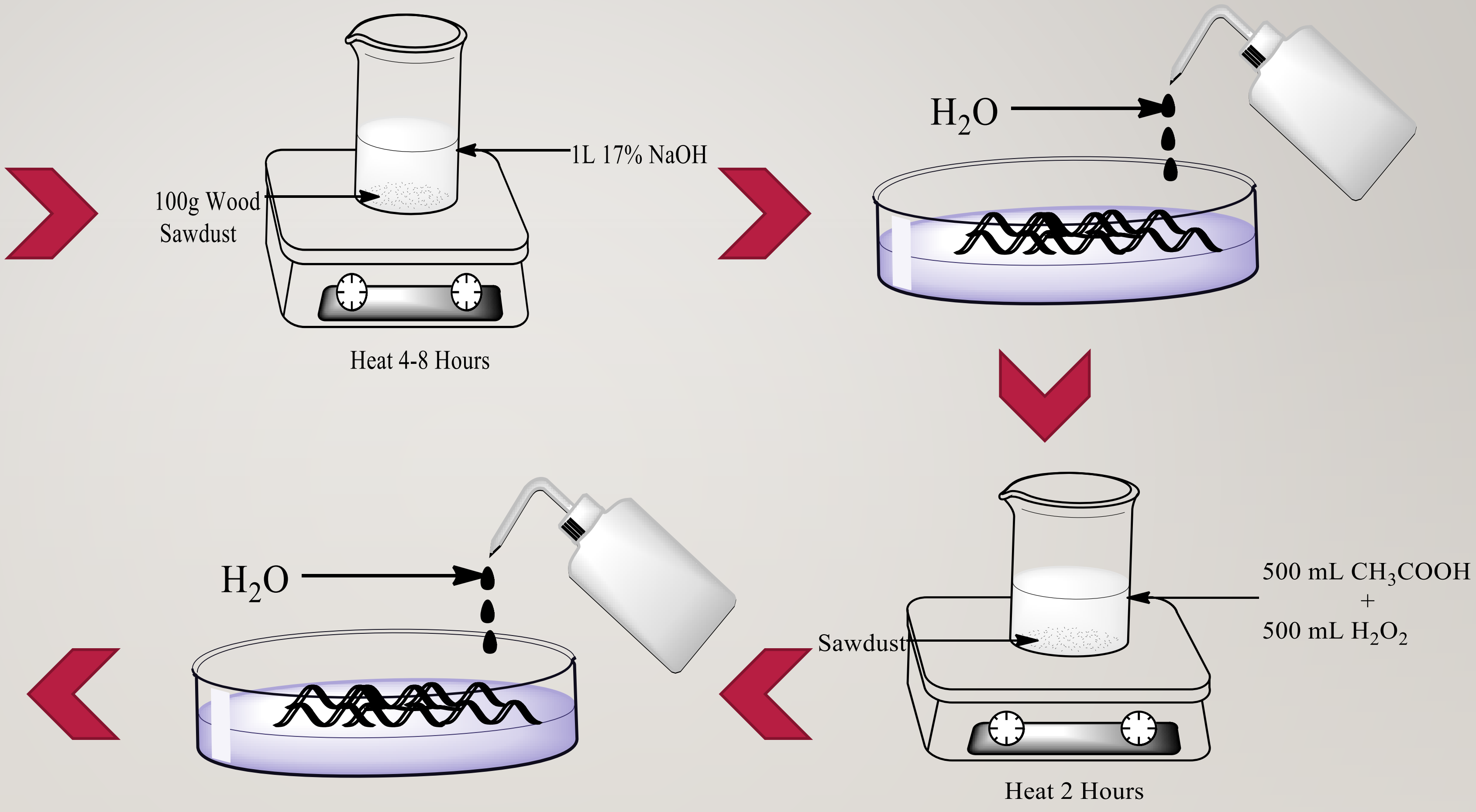
OBJECTIVES

- To extract the cellulose from the agro-waste (pandanus fruit fibre) and utilize to synthesize a poly(amidoxime) ligand,
- To prepare heterogeneous copper catalysts from the cellulose-supported amidoxime ligands,
- To evaluate the catalytic ability and reusability of synthesize catalyst in Ullmann cross-coupling reaction.

METHODOLOGY

Cellulose Extraction

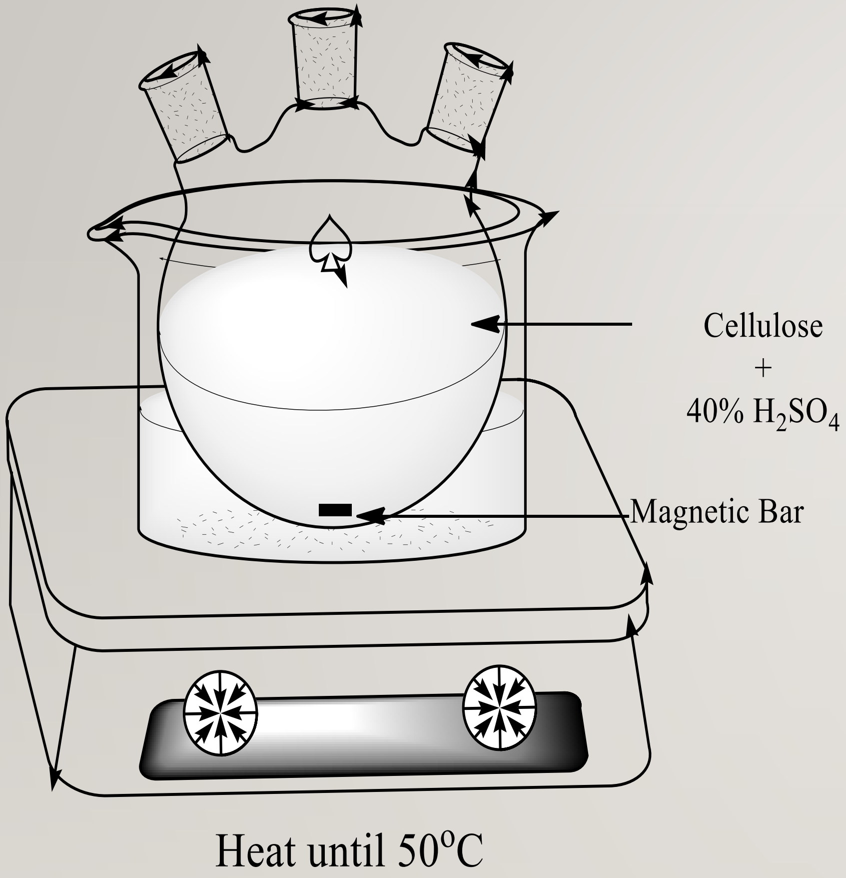
Filter the wood sawdust and weight 100g of fiber.



Dry the cellulose with oven at 50°C for one day and weight the mass of cellulose obtain

(Sources: Rahman *et al.*, 2016)

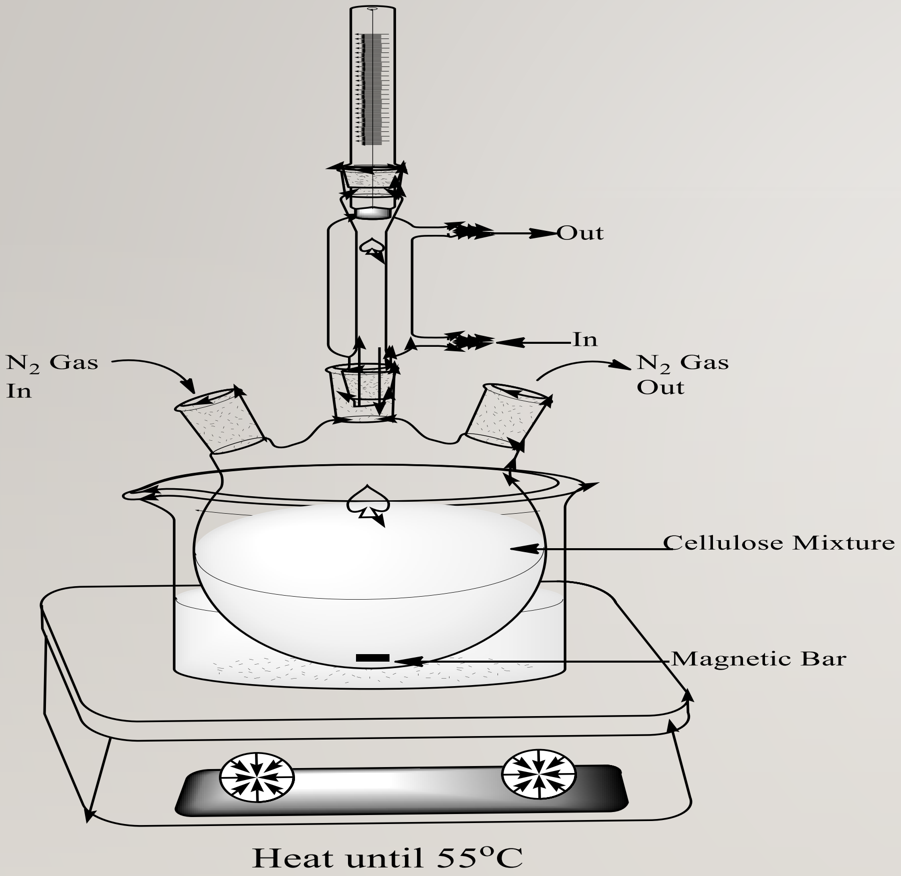
Synthesize nanocellulose



Procedure:

1. Boil the cellulose with 40% of H_2SO_4 for 1 hours.
2. Pour the mixture into the cool water after reaction done.
3. Neutralize the solution using NaOH .
4. Wash and dry.

Graft Copolymerization (Poly(acrylonitrile))

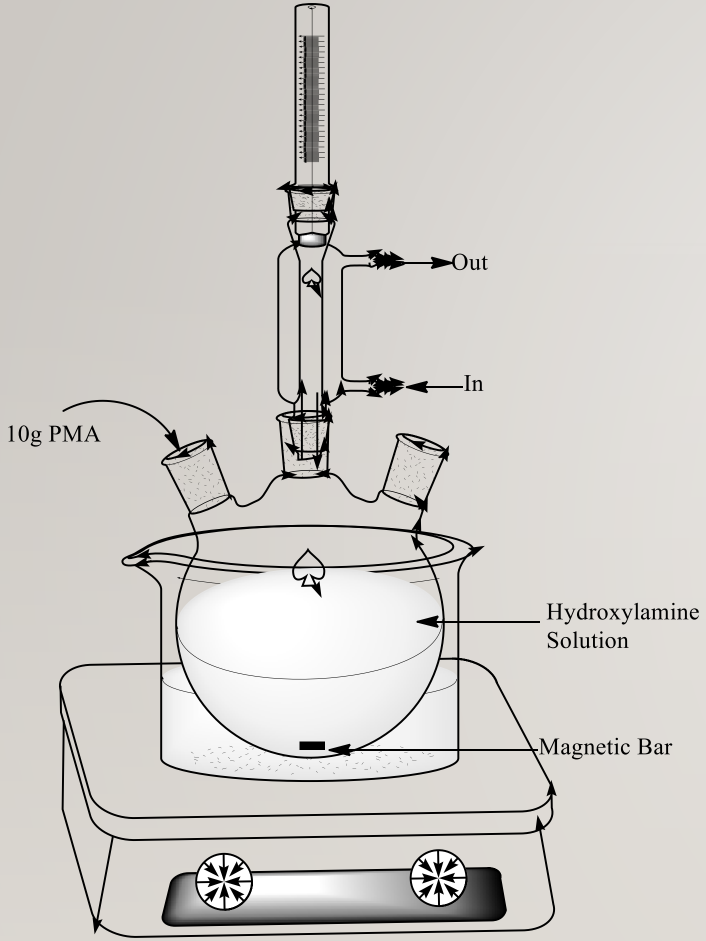


Procedure:

1. Hydrolyze cellulose react with ceric initiator in inert condition for 15 min
2. Purified monomer (methyl acrylate) is added.
3. Heat for 4 hours at 55°C.
4. Wash and dry

(Sources: Mandal *et al.*, 2016)

Synthesis of Poly(amidoxime) Ligand

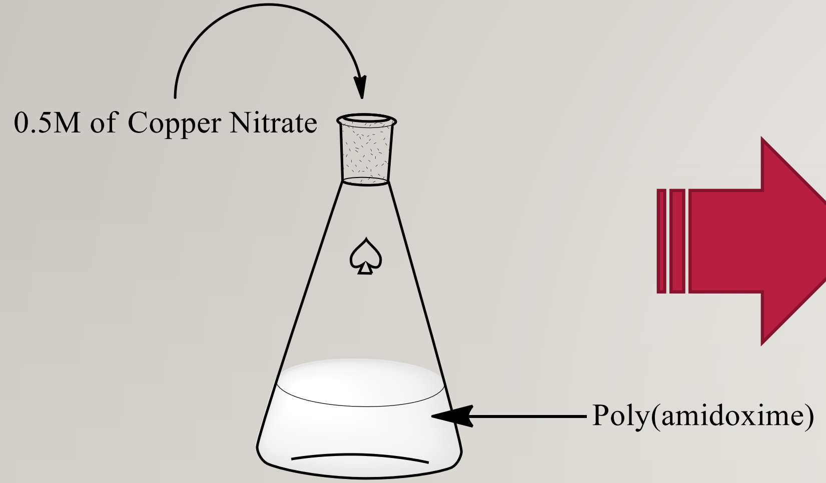


Procedure

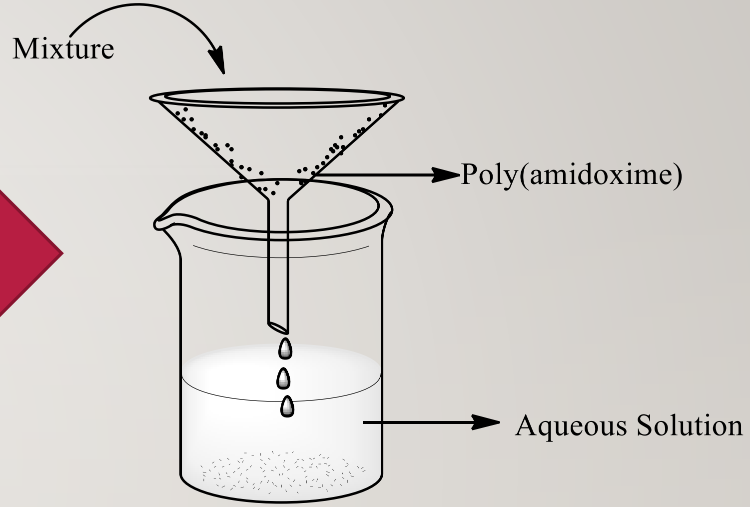
1. Hydroxylamine hydrochloride is dissolved into 4:1 methanolic solution.
2. PMA is added into the hydroxylamine solution and heat for 6 hours at 70℃.
3. PHA ligand is washed by methanolic solution.
4. In order to cover chelating polymeric ligand into H-form ligand, the ligand was treating with 100 mL of 0.1 M of hydrochloric acid (HCl) in methanolic for five minutes.
5. Wash and dry.

(Sources: Shaheen *et al.*, 2016)

Preparation Of Metal Catalyst (Cu^{2+})



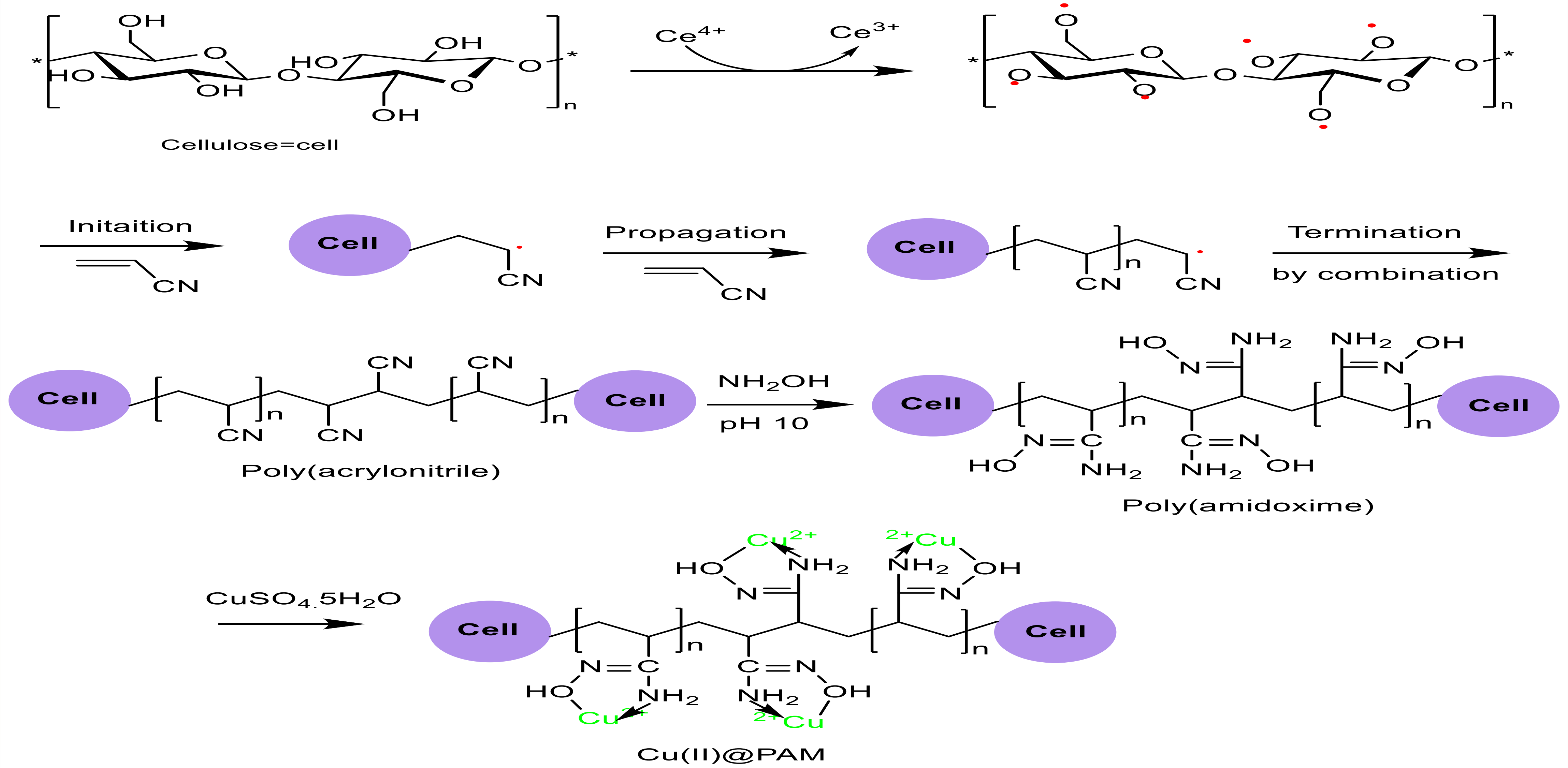
Shake for 2 hours with 180 rpm Agitation speed



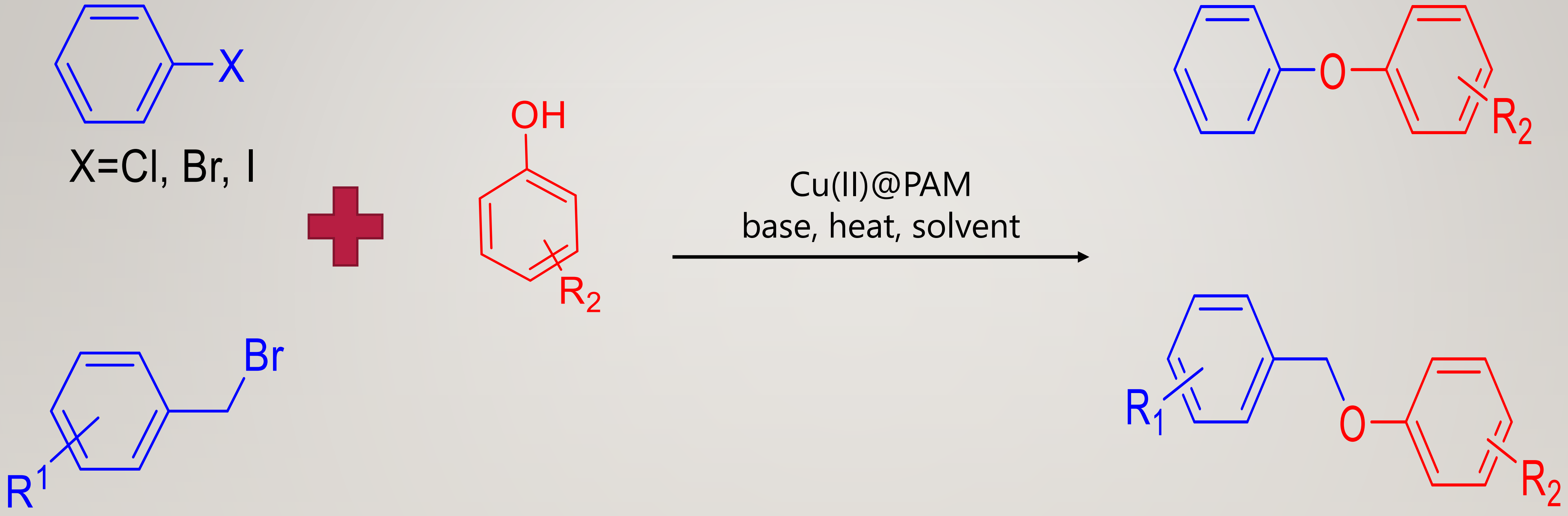
Wash the ligand and dry it. The ICP-OES analysis should be used to estimate the copper adsorbed

(Sources: Rahman *et al.*, 2016)

Reaction Mechanism



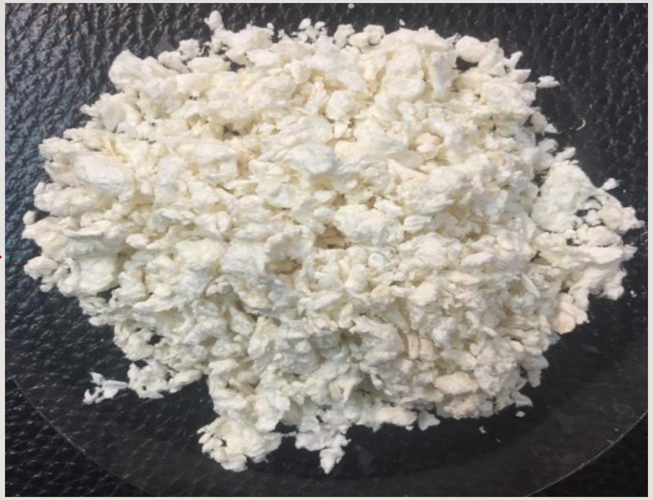
Ullmann Reactions



RESULT

Product

Pandanus fruit and its fibre

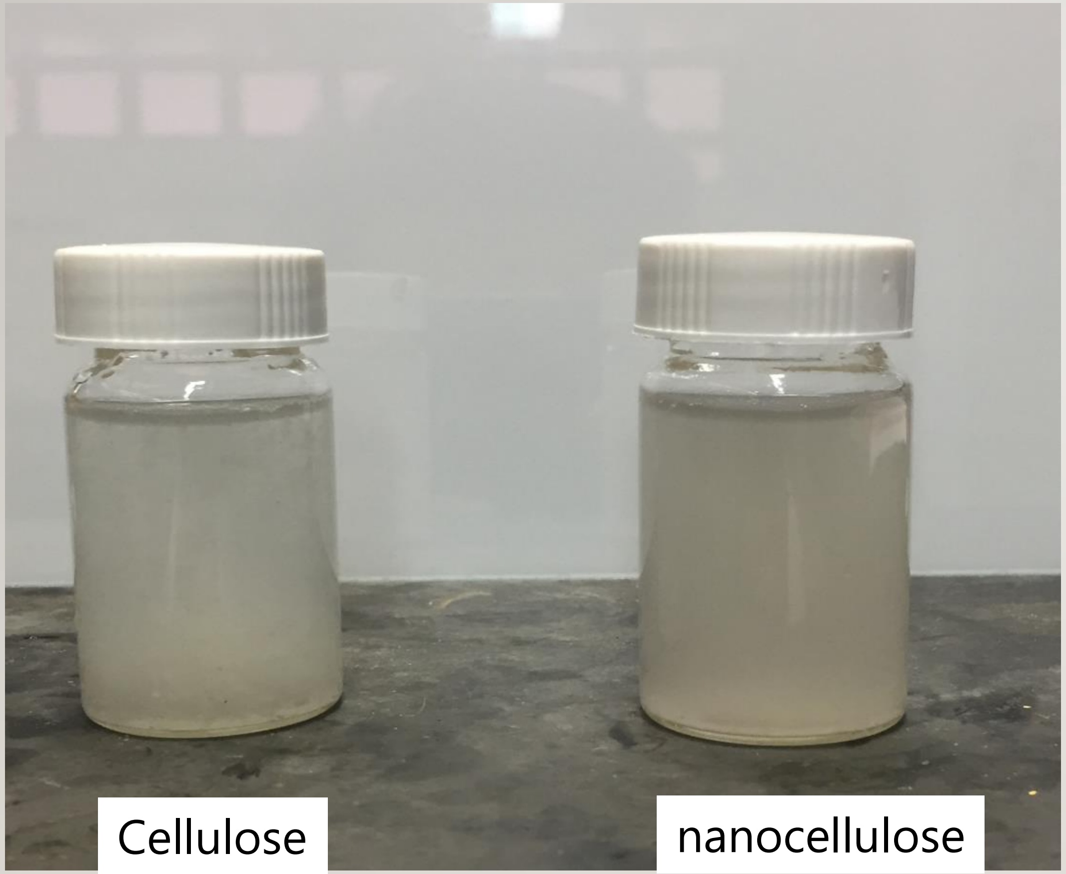


Cellulose from Pandanus fruit fibre

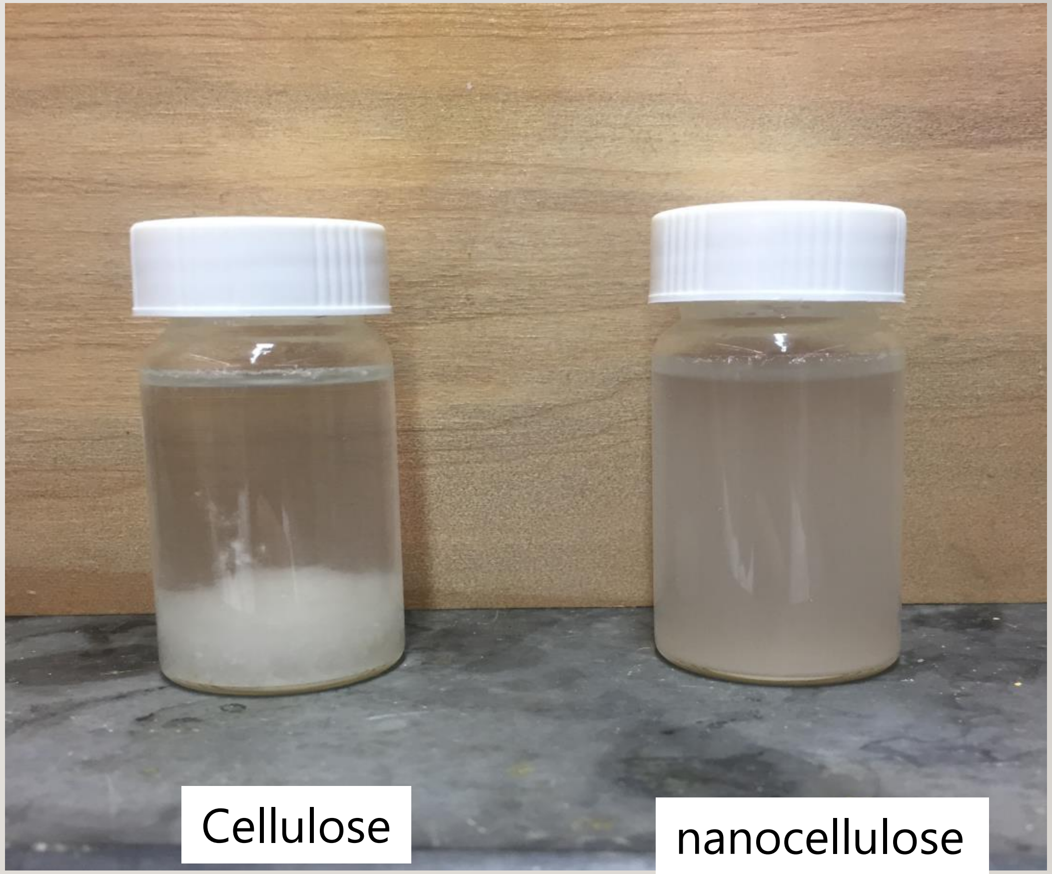
Extraction: 49.5 ±1.0g from 100g dried fruit fibre
Yeld: (≈ 50%)

(nanocellulose)

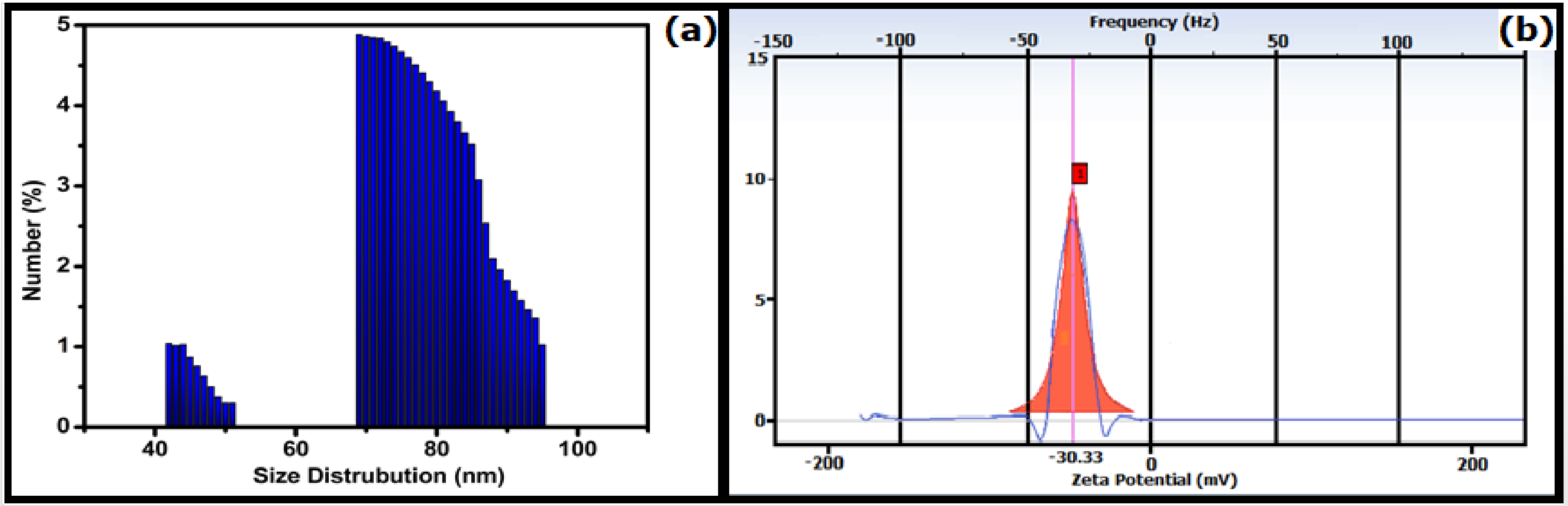
Physical stability of cellulose and nanocellulose



15 min String

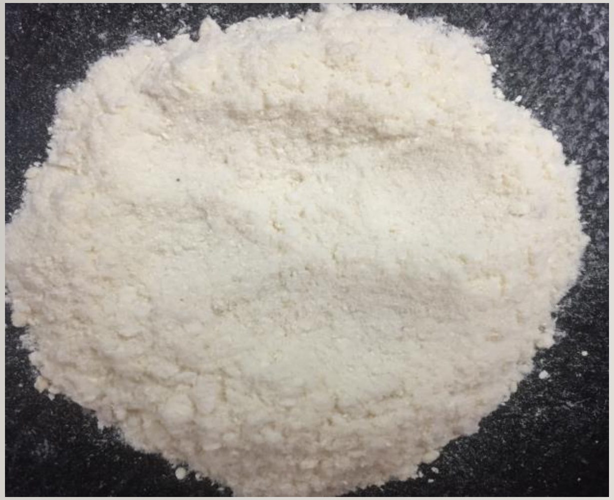


Leave For 3 hour



Particle size and zeta potential analysis

Product

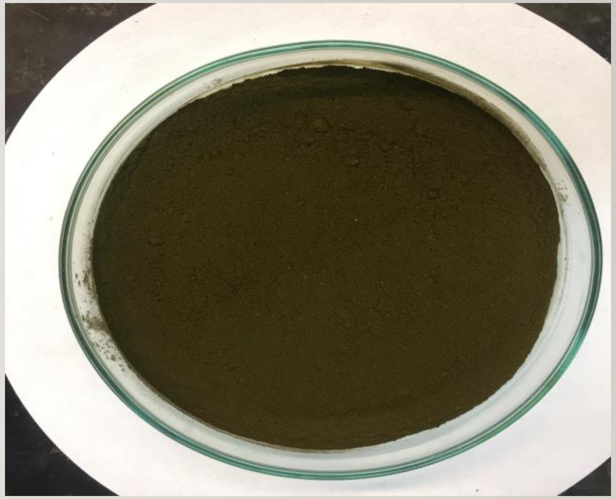


Poly(acrylonitrile)

Yield: **18.15 g** from 10g dried nanocellulose

Poly(amidoxime) Ligand

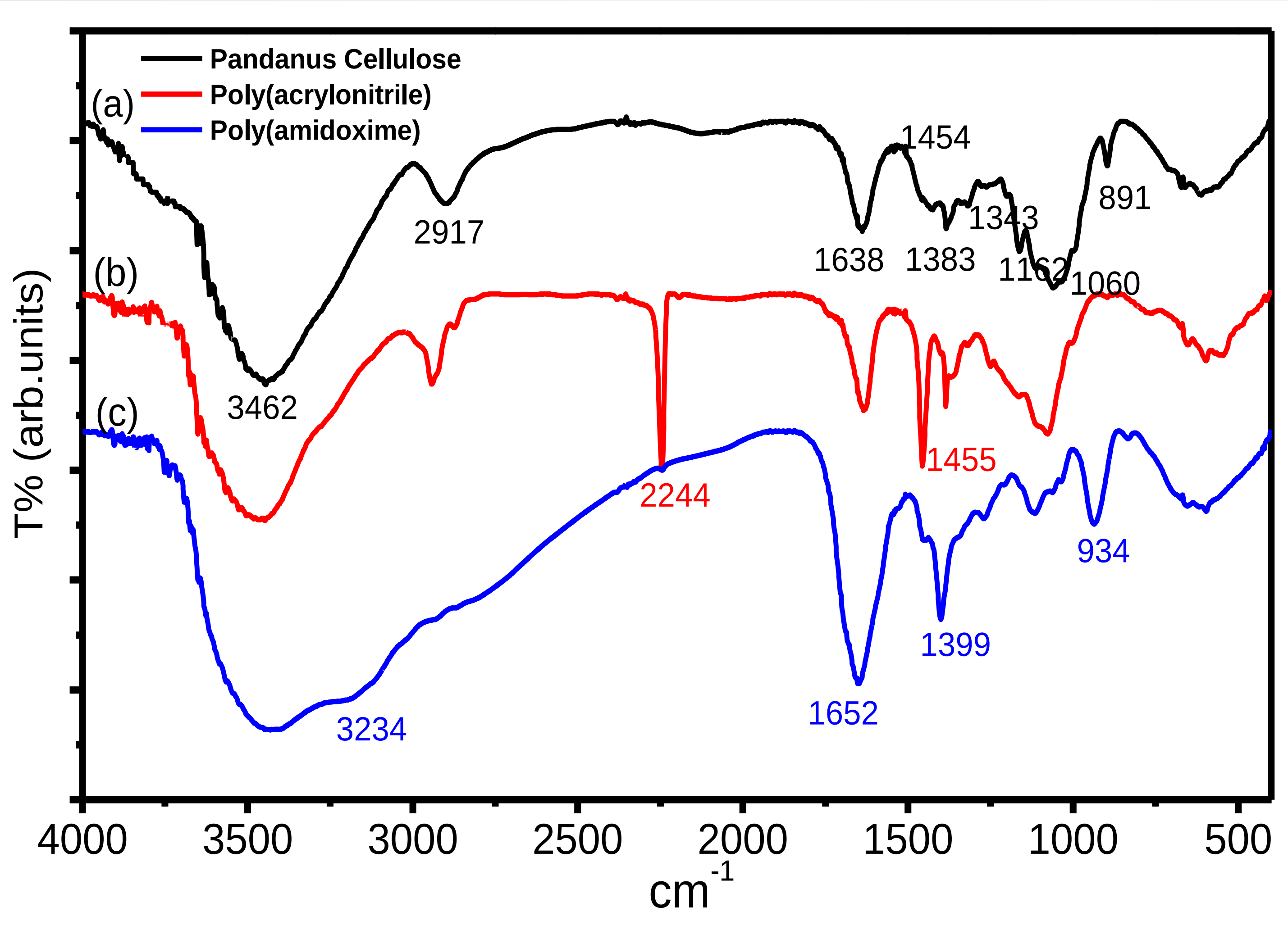
Yield: **28.50g** from 10g dried poly(acrylonitrile)

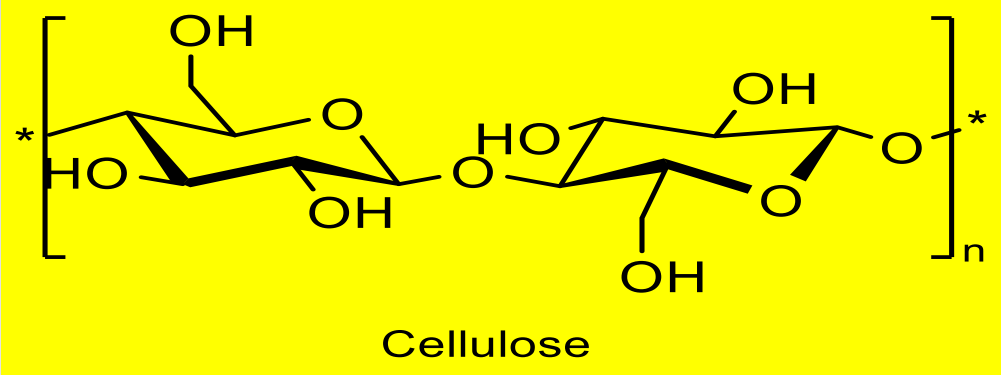


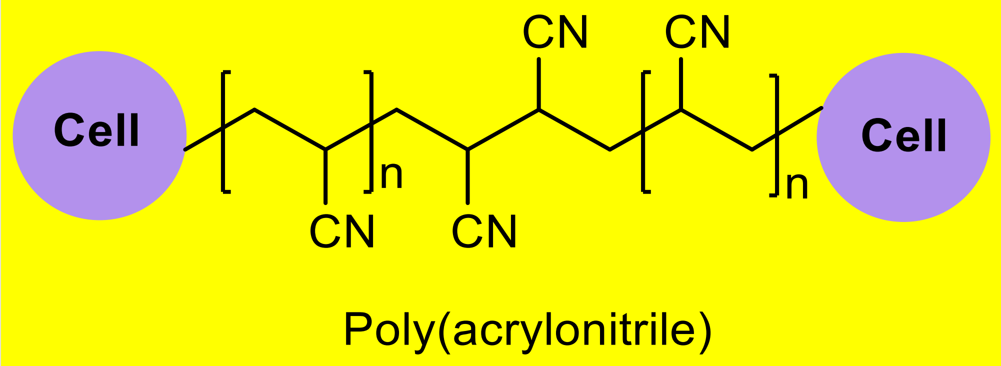
Cu(II)@PAM

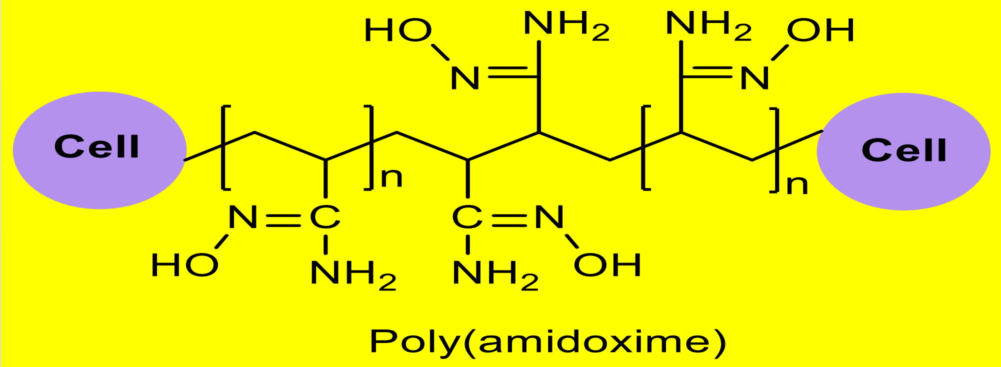
ICP-OES= 0.50mmol/g of copper

FT-IR Analysis

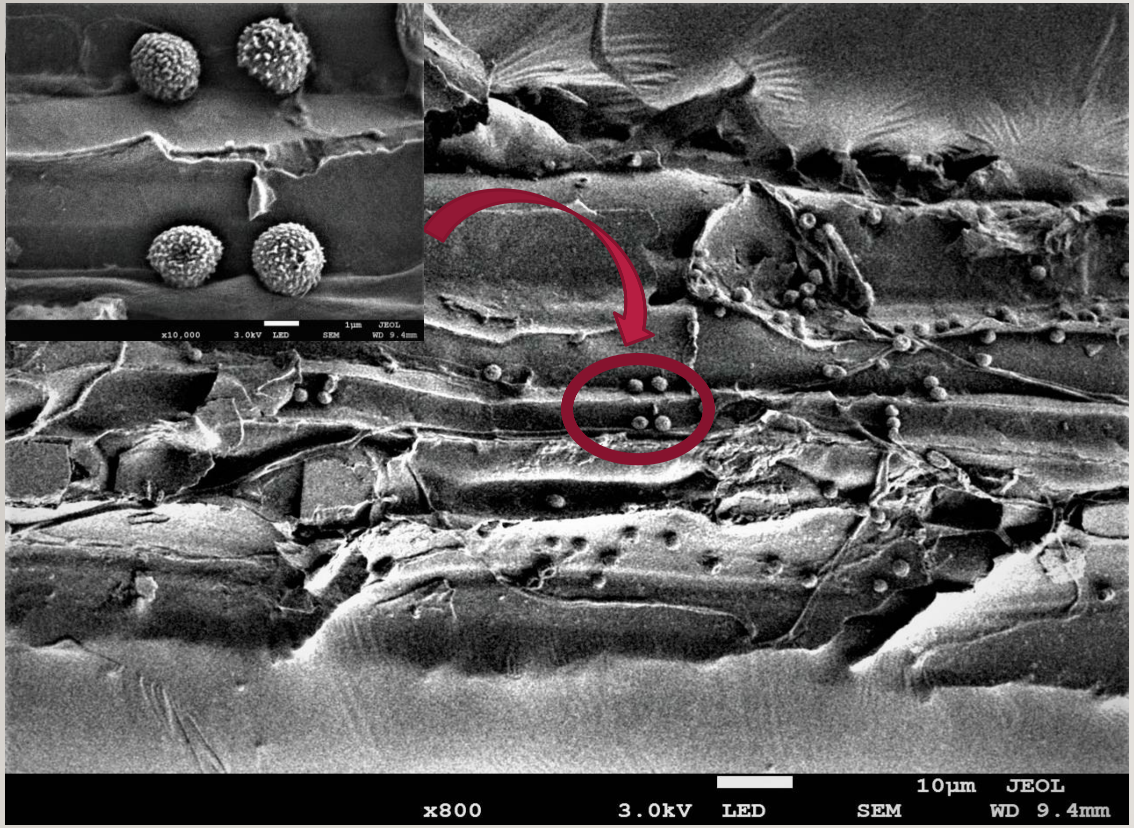




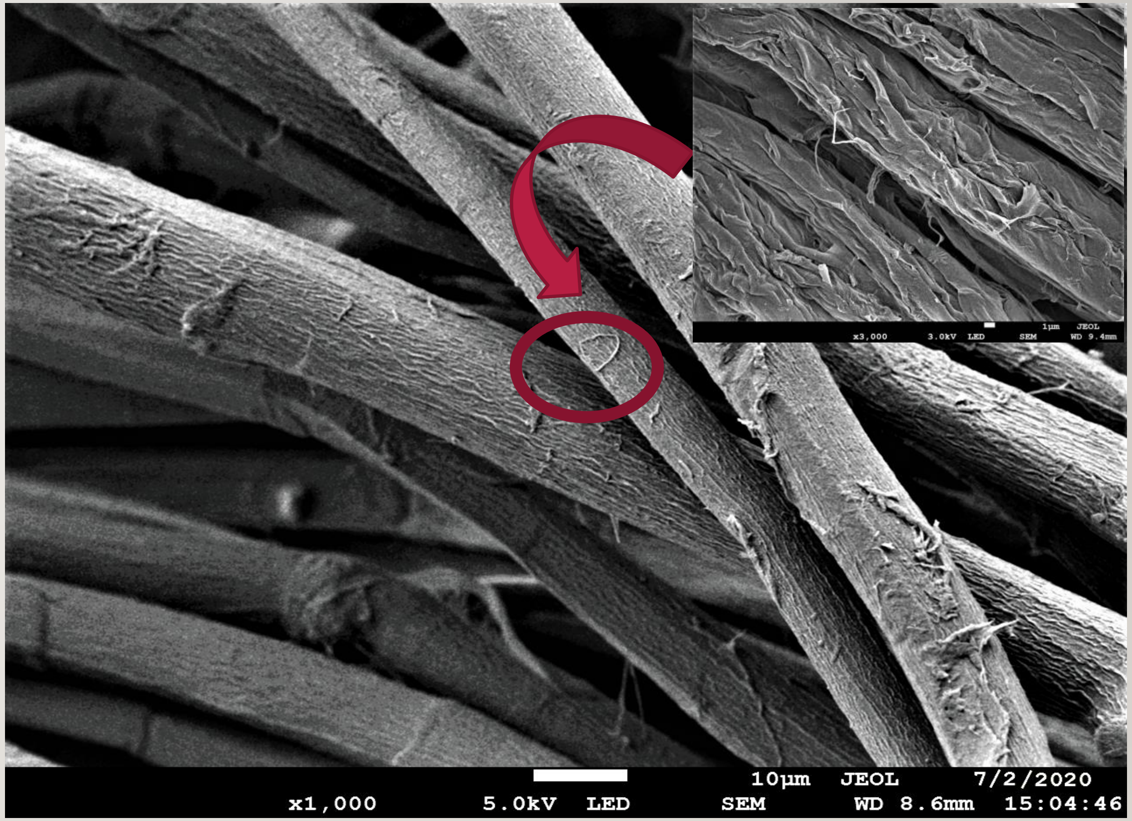




FE-SEM Analysis



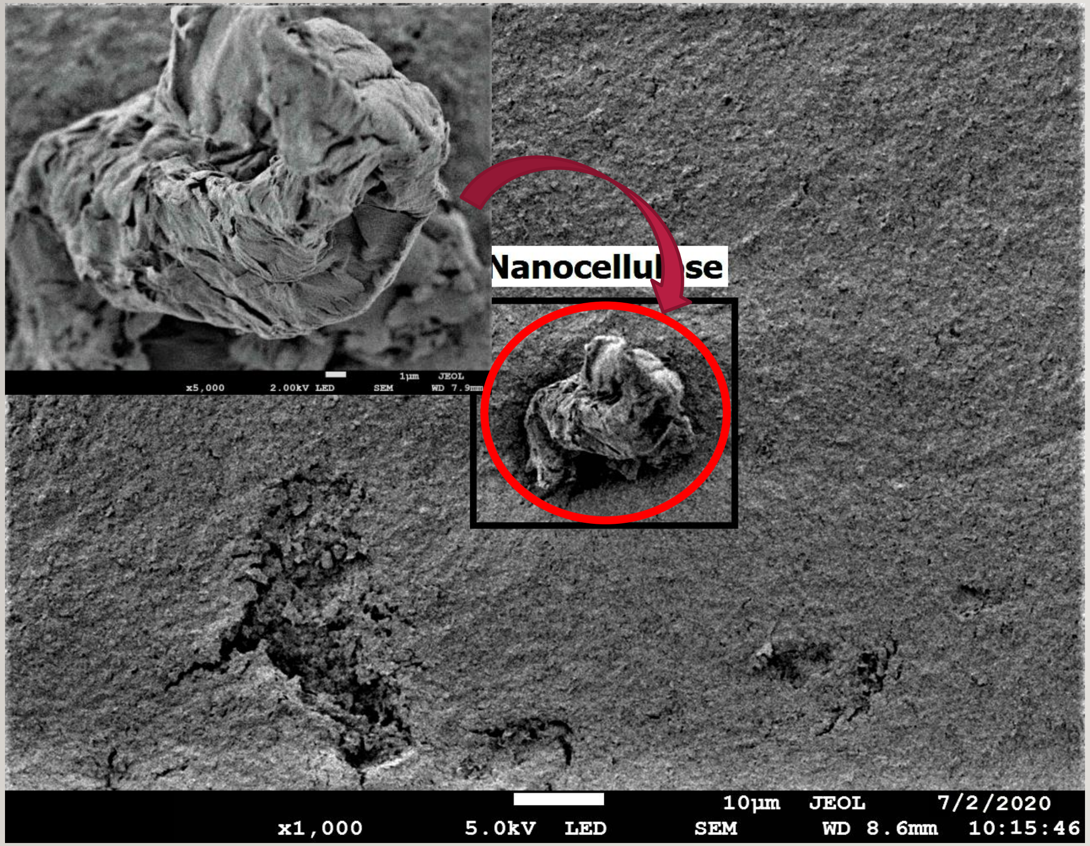
Pandanus fruit fiber



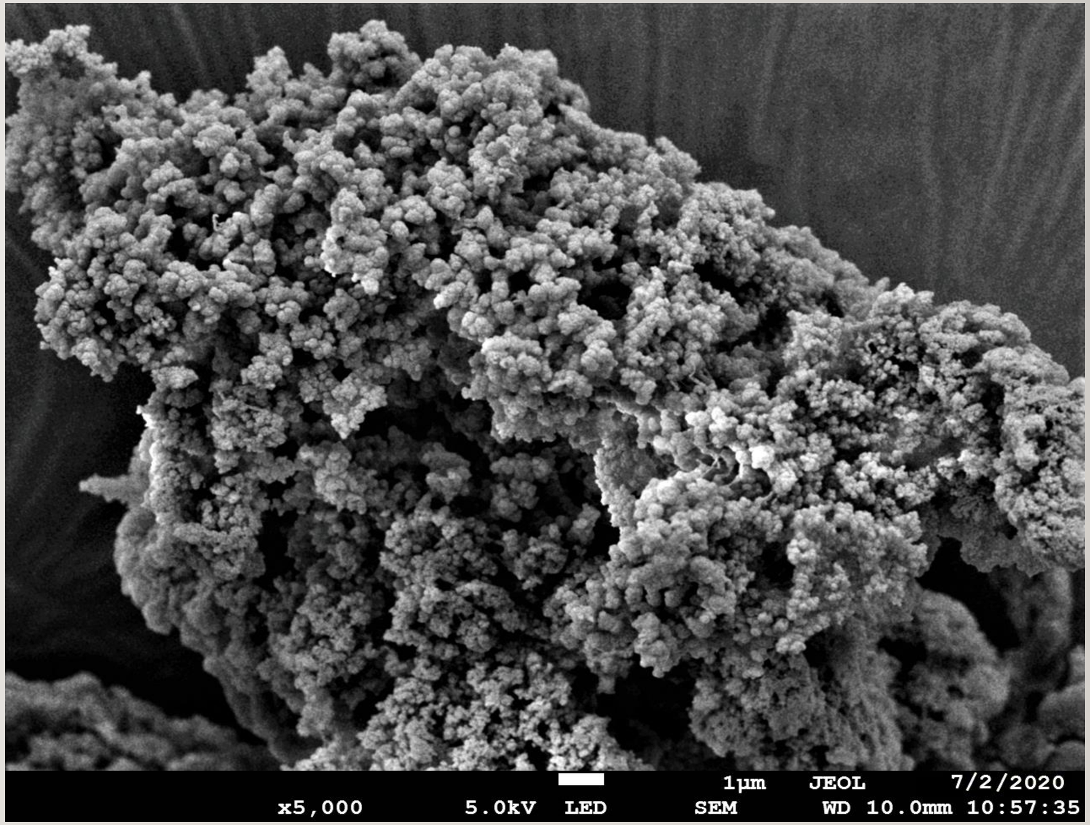
Pandanus-cellulose

Magnification: 1000X

FE-SEM ANALYSIS

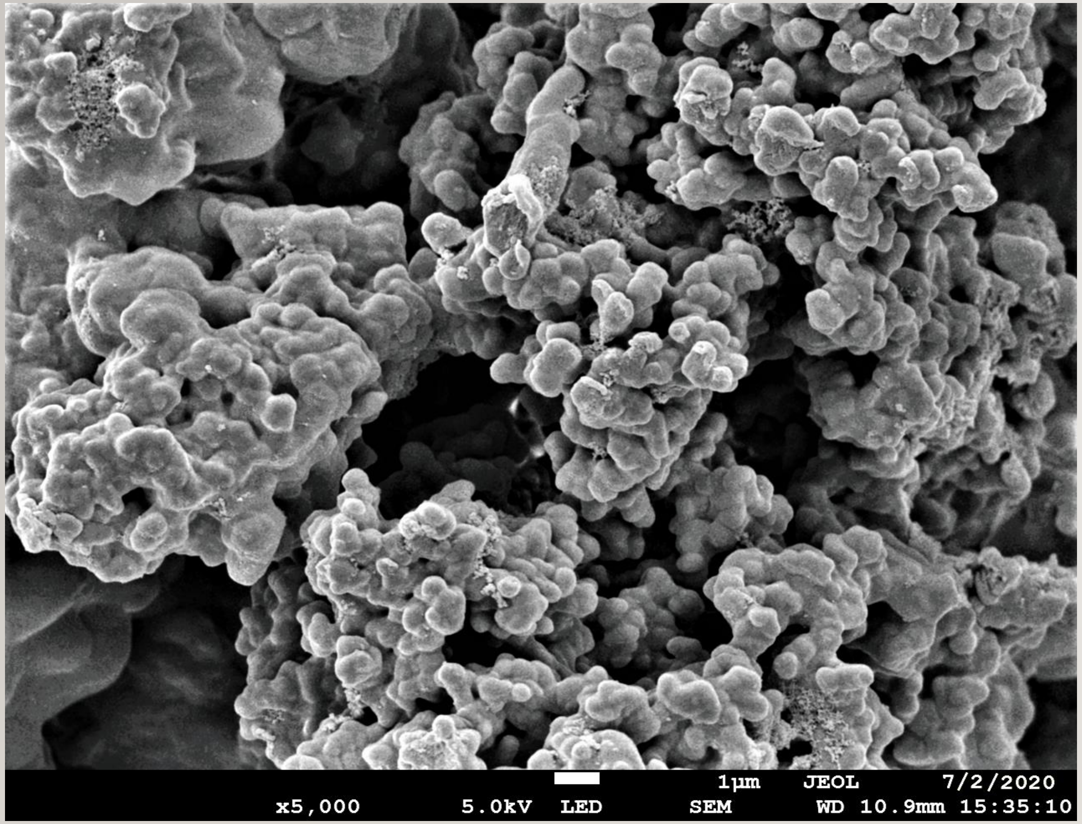


nanocellulose
Magnification: 1000X

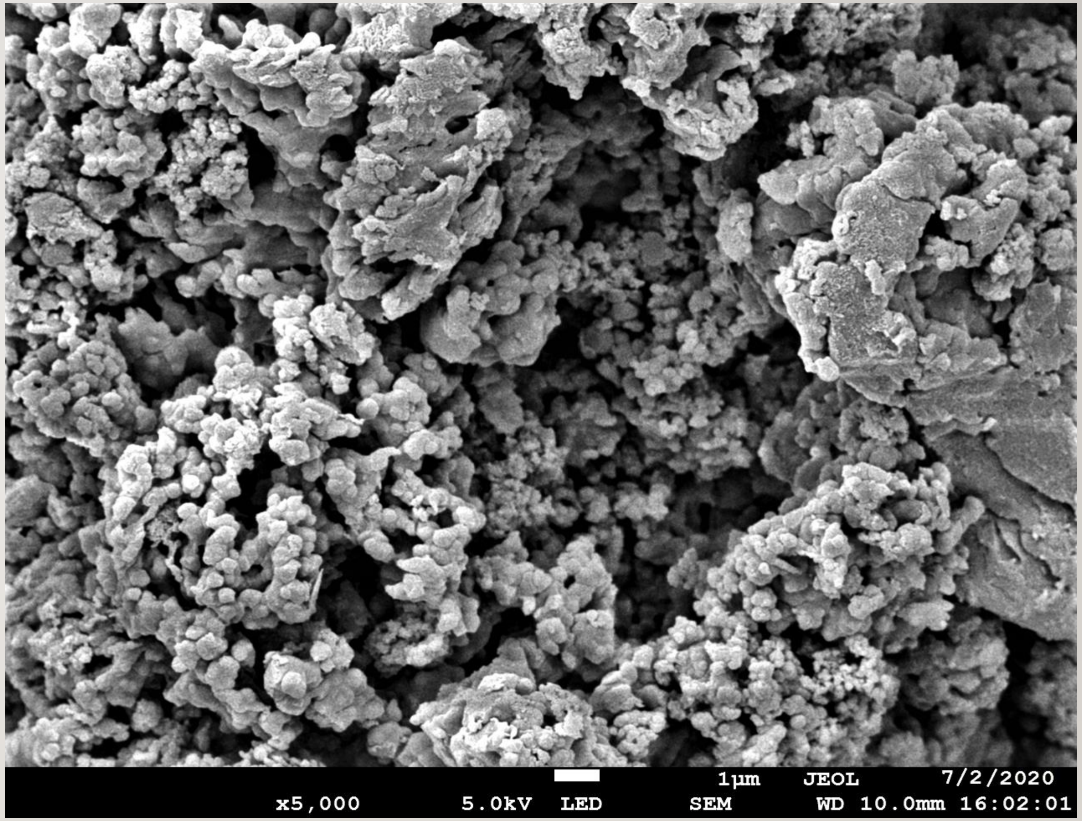


Poly(acrylonitrile)
Magnification: 5000X

FE-SEM Analysis



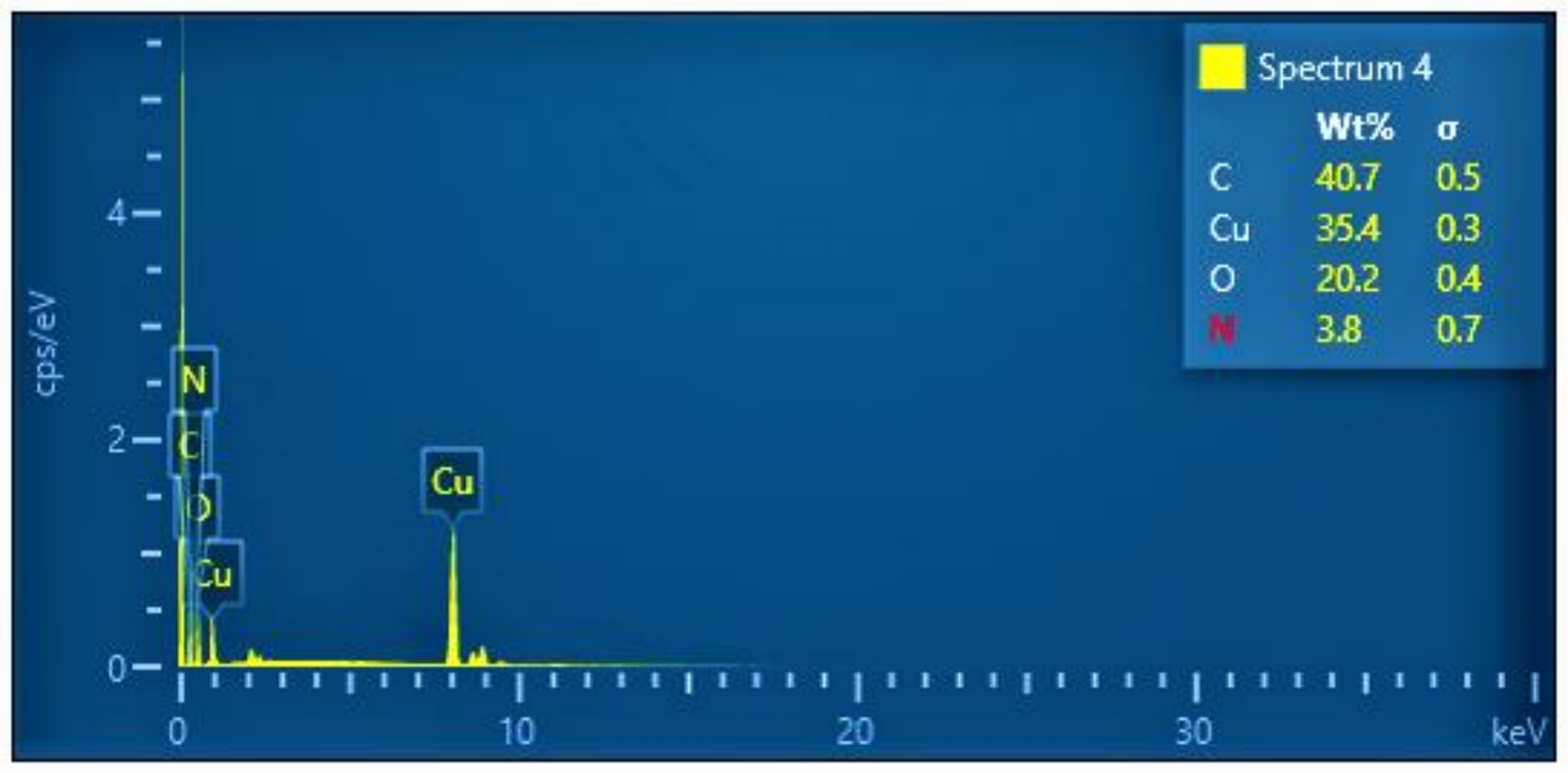
Poly(amidoxime)



Cu(II)@PAM

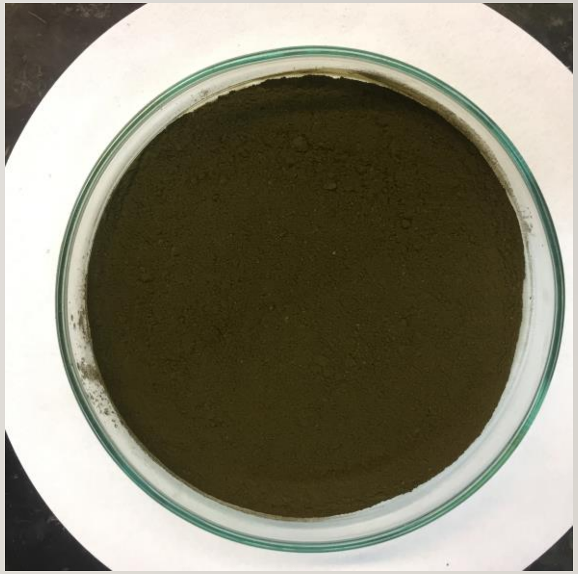
Magnification: 5000X

Energy Dispersive X-ray Diffraction (EDX Analysis)

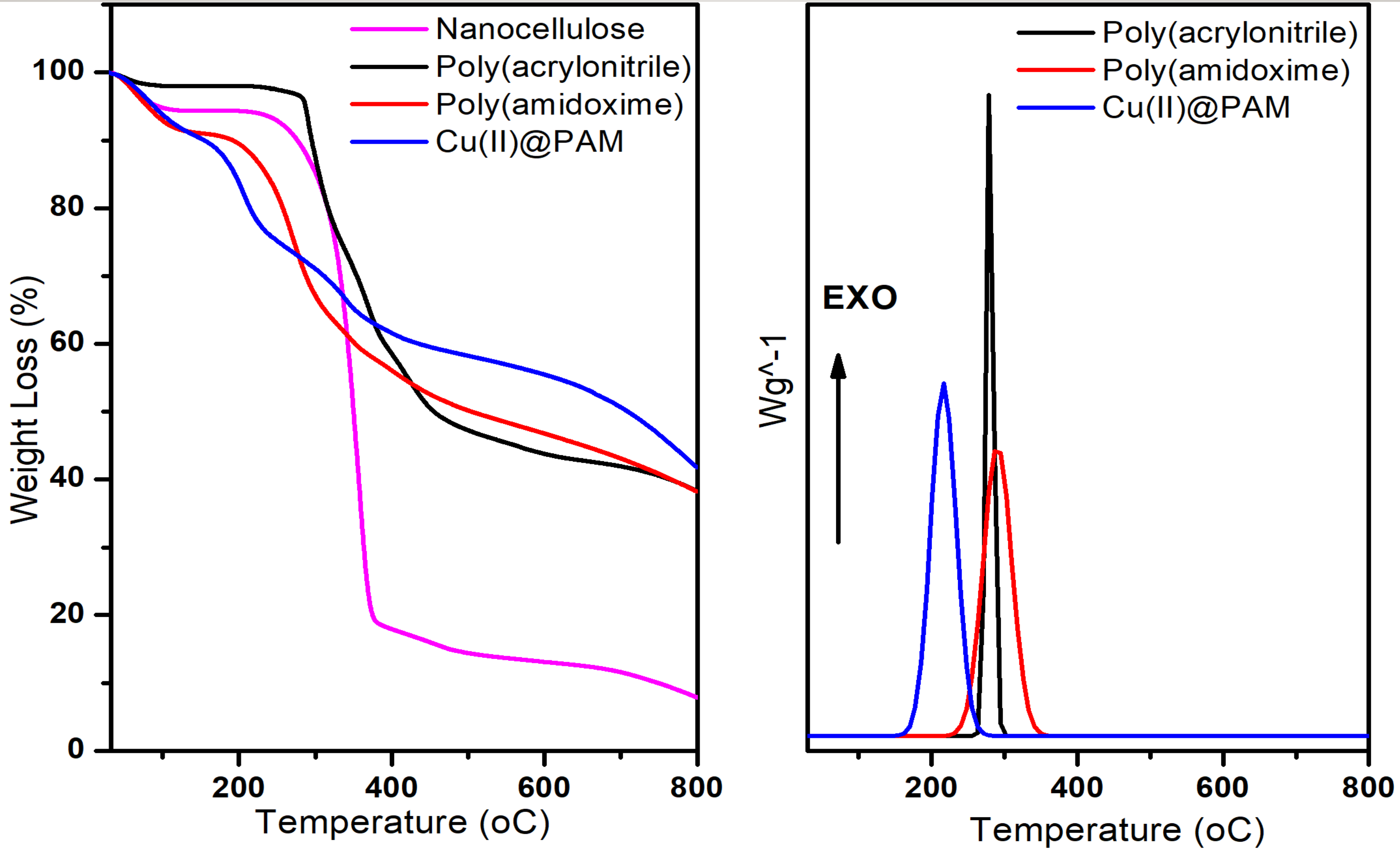


Cu(II)@PAM

Copper = 35.4%
Carbon = 40.7%
Oxygen = 20.2%
Nitrogen= 3.8%

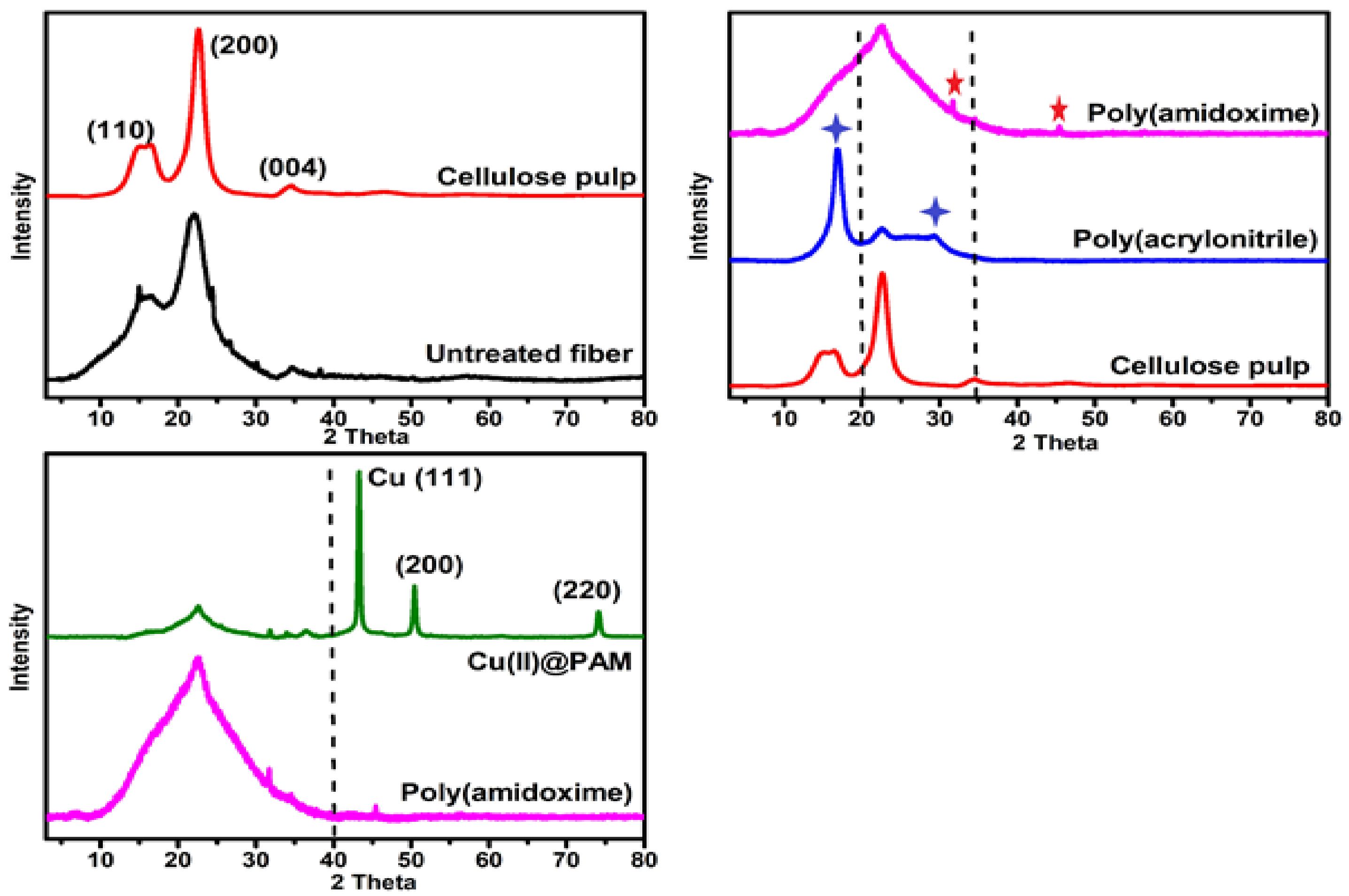


TGA & DSC



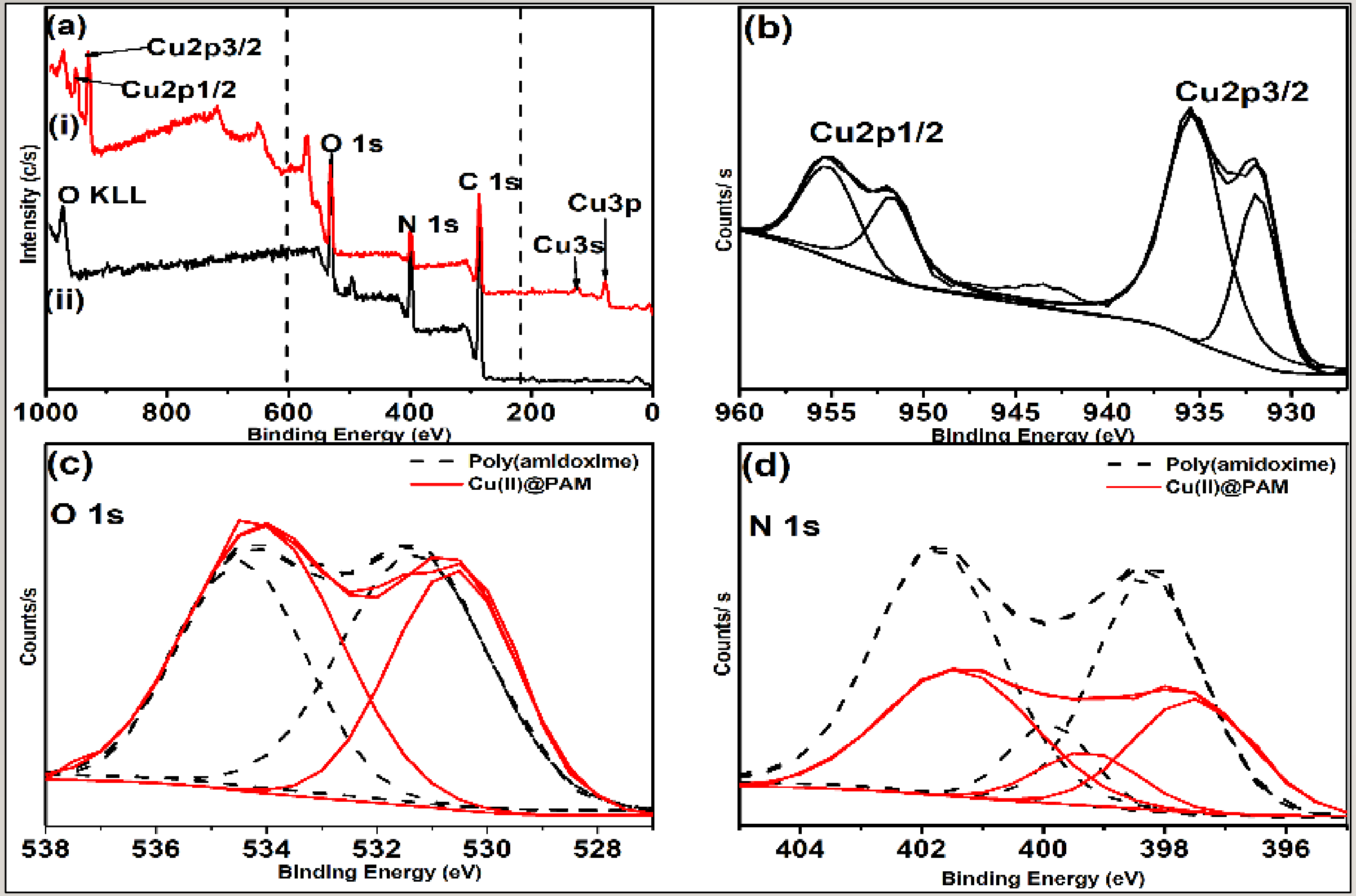
Nanocellulose
Poly(acrylonitrile)
Poly(amidoxime)
Cu(II)@PAM
100
80
60
40
20
0
200
400
600
800
Weight Loss (%)
Temperature (oC)
Poly(acrylonitrile)
Poly(amidoxime)
Cu(II)@PAM
EXO
Wg^-1
200
400
600
800
Temperature (oC)

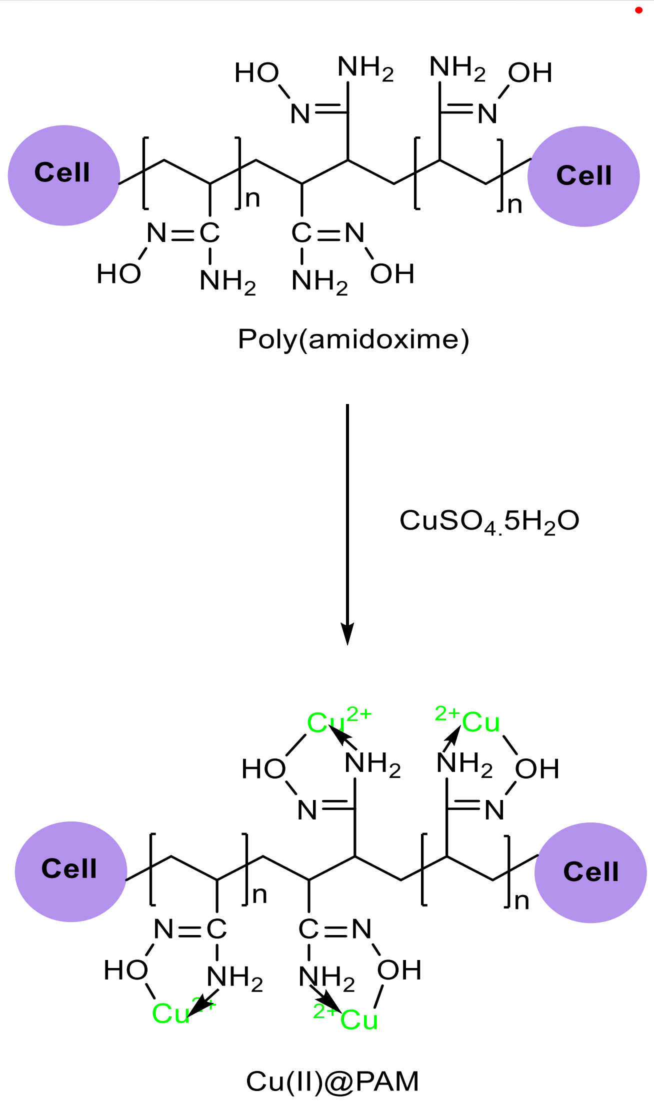
XRD RESULT



(200)
(110)
(004)
Cellulose pulp
Untreated fiber
Intensity
10 20 30 40 50 60 70 80
2 Theta
Poly(amidoxime)
Poly(acrylonitrile)
Cellulose pulp
Intensity
10 20 30 40 50 60 70 80
2 Theta
Cu (111)
(200)
(220)
Cu(II)@PAM
Poly(amidoxime)
Intensity
10 20 30 40 50 60 70 80
2 Theta

XPS ANALYSIS



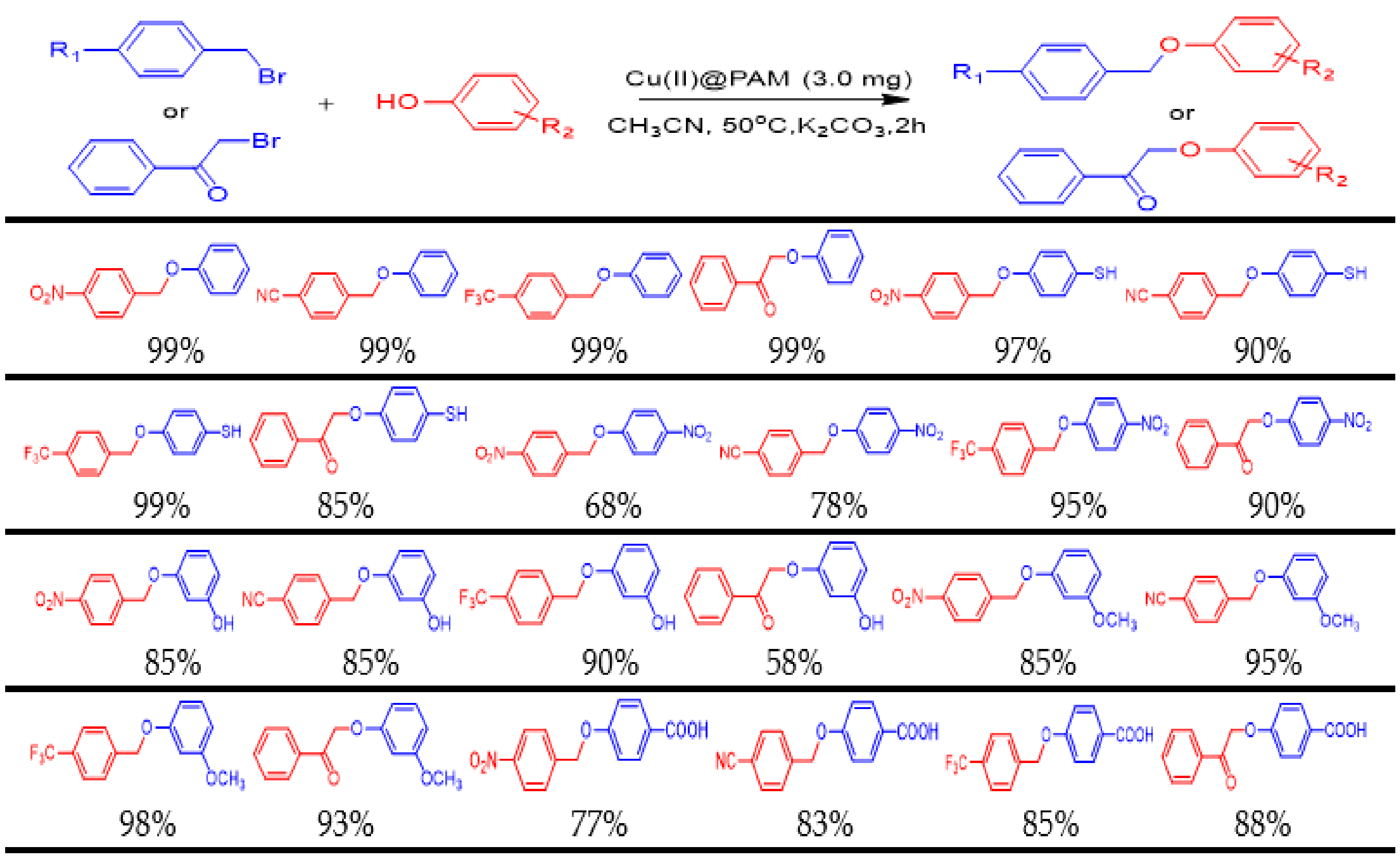


Optimization Of Ullmann Reaction

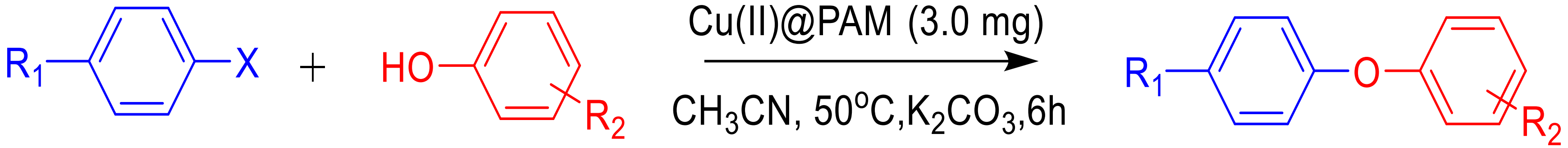
Entry	Cu(II)@PAM (mg)	Temperature (℃)	Time (h)	Yield (%)
1	15	80	8	98
2	5	50	8	99
3	3	50	2	99
4	1.5	50	2	89

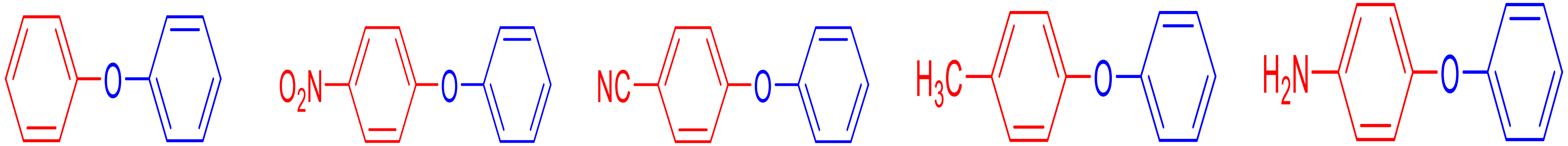
- Conditions: 4-nitrobenzyl bromide (1 mmol), phenol (1.2 mmol), a catalytic amount of complex copper and 3 mol equiv. of K_2CO_3 in 5 mL of acetonitrile.

REACTION



- Conditions: Benzyl halide (1 mmol), phenol (1.2 mmol), ±3.0 mg of Cu(II)@PAM and 3 mol equiv. of K_2CO_3 in 5 mL of acetonitrile. All the compound was determined by GC-MS and NMR.





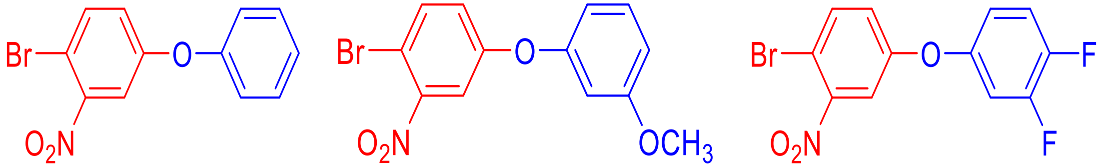
I= 60%; Br= 55%; Cl= 20%

I= 77%; Br= 69%; Cl= 51%

I= 90%; Br=82%; Cl= 60%

I= 65%; Br= 50%; Cl= 20%

I= 50%; Br= 45%; Cl= 15

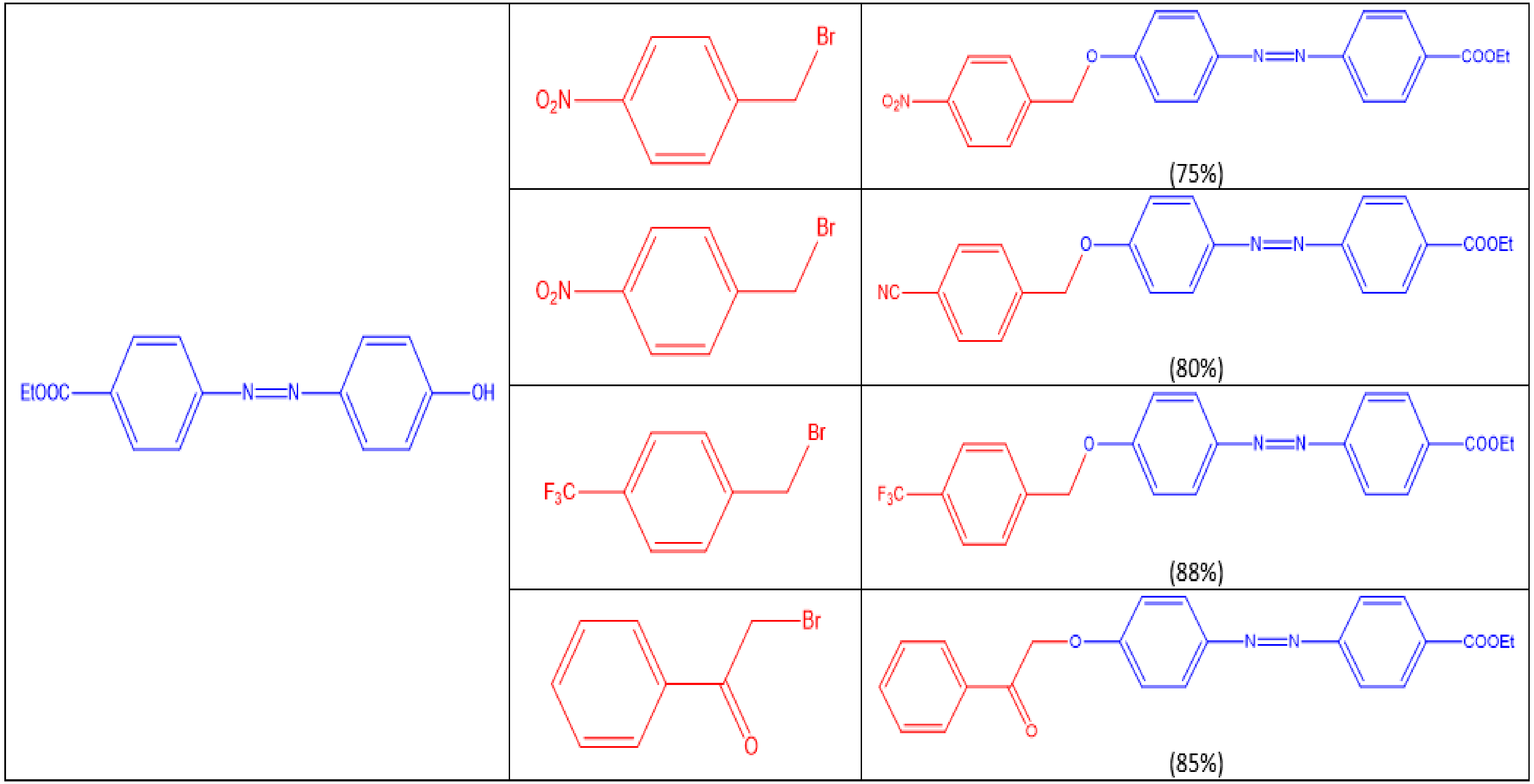


Br= 67%

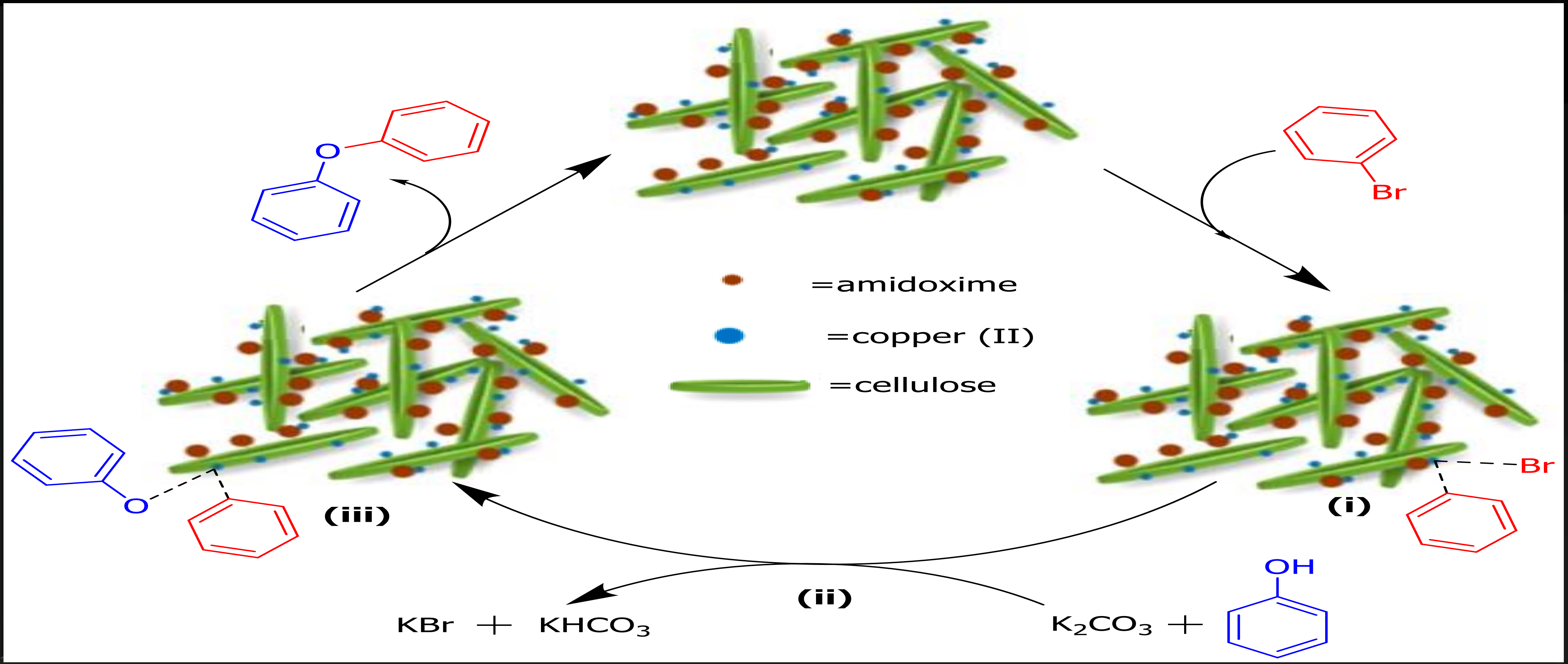
Br= 75%

Br= 65%

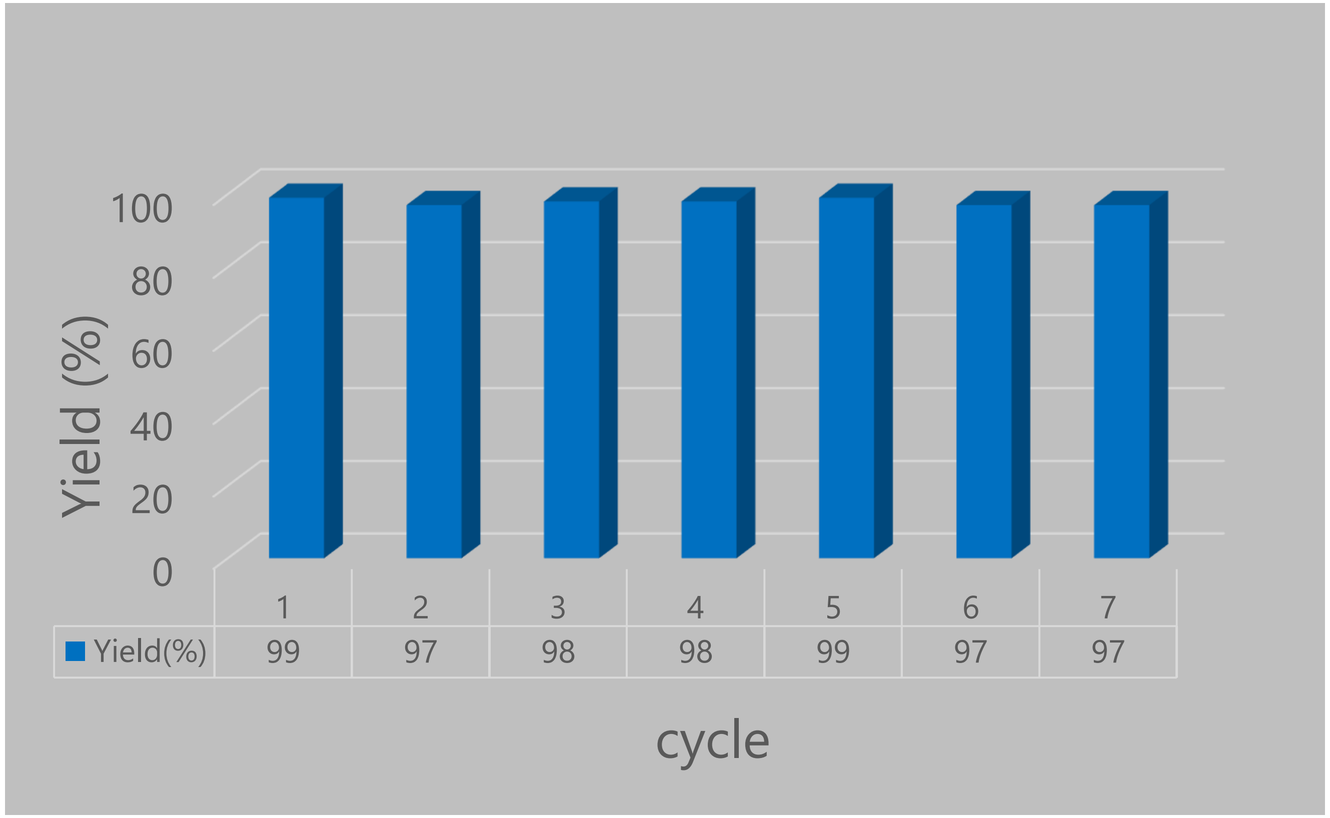
- Conditions: Benzyl halide (1 mmol), phenol (1.2 mmol), ±3.0 mg of Cu(II)@PAM and 3 mol equiv. of K_2CO_3 in 5 mL of acetonitrile. All the compound was determined by using GC-MS and NMR.


EtOOC
N=N
OH
O2N
Br
O2N
Br
F3C
Br
Br
O
O2N
O
N=N
COOEt
(75%)
NC
O
N=N
COOEt
(80%)
F3C
O
N=N
COOEt
(88%)
O
O
N=N
COOEt
(85%)

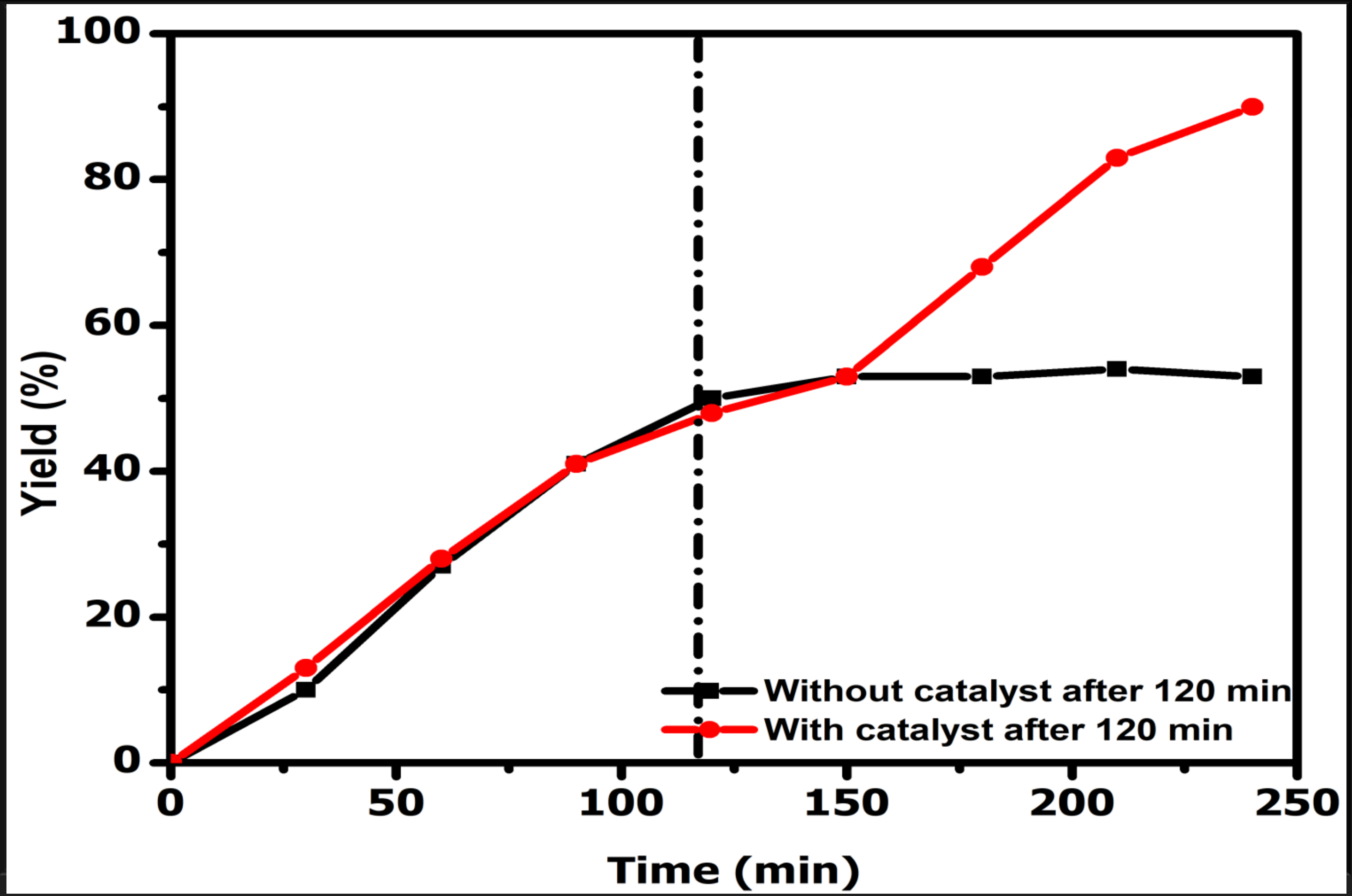
Mechanism for Ullmann Reaction



REUSABILITY



LEACHING STUDY



CONCLUSION

Successful synthesis high active, stable and safe copper catalyst for Ullmann etherification reaction.

The synthesized copper catalyst can afford the Ullmann etherification in good to high yield of product.

FUTURE WORK

- Test the synthesize catalyst in other cross-coupling reaction (C-C, C-N, C-S, etc.)
- Utilize the Cu(II)NPs@PAM in total synthesis of natural product, medicine compound.

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Thank
you