# Khaya Cellulose Supported Copper Nanoparticles for Chemo Selective Aza-Michael Reactions

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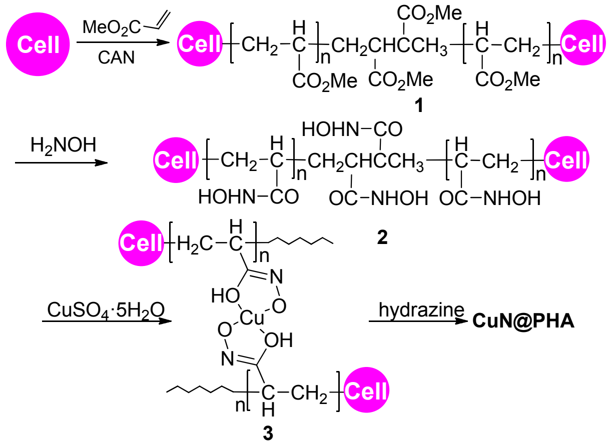
***Abstract*—**We prepared a highly active Khaya cellulose supported poly(hydroxamic acid) copper nanoparticles by the surface modification of Khaya cellulose through graft co-polymerization and subsequently amidoximation. The Cu-nanoparticle (0.05 mol% to 50 mol ppm) was selectively promoted Aza-Michael reaction of aliphatic amines to give the corresponding alkylated products at room temperature in methanol. The supported nanoparticle was easy to recover and reused seven times without significance loss of its activity.

***Keywords*—**Aza-Michael, Copper, Cellulose, Nanoparticles, Poly(hydroxamic acid)

**Introduction:** The conjugate Michael addition reaction has drawn high attention in the synthesis of biological active natural products as well as the synthetic precursors of antibiotics, pharmaceutical intermediates, β-amino alcohols. In most of the Michael reactions homogeneous Lewis acids, such as $AlCl_3$, $PtCl_4{\cdot}5H_2O$, $InCl_3$/TMSCl, $Bi(NO)_3$ have been used. The dificulty of purification of the product in homogeneous system, thus heterogeneous metal catalysts have gained a specific attention and a plenty of heterogeneous metal catalysts such as MOF-99, polystyrene supported CuI-imidazole complex, silica sulphuric acid, nanocrystalline copper(II) oxide have been used. From the viewpoint of economic and sustainable protocols involved in the development of green processes, scientists are looking into low cost environmental friendly and renewable resources as well as sustainable processes. In this respect, cellulose could be the most satisfactory material due to some advantages like large abundance in nature, low-density, bio-renewability, universal availability, low cost, moreover cellulose backbone can be effectively chemically modified and suitable chelating ligands can be incorporated. In this work, we report synthesis of khaya cellulose supported poly(hydroxamic acid) copper nanoparticles (**CuN@PHA**) and efficiently applied to Michael addition reaction of aliphatic amines with α,β-unsaturated carbonyl/cyano compounds in methanol at room temperature. **CuN@PHA** catalyst showed high catalytic activity (50 mol ppm) as well as regioselectivity with easy recyclability and reusability.

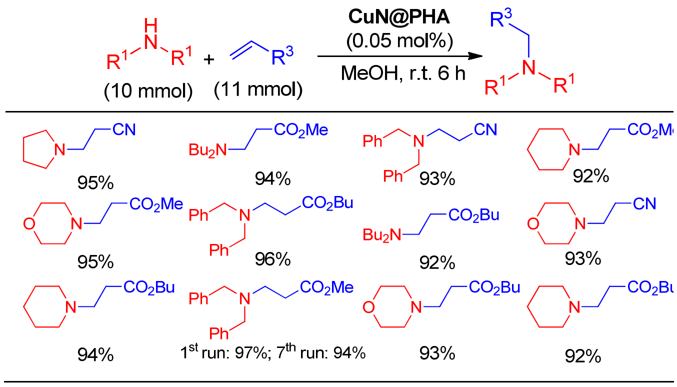
**Preparation of poly(hydroxamic acid) copper complex 3:** To a stirred suspension of **2** in water was added an aqueous solution of $CuSO_4{\cdot}5H_2O$ at room temperature. The blue $CuSO_4$ was immediately turned into green colour copper complex and the mixture was stirred for 2 h at room temperature. The poly(hydroxamic acid) copper complex **3** was filtered, washed several times with excess amount of ammonium chloride, water, MeOH and dried at 60 °C for 2 h. The ICP-AES analysis showed that 0.5 mmol/g of copper was adsorbed by the poly(hydroxamic acid) ligand (Scheme 1).

**Preparation of poly(hydroxamic acid) CuN@PHA:** Poly(hydroxamic acid) copper complex **3** was dispersed in deionized water and then hydrazine hydrate was added. The resulting dark brown color **CuN@PHA** materials (Ø = 6.4 ± 3 nm) were collected by filtration, washed with methanol, and dried under vacuum at 100 °C for 3 h and stored under nitrogen atmosphere.




**Scheme 1.** Preparation of cellulose supported **CuN@PHA**

**Table 1**. Aza-Micheal reaction




**Conclusion**

We have successfully prepared highly active **CuN@PHA** and applied to the Michael addition reaction which selectively provide alkylated products in up to 97% yield and could be used seven times without significance loss of activity.

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