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# Journal Name

# COMMUNICATION

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# solvent-free synthesis of dipyrromethanes and aromatic amines Sengan Megarajan, Khan Behlol Ayaz Ahmed, Rajamani Rajmohan, Pothiappan Vairaprakash\*,

Easily accessible and recyclable copper nanoparticle catalyst for

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A facile method to prepare reusable copper nanocatalyst was reported. Transmission electron micrograph showed that the CuNPs are spherical in nature and reside in the nanoscopic template of the capping agent, guar gum. Powder x-ray diffraction studies support the crystalline nature of the CuNPs. The catalytic efficiency and recyclability of synthesized CuNPs were demonstrated through the synthesis of dipyrromethanes (DPMs) and aromatic amines. Various DPMs are obtained in very good yield under solvent-free condition and nitroarenes are converted to corresponding amino compounds within 10 min, as evidenced by the kinetic study.

Veerappan Anbazhagan\*

## Introduction

The physiochemical nature of a material gets modified when translated into nanodimension and offer improved physical, chemical and biological activity. For example, gold is considered as an inert metal in its bulk form, at the same time nanogold exhibits excellent catalytic activity in several organic transformations.<sup>1</sup> Nanocatalysts are highly advantages than regular catalyst because it provides increased catalytic surface to volume ratio thereby minimize the catalytic loading. Of late, the catalytic activities of copper nanoparticles (CuNPs) are explored in Ullman reactions, Heck reactions, Sonogashira reactions,<sup>1</sup> dipolar cycloaddition, Huisgen [3+2]-cycloaddition and so forth.<sup>2</sup> Economical and eco-friendly access and reusablilty facilitates the materials to be easily adaptable in industry. Herein, we report an easy method to synthesis CuNPs using biopolymer, guar gum as capping agent. The choice of guar gum was based on their benign nature and easy to obtain from the renewable resources.<sup>3</sup> The synthesized CuNPs were characterized by transmission electron microscopy, powder Xray diffraction and energy dispersive X-ray spectroscopy. The effectiveness and reusability of the catalyst were

molecules such as BODIPY dyes,<sup>4</sup> porphyrins,<sup>5</sup> chlorins,<sup>6</sup>  $corroles^7$  etc for photonics/electronics applications including (i) photo-induced electron transfer,<sup>8</sup> (ii) molecular switches,<sup>9</sup> (iii) spin switching,<sup>10</sup> (iv) triplet sensitized conjugated polymers,<sup>11</sup> (v) dyes,<sup>12</sup> (vi) bio-imaging,<sup>13</sup> (vii) photodynamic therapy,<sup>14</sup> (viii) electrocatalytic oxygen reduction,<sup>15</sup> (ix) sensors,<sup>16</sup> (x) fluorescent probe<sup>17</sup> etc. Traditionally, DPMs are synthesized in a reaction of pyrrole with aldehydes, catalyzed by Lewis or Brønsted acids including HCl, CF<sub>3</sub>COOH, InCl<sub>3</sub>, I<sub>2</sub>/AcOH, CAN, BF<sub>3</sub>-etherate, TsOH and cation exchange resins.<sup>18</sup> These reactions hardly stop at dipyrromethane stage and proceeds to oligomeric/polymeric compounds, necessitating tedious purification processes and also resulting in low yield. To avoid the formation of polymeric byproducts and selectively stop the reaction at dipyrromethane stage, several modifications has been introduced in the synthesis as (i) employing 2,4substituted pyrrole,<sup>19</sup> (ii) solventless synthesis employing pyrrole as reagent and solvent.<sup>20,21</sup> The former case is only applicable to the synthesis of BODIPY dyes, as substituted DPMs were obtained and these substituted DPMs cannot be converted into tetra-pyrrolic macrocycles. In the later case, use of the excess pyrrole limits the versatility of this methodology. In these reactions, the acidity of the catalyst has a significant impact on reaction outcome and selectivity.<sup>21</sup> Among the catalysts reported for DPM synthesis, promising results were obtained in reaction employing more expensive  $InCl_3$  catalyst and 100 equivalent of pyrrole.<sup>21</sup> The milder acidity of  $InCl_3$ resulted in the selective formation of DPM.<sup>21</sup> Recently, we have disclosed the synthesis of dipyrromethane analogs from fructose derived HMF using celite supported InCl<sub>3</sub> as a recyclable catalyst.<sup>22</sup> Herein we are reporting simple, easily accessible and recyclable copper nanoparticles for DPM synthesis. These CuNPs are providing more selectivity towards DPM synthesis. In addition to DPM synthesis, our catalyst system is found to be more efficient in reducing aromatic nitro compound to the corresponding amines.

demonstrated through the synthesis of dipyrromethanes and aromatic amines. Dipyrromethanes (DPMs) are versatile key

intermediates in constructing various functional organic

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The reduction of aromatic nitro compounds to the corresponding amine is an active area of research; as the amines and their derivatives are important starting material for the synthesis of chemicals including dyes, pharmaceuticals, and anticorrosive lubricants.<sup>22</sup> In light of the commercial importance, many methods are developed for the production aromatic amines which include catalytic hydrogenation of aromatic nitro compound with hydrogen gas in the presence of Pd, Pt, Ni and Rh metal.<sup>23</sup> In recent years, instead of H<sub>2</sub> gas, sodium borohydride has been used as a hydrogen source with metal nanoparticles as the catalyst.<sup>24</sup> Among the available methods for the synthesis of aromatic amines, nitroarene reduction using NaBH<sub>4</sub>/metal nanoparticles is considered trusted model reaction to explore the catalytic activity of nanoparticles.<sup>25</sup> In this work, we exploited the chromophoric nature of the aromatic NO<sub>2</sub> group and determined the rate of the reduction using absorbance spectroscopy and the results are discussed.

## **Results and Discussion**

## Synthesis of copper nanoparticles

The reusable copper nanocatalyst (CuNPs) was synthesized by bottom-up approach using the precursor copper sulfate and the biopolymer guar gum and hydrazine as capping and reducing agent, respectively. The aqueous CuNPs was dehydrated by heating at 100 °C. The colloidal reddish brown solution turns to brownish black precipitate confirms the removal of water (Fig. 1). The obtained precipitate is insoluble in water indicating that the average strength of biopolymerbiopolymer interaction is significantly increased than the water-polymer interaction.



Fig. 1 Photograph representing the preparation of reusable CuNPs catalyst.

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Energy dispersive X-ray spectroscopy (EDS) confirms the presence of copper in our preparation (Fig. 2A). The noticeable amount of oxygen in EDS can be attributed to the oxygen rich capping agent. X-ray diffraction showed diffraction pattern peaks at  $43.32^{\circ}$ ,  $50.39^{\circ}$  and  $74.08^{\circ}$ , which corresponds to the crystal planes (111), (200) and (220), respectively (Fig. 2B). The absence of diffraction peaks corresponds to copper oxides (CuO, Cu<sub>2</sub>O), suggested that the prepared NPs is composed of metallic copper. Transmission electron microscopy (TEM) revealed that the particles are spherical nature with the size range from 100 to 300 nm. TEM images clearly showed that CuNPs are residing in the nanoscopic template of the capping agent (Fig. 3). The observed ring pattern in the selected area diffraction confirms the crystalline nature of the prepared CuNPs.

## Synthesis of dipyrromethanes

The catalytic behavior of the CuNPs was explored in the synthesis of dipyrromethanes and aromatic amines. In the synthesis of DPM, a mixture containing anisaldehyde and pyrrole (10 equiv) was treated with a suspension of CuNPs in water at 30 °C. Under this condition, aldehyde was consumed completely in 8 h. Analysis of reaction mixture showed the formation of more byproducts and DPM was obtained in very low yield (~5%, Table 1, entry 1). When the reaction was repeated under solventless condition using 10 equiv of pyrrole, complete consumption of aldehyde was observed after 15 h with very good selectivity towards product and the corresponding DPM was obtained in 63% isolated yield (Table 1, entry 2). Formation of DPM in trace quantities in an experiment carried out without CuNPs evidently indicated the role of CuNPs as a catalyst in DPM synthesis (Table 1, entry 3). The catalytic behavior of CuNPs is attributed to the increase in nucleophilicity of pyrrole on adsorption over CuNPs.



**Fig. 2** (A) EDS spectra and (B) Powder x-ray diffraction pattern of CuNPs. The sharp peaks (blue star) can be attributed to the capping agent guar gum, which is known for crystalline nature.

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Fig. 3 Transmission electron micrograph of CuNPs at scale bar (A) 500 nm and (B) 200 nm. Inset corresponds to the SAED pattern.

On adsorption over CuNPs, the nucleophilicity of pyrrole is increased and reacted with electrophilic carbon of aldehyde. The resulting intermediate reacts with another pyrrole adsorbed on CuNPs to yield dipyrromethane after removal of the water molecule. The reactivities of other aryl aldehydes were tested at this temperature (Table 1, entries 4 - 8). Electron withdrawing substituent present in aldehyde facilitated the better conversion to DPM. Among various aldehydes, the better conversion was obtained with 3nitrobenzaldehyde and the product was obtained in 77% yield (Table 1, entry 8). In all experiments, the catalyst was recovered by diluting reaction mixture with dichloromethane (5 mL), followed by centrifugation for 15 min and catalyst was recovered as a residual fraction. The recovered catalyst showed similar catalytic activity without any deterioration in yields up to 4 cycles (Table 1, entries 8-11). In an experiment using 2,4-dimethylpyrrole, 3-nitrobenzaldehyde was consumed with in 30 mins and the corresponding DPMs were obtained in 75% yields (Table 1, entry 12). Use of 2,4-dimethylpyrrole in stoichiometric amount (3 equiv) did not deteriorate the product yield (Table 1, entry 13). In the copper nanoparticle catalyzed reaction of pyrrole with aromatic and aliphatic ketones, the corresponding dipyrromethanes were not

obtained even after 24 hrs stirring at room temperature (Table 1, entries 14 and 15).

Table 1 Solvent free synthesis of dipyrromethanes <sup>a</sup>					
Entry	Reactant	Product	Time (h)	Yield (%)	
1 <sup>b</sup>	OMe ↓	OMe	8	5	
2	Q	$\square$	15	63	
3°	СНО		24	Trace	
4	СНО	NH HN	15	65	
5	СНО		15	71	
6	CHO F	F NH HN	15	63	
7	NO <sub>2</sub> CHO		12	75	
8			12	77	
9 <sup>d</sup>	NO <sub>2</sub>	NO <sub>2</sub>	12	73	
10 <sup>e</sup>	СНО		12	71	
11 <sup>f</sup>		≫́йн нй 🗸	12	74	
12 <sup>g</sup>	NO <sub>2</sub>	NO <sub>2</sub>	0.5	75	
13 <sup>h</sup>	СНО	NH HN	0.5	72	
14	Acetophenone		24		
15	Cyclohexanone		24		

<sup>a</sup>A mixture of aldehyde (0.5 mmol), pyrrole (5 mmol, 10 equiv.) and copper nanoparticle (5 mg) was stirred at 30 °C. After the completion of reaction, reaction mixture was diluted with dichloromethane (5 mL), centrifuged and the catalyst was recovered as residual fraction. The supernatant was purified by column chromatography. <sup>b</sup>Reaction was carried out in water. <sup>c</sup>Reaction without CuNPs. <sup>d</sup>Recycled catalyst (II cycle). <sup>e</sup>Recycled catalyst (III cycle). <sup>f</sup>Recycled catalyst (IV cycle). <sup>g</sup>A mixture of 3-nitrobenzaldehyde (0.5 mmol), 2,4-dimethylpyrrole (5 mmol, 10 equiv.) and copper nanoparticle (5 mg) was stirred at 30 °C. <sup>h</sup>Experiment was carried out with 3 equiv of 2,4dimethylpyrrole.



Fig. 4 (A) UV-Vis spectra for the reduction of nitrophenol to aminophenol in the presence of CuNPs catalyst and NaBH<sub>4</sub> in water. 100  $\mu$ M nitrophenol, 1 mg CuNPs, 20 mg NaBH<sub>4</sub> (B) time-dependent absorption of nitrophenolate ion at 400 nm, with an induction period of t<sub>0</sub>. The line corresponds to the linear section, from which *k* was determined.

#### Nitroarenes reduction kinetics

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In the synthesis of aromatic amines, nitroarenes are allowed to react with NaBH<sub>4</sub> in the presence of CuNPs at room temperature. Under this condition, nitroarenes were converted to corresponding amines within 10 min. Taking advantage of the chromophoric nature of the nitroaromatics, the reaction was followed by UV-Vis spectroscopy. During the subsequent addition of CuNPs, the absorbance peak at 400 nm disappears with an appearance of a new peak at 300 nm, indicating the conversion of nitrophenol to aminophenol. In a typical reaction of 4-nitrophenol, the addition of NaBH<sub>4</sub> induces a bathochromic shift from 317 nm to 400 nm due to the formation of nitrophenolate ion (Fig. 4).

Interestingly, neither NaBH<sub>4</sub> nor CuNPs alone reduces the nitroaromatics, suggesting that the CuNPs and NaBH<sub>4</sub> serve as a catalyst and reducing agent, respectively and both are required for this chemical transformation. The change in the absorption peak during the progress of the reduction reaction allowed us to determine the kinetics of the reduction process the reduction process using the absorption spectroscopy. The kinetic experiment was initiated by adding NaBH<sub>4</sub> and CuNPs to the nitrophenol aqueous solution and followed the time-dependent change in the absorbance at 400 nm. Initially, an induction time ( $t_0$ ) was observed, which is typical for a heterogeneous catalytic process and commonly attributed to activation or restructuring of the metal surfaces by the substrate before initiating the reaction.<sup>26</sup>

After t<sub>0</sub>, the reduction reaction starts as evidenced by the decrease in the absorbance at 400 nm and stops changing after all the substrate converted to the product (Fig. 4A). In this catalytic reaction, the concentration of NaBH<sub>4</sub> was much higher than that of the substrate. Therefore, the reduction kinetics can be described by *pseudo* first-order rate law:  $ln(A_t/A_0) = -kt$ , where k is the apparent first-order rate

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constant, t is the reaction time. At and Ao are the absorbance of the substrate at time t and 0, respectively. Fig. 5B shows the plot of  $ln(A_t/A_0)$  versus reaction time for the reduction of nitrophenol. The rate constant, k was obtained directly from the slope of the linear part of the kinetic trace and presented in Table 2. Nitroarene reduction was preceded through IV steps as described in Fig. 5.<sup>26</sup> In the first step, hydrogen released from NaBH<sub>4</sub> gets adsorbed on nanoparticle surfaces followed by adsorption of nitroarenes on nanoparticle surfaces through the nitro group (Step II). Then, nitroarenes on the nanoparticle surfaces were reduced by adsorbed hydrogen to aromatic amines. The scope of the catalytic system was tested with several other nitroaromatic compounds (Table 2). Formation of amine is confirmed by <sup>1</sup>H NMR spectroscopic analysis of resulting crude mixture (Table 2, entries 2 & 8; Fig S20 & S21).

Table 2 Catalytic activity of CuNPs for nitroaromatic reduction

Entry	Reactant	Product	Induction time (s)	<i>k</i> (s <sup>-1</sup> )
1.	NO <sub>2</sub> OH	NH <sub>2</sub> OH	40.2	0.00267 <sup>b</sup> 0.00198 <sup>c</sup> 0.00288 <sup>d</sup> 0.00258 <sup>e</sup> 0.00199 <sup>f</sup>
2.		NH <sub>2</sub>	70.2	0.00343
3.	NO <sub>2</sub> NH <sub>2</sub>	NH <sub>2</sub>	79.8	0.00077
4.	NO <sub>2</sub> NH <sub>2</sub>	NH <sub>2</sub> NH <sub>2</sub>	110.4	0.00211
5.	NO <sub>2</sub> NH <sub>2</sub> CH <sub>2</sub>	NH <sub>2</sub> NH <sub>2</sub> CH <sub>3</sub>	110.4	0.00237
6.	NO <sub>2</sub> NHCOCH <sub>3</sub>	NH <sub>2</sub> NHCOCH <sub>3</sub>	170.4	0.00659
7.		H <sub>2</sub> N H <sub>2</sub> N H <sub>2</sub> N H <sub>2</sub> N H <sub>2</sub> N H <sub>2</sub>	110.4	0.00236
8 <sup>g</sup>		NH <sub>2</sub>		
<u>.</u>	ĊO₂Me	ĊO₂Me		

<sup>a</sup>NaBH<sub>4</sub> (20 mg) and copper nanoparticle (1 mg) was added to 3 mL of aqueous solution/suspension of nitrocompound (0.1 mmol) and followed the absorption spectra changes with respect to time. Kinetic trace was fitted with pseudo first order equation and k value is reported. <sup>b</sup>Using fresh catalyst. <sup>c</sup>Using recycled catalyst (II Cycle). <sup>d</sup>Using recycled catalyst (III Cycle). <sup>e</sup>Using recycled catalyst (IV cycle). <sup>f</sup>Using recycled catalyst (V cycle). <sup>g</sup>No appreciable change in absorbance spectrum on nitro-reduction, hence monitored by TLC analysis and confirmed by <sup>1</sup>H NMR spectroscopy.



Fig. 5 Nitro-reduction over CuNPs using NaBH<sub>4</sub>

In all experiments, the catalyst was recovered by centrifugation and the residue was subjected to acetone wash prior to use in the next cycle. The reusability of the catalyst was studied with nitrophenol system. The recovered catalyst efficiently converted nitrophenol to aminophenol upto five cycles as evidenced by the similar rate constant  $(10^{-3} s^{-1})$ . The XRD and TEM analysis of the recovered catalyst after 5<sup>th</sup> cycle affirmed that there is not a considerable change in the morphology of the catalyst (Figure S18). As noted from Table 2, irrespective of the substituent, all the tested nitro-aromatic compounds showed a rate constant in the order of  $10^{-3}$  s<sup>-1</sup> which is consistent with that of substrate-supported metallic nanoparticles catalyzed reactions reported in the literature.<sup>27</sup> The difference in the induction time observed for the different substrate can be attributed to the steric hindrance, which may delay the activation or restructuring of the substrate on the metal surface. Nevertheless, the procedure described here is simple to prepare amino compounds from nitroarenes in the shorter time. With our recyclable and easily accesible copper catalyst system, we have obtained rate consant values for nitro reduction reactions as comparable with that of previously reported nano catalystic systems (Table 3).<sup>28</sup>

Table 3. Comparison of Rate Kinetics							
Entry	Nanocatalyst	Rate constant (s <sup>-1</sup> )	Ref (year)				
1	Au NPs	0.00919	27a (2011)				
2	Ag NPs	14.57	27b (2013)				
3	G6-OH(Pd <sub>28</sub> Cu <sub>28</sub> )DENs	0.12	27c (2013)				
4	Ag NPs	0.033	27d (2014)				
5	Au NPs	4.35	27e (2016)				
6	Ag NPs	0.00212	27f (2016)				
7	Cu NPs	0.00267	this study				

#### Conclusions

In summary, we have developed an easy access to dry copper nanoparticles with retained morphology of solution state. The isolated nanoparticle has been tested in the synthesis of dipyrromethanes and aromatic amines. In the synthesis of DPMs, nucleophilicity of pyrrole is enhanced on adsorption over the CuNps and reacted at the electrophilic site of aldehyde. The corresponding DPMs were obtained in very good yields. In addition, the catalytic efficiency of the CuNPs was investigated with well-known 4-nitrophenol reduction kinetics experiment and extended to nitroarenes. Irrespective of the substituent, all the tested nitroarenes get reduced to amino compounds in less than 10 min. The recyclability of CuNps was exhibited evidently in both the synthesis. These findings on easy access to CuNPs and their use in synthesis of dipyrromethane and aromatic amines will provide a boost for the exploration of applications of simply accessed CuNPs in various organic syntheses.

#### Experimental

#### **General information**

<sup>1</sup>H NMR (300 MHz) spectra were recorded on Bruker-300-AVANCE II spectrometer, with chloroform-d as solvent and tetramethylsilane (TMS) as reference ( $\delta = 0$  ppm). The chemical shifts are expressed in  $\delta$  downfield from the signal of internal TMS. All yields reported are of isolated materials judged homogeneous by TLC, and NMR spectroscopy. The size, morphology and crystallinity were characterized by highresolution transmission electron microscopy (HR-TEM) (JEOL-JEM 1011, Japan) with an accelerated voltage of 200 kV. Samples of TEM measurements were prepared by placing a drop of NP solution on the graphite grid and drying it in a vacuum

Preparation of recyclable CuNPs catalyst: About 500 mg of guar gum was suspended into 50 mL of double distilled water. To the aqueous suspension, 85 mg of copper(II) chloride was added slowly under vigorous stirring at room temperature. After the complete solubilization of CuCl<sub>2</sub>, 1 mL of concentrated ammonia solution was added. The color changes from greenish blue to blue due to the formation of copperammonia complex. After 5 min of gentle mixing, 2 mL of hydrazine hydrate was added as a reducing agent. After stirring the solution for 5 min, the reaction was allowed to proceed at room temperature for 3 h without stirring. The formation of copper nanoparticles was easily noticeable due to the change in the color of the solution to wine red - the characteristic color of the copper nanoparticles (CuNPs). As prepared CuNPs was coated on a thin glass plate and dried in the pre-heated hot air oven set at 100  $^{\circ}$ C. After 3 h, the plate was removed and cooled to room temperature and the dried material was collected by simple scratching. The obtained material was grounded well with the help of mortar and pestle and washed three times with absolute ethanol and then dried at 60 °C for 2 h to obtain 310 mg of copper nanocomposite. The amount of metallic copper present in nanocomposite was

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determined by atomic absorption spectroscopy. About 0.28 mg of copper was present in the 5 mg of the nanocomposite. The morphology, size and crystallinity of CuNPs were measured by transmission electron microscope (TEM). Samples for TEM were prepared by placing a drop of NP solution on the graphite grid and drying it in the vacuum. The EDS spectrum of the solution containing CuNPs confirmed the presence of an elemental copper signal without any peaks of impurities. Powder X-ray diffraction (XRD) measurements of CuNPs were done on an XRD-Bruker D8 Advance X-ray diffractometer using monochromatic Cu Kα radiation.

**General procedure for synthesis of dipyrromethane:** A mixture of aldehyde (0.5 mmol), pyrrole (5 mmol, 10 equiv.) and copper nanoparticle (5 mg) was stirred at 30 °C for a stipulated period of time. After the complete consumption of aldehyde, the reaction mixture was diluted with dichloromethane (5 mL), centrifuged and the catalyst was recovered as a residual fraction for reuse. The supernatant was concentrated by rotary evaporation under reduced pressure and the resulting mixture was purified by column chromatography. The product was characterized by <sup>1</sup>H NMR spectral analysis. The NMR data are well in accordance with literature data.

**Hydrogenation of nitroarenes:** Typically, 20 mg of NaBH<sub>4</sub> and 1 mg of CuNPs were added to 3 mL aqueous solutions of nitrocompounds (100  $\mu$ M) aqueous solution and measured the absorbance changes. The change in absorbance was used for kinetic analysis. All experiments were performed in triplicate and the average value is reported. To rule out the possibility of formation of the metal oxide layer and catalytic surface poisoning, the samples were carefully degassed before adding NaBH<sub>4</sub>.

To calculate rate constant, the obtained kinetic trace was analyzed by pseudo first-order rate law: ln(At/A0) = -kt(1)

where k is the apparent first-order rate constant, t is the reaction time. At and AO are the absorbance of substrate at time t and 0, respectively (Fig. 5B). The rate constant, k was obtained directly calculated from the slope of the linear part of the kinetic trace

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