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Volume 40 | Number 1 | January 2016 | Pages 1–846

NJC

New Journal of Chemistry
www.rsc.org/njc

A journal for new directions in chemistry

ISSN 1144-0546

ROYAL SOCIETY OF CHEMISTRY

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PLA-TiO_2 particle brush as novel support for CuNPs: A catalyst for fast sequential reduction and N-arylation of nitroarenes

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Abstract

The present study describes the synthesis and characterization of dispersible copper nanoparticles on PLA-TiO_2 particle brush and its catalytic efficiency in conducting sequential reactions. The prepared CuNPs@ PLA-TiO_2 was characterized by various techniques like SEM, TEM, EDAX, FT-IR, TGA, XRD and UV-Vis spectroscopy. The support controlled the size of nanoparticles between 2-6 nm and prevented their agglomeration during catalysis. Zeta potential of -70.3 mV was measured for the dispersed catalyst which indicated its high stability in solution. The nanoparticles were effectively used for the synthesis of biphenyl amines from nitro arenes by sequentially carrying out reduction and N-arylation in a single pot. Short reaction time of N-arylation and recyclability are the hallmark of developed catalytic system.

Keywords: Copper nanoparticles, PLA-TiO_2 particle brush, Catalytic activity, Secondary aromatic amines, Sequential reduction and N-arylation of nitroarenes, microwave heating

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1. Introduction

Catalysis of various organic transformations in industry is of fundamental importance in order to minimize waste and to avoid toxic chemicals. Usage of nanoparticles in organic synthesis in the past few decades have made noteworthy contributions in this direction. Among transition metals copper was first to be used in coupling reactions as it is essential to all life forms and is generally harmless. But, due to its poor recyclability compared to palladium its application as heterogeneous catalyst decreased. With the advent of nanotechnology and greater understanding of means of particle stabilization, interest in copper as catalyst has increased once again. Copper nanoparticles are being used for various organic reactions. Copper at nano-scale is highly reactive and difficult to stabilize as large number of active sites compared to bulk material make them agglomerate and oxidizes quickly. Thus, stabilizing copper nanoparticles is a challenging area of research.[1-3] Due to high catalytic activity of nanoparticles, heterogenization of nanoparticles by suitable support can enhance sustainability of the resources by facilitating their recovery and reuse.[4-7] The choice of the support material is one of the most important factors affecting physicochemical behavior of the metal nanoparticles.[8] Both, thermal and chemical stability the nanoparticles has been enhanced by stabilizing them onto various inorganic and organic supports. Of late synthesis of inorganic-polymer hybrid material as support for nanoparticles have emerged as an immense research area to investigate structure-property relationship at nanoscale and to obtain material with potential applications in photonics, catalysis, energy, drug delivery etc.[9-13] One such hybrid support is polymer-metal oxide particle brush which offers large surface area for the stabilization of catalysts and encapsulation of drugs.[14-17] This hybrid material can be synthesized by grafting polymers on the surface of inorganic nanoparticles. Literature studies showed that metal oxides such as silica[18], ferrite[19,20],

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TiO_2[21] etc. have been grafted by various polymers for stabilizing them or to achieve some special applications.

In nature most of the reactions occur sequentially, in the same reaction medium. In industry also, one pot reactions that can be carried out by successively adding reactants are very important as they enhance efficiency. In context of sustainability and green synthesis, these protocols are very important as lengthy separation and purification of intermediates can be avoided. These are especially useful when intermediates are sensitive and may decompose. A number of requirements need to be fulfilled to development such protocols. The reactions should occur in a common solvent which require optimization if reactants of different steps have different polarity. In case of heterogeneous catalysis supporting material should be such that reactants with different polarities have accessibility to catalytic sites. With this aim in our mind, we decided to synthesize a dispersible yet filterable nano-catalyst and used it for synthesis of diphenyl amines from nitro amines in a sequential reaction to avoid isolation of intermediate primary amines. A TiO_2-polylactic acid (TiO_2-PLA) particle brush was synthesized and used as support for copper nanoparticles. PLA was chosen as it is derived from bioresources and TiO_2 is a semiconductor which can strongly attach to PLA through co-ordination of surface Ti atoms with free carboxylate group of latter[22]. PLA fibers were grown on TiO_2 surface by a method developed in our lab which involved polycondensation of lactic acid assisted by azeotropic separation of water[23]. The assembly thus synthesized was used to stabilize copper nanoparticles (CuNPs). The prepared CuNPs@PLA-TiO_2 catalyst was characterized by various instrumental techniques viz. UV-visible spectroscopy, TEM-EDAX, SEM, XRD, FT-IR, TGA and AAS etc. and employed to study reduction of nitro arenes and N-arylation of aromatic amines. All the

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reaction parameters for the two reactions were optimized individually, prior to setting up a one pot sequential reaction for the direct synthesis of secondary amines from nitro amines.

2. Experimental

2.1. Materials and instruments

Chemicals used were of the analytical grade or of the highest purity available. Copper nitrate, aryl halides, aryl boronic acid and aryl amines were purchased from Aldrich or Merck. Ethyl acetate, methanol, $NaBH_4$ and K_2CO_3 were purchased from Finar Chemicals and hydrazine hydrate was purchased from Ranbaxy Laboratories Ltd. Water used in all experiments was purified by Millipore-Q system. Freshly prepared 3:1 HCl/HNO_3 (aqua regia) was used to clean all glassware thoroughly cleaned before use.

UV–Visible absorption spectra were acquired on a Jasco V-570 UV–visible spectrophotometer. JEOL JEM 2100 instrument and were used for particle size measurement through High resolution transmission electron microscopy (HR-TEM) as well as Energy dispersive atomic X ray analysis (EDAX). A drop of methanol with dispersed catalyst was placed onto a 200 mesh carbon coated copper grid. The water was evaporated and particle size measurement was done. The powder XRD of the catalyst was recorded on Brucker D_2 Phaser using Cu Kα radiation (λ = 1.54184 Å) and a filter of nickel at 30 kV and 10 mA with step size 0.03 and count time 0.1s. Scanning Electron microscopy analysis (SEM) was carried out through JSM 6100 (JEOL) with acceleration voltage range 0.3 to 30 kV and working distance of 6 to 48 mm. Atomic absorption spectroscopy (AAS) measurements were carried out on an Atomic absorption spectrophotometer SL-243 Elico instrument: Voltage 619 V, nebulizer flow 7 ml / min, wavelength 324.8 nm, slit width 0.5 nm, current 5.0 mA, air-acetylene flame. IR spectra were recorded on Bruker FT-IR

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spectrophotometer using KBr pellets. The disc containing 1 mg of sample was scanned within a range of 600 to 3600 cm^{-1}. Zeta potential and particle size measurement were carried out on Malvern Zetasizer Nano Z. ^{1}H NMR spectra were measured in Bruker AV 400 MHz using $CDCl_3$ as solvent and TMS as internal standard. Mass spectra were recorded by injecting the samples in ESI ionizer of Shimadzu LCMS 2010 with single quadruple analyzer.

Synthesis of TiO_2 nanoparticles and TiO_2/Poly lactic acid (PLA) nanocomposites are discussed in Electronic supplementary information (ESI).

2.2. Synthesis of CuNPs@PLA- TiO_2 nanocomposites

Into a 100 ml RBF TiO_2-PLA nanocomposites (1.0 g) was stirred in 20 mL deionized water. A solution of $CuNO_3.3H_2O$ (0.241 g, 1.0 mmol) in 20 ml water was added. After 10 min, reducing agent hydrazine hydrate (0.1 g, 2.0 mmol) was added in one portion. The stirring was continued for 4 h. The resulting colloidal solution was centrifuged and washed with deionized water. The catalyst was re-dispersed in 10 mL water and stored under inert conditions.

2.3. General procedure for reduction of nitroarenes

Into a 25 ml RBF, nitrobenzene (1mmol) was dissolved in a 5 ml (4:1) methanol/water mixture, and 100 mg catalyst (CuNPs@PLA-TiO_2) was added followed by $NaBH_4$ (5 mmol). The reaction mixture was vigorously stirred at room temperature.

2.4. General procedure for N-arylation of nitroarenes

Into a 25 ml RBF, Aryl halide (1mmol), K_2CO_3 (3 mmol) and aryl amine (1.2 mmol) were dissolved in a 5 ml (4:1) methanol/water mixture, catalyst (100 mg CuNPs@PLA-TiO_2) was added. The reaction mixture was heated at reflux temperature for 6 hours.

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2.5. General procedure for Sequential reduction and N-arylation of nitroarenes

2.5.1. Microwave method

Into a 10 ml vial, nitrobenzene (1mmol), 100 mg CuNPs@PLA-TiO_2 were taken in 5 ml (4:1) methanol:water mixture and $NaBH_4$ (5 mmol) was added. The reaction mixture was vigorously stirred at room temperature. After 30 min reaction was monitored by TLC to check completion of reduction and aryl halide (1 mmol) or aryl boronic acid (1 mmol), K_2CO_3 (3 mmol) were added and the reaction mixture was heated in a CEM microwave (100 °C, 50 W) for 30 min.

2.5.2. Conventional method

In a 25 ml RBF, nitrobenzene (1mmol), 100 mg catalyst (CuNPs@PLA-TiO_2) were taken in a 5 ml (4:1) methanol/water mixture followed by addition of $NaBH_4$ (5 mmol). The reaction mixture was vigorously stirred at room temperature. After 30 min, aryl halide (1 mmol) or aryl boronic acid (1 mmol) along with K_2CO_3 (3 mmol) were added. The reaction mixture was heated at reflux temperature for 6-8 hours.

The progress of all the reactions was monitored by TLC. After completion of reaction, the reaction mixture was centrifuged. The catalyst was separated and washed with methanol and re-dispersed in water. Washings along with the filtrate were combined and methanol was distilled off using rotary evaporator. After a work up with dichloromethane and water, the organic layer was separated, dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to get the crude product. The crude products were purified by column chromatography (ethyl acetate: hexane) to afford the pure products which gave satisfactory mass and NMR spectral data [see ESI].

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3. Result and discussion

3.1. Characterization of CuNPs@PLA-TiO_2 nanocomposites

Support plays a vital role in the stabilization and catalytic efficiency of nanoparticles. Copper nanoparticles have been supported on many conventional inorganic/organic supports such as Al_2O_3,[24] alumina/gallium oxide,[25] Ferrite,[26-28] silica,[29,30] PEG,[31] PVP,[32] CMC,[33] PVC,[34] polystyrene composites[35] etc. To the best of our knowledge PLA-TiO_2 assembly has never been used for stabilizing copper nanoparticles. Though, in a report by Kaur et al., copper nanoparticles decorated onto polyaniline-zeolite hybrid material have been used to prepare hydrazine sensor[36]. In another report, palladium nanoparticles have been synthesized on PLA grafted carbon nanotubes and used to study C- C coupling reactions[37]. In the present studies CuNPs synthesized on PLA-TiO_2 particle brush were synthesized and analyzed extensively by various instrumental techniques and the results are discussed below.

Size of nanoparticles is the most crucial requirement for its catalytic activity and efficiency. Surface plasmon resonance (SPR) absorption is a phenomenon which is characteristic of metal particles at nanoscale only. This can be easily observed by UV-visible spectrophotometer and used to estimate size of nanoparticles[38] as the absorption maximum is size specific according to Mie theory, although; absorption maxima may vary depending upon the nature of support.[39] In the present case characteristic SPR was observed at 582 nm and hence, stepwise synthesis of CuNPs was conveniently monitored by UV-visible spectroscopy (Fig. 1). A series of CuNPs were prepared by varying the precursor to support ratio and the results are shown in figure 2. Interestingly, the value of SPR band was not drastically shifted with the change in the precursor to nanocomposite ratio, though, the intensity of the peak was found to

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increase with increasing metal percentage. This indicated that average particle size remained constant even when the quantity of support increased. This may be due to the brush like architecture of nanocomposite that controls the size rather than its quantity. Standard catalyst prepared by the method given in section 2.4 was used for all other analysis and for the catalysis. AAS analysis of the catalyst showed 0.85 mmol of copper per gram of catalyst.

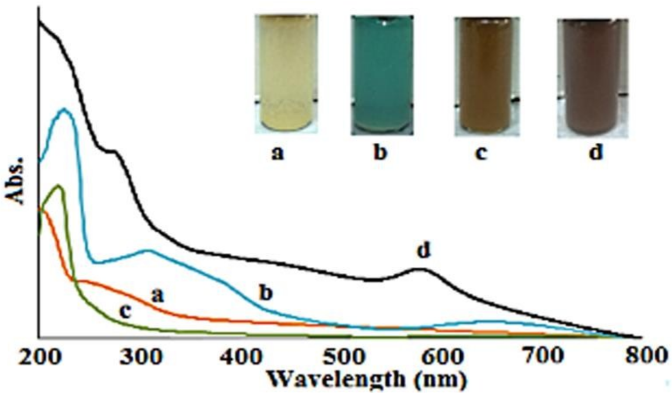

Fig. 1. Stepwise study of CuNPs synthesis by UV-Visible spectroscopy a) PLA-TiO_2 nanocomposites b) after addition of copper nitrate c) immediately after addition of hydrazine hydrate d) after 4 hrs.

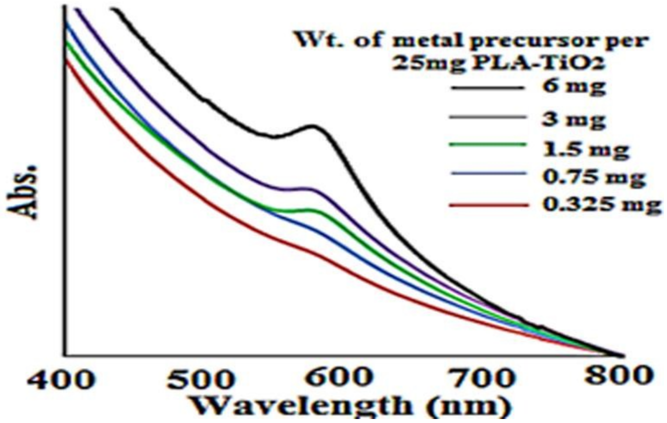

Fig. 2. Effect of variation in metal precursor concentration on SPR

High resolution tunneling electron microscopy (HR-TEM) is another powerful tool to study the size and shape of nanoparticles. TEM pictures of catalyst dispersed in water were taken and the

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results are shown in figure 3. Average diameter of CuNPs was 2-6 nm and they were mostly spherical in shape. The TEM pictures of PLA-TiO_2 were also taken which showed average diameter of TiO_2 nanoparticles was 1-2 nm (Fig. S2, ESI). A typical EDX analysis (Fig. S3, ESI) showed only Cu and Ti metal peaks in the catalyst while absence of any other peaks negated the possibility of other metallic impurities. The nature of spectra was found to be similar to the earlier reported studies.[40,41]

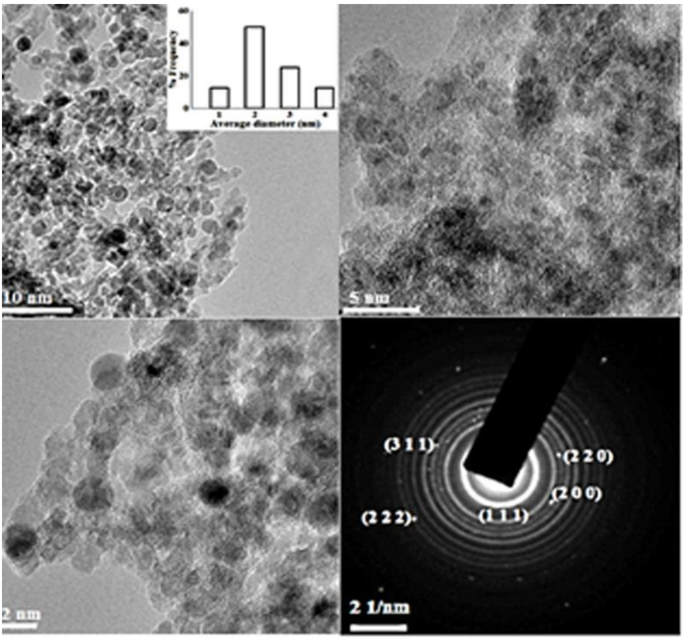

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Fig. 3. HRTEM- ED studies of CuNPs @PLA-TiO_2

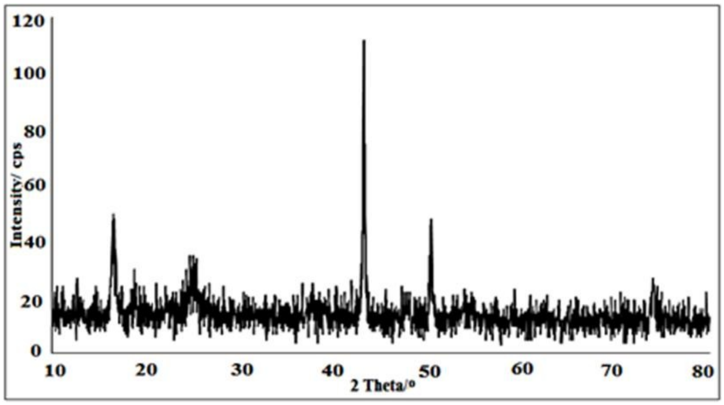

Fig. 4. XRD spectrum of CuNPs @PLA-TiO_2

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XRD analysis of the catalyst was carried out to analyze its constituents. The results shown in figure 4 clearly indicated that copper was in zero oxidation state. The peaks at 43.2033 (111), 50.4025 (200) and 74.0049 (220) were assigned to copper nanoparticles (JCPDS No. 04-0836) and correspond to the FCC lattice of copper (0). Average size of CuNPs calculated from the Debye-Scherrer equation was 4.54 nm from the reflection at $2\theta = 43.2033$ which is close to results obtained from HR-TEM analysis. Two other peaks were also observed. The one at 25.0382 (101) (JCPDS No. 21-1272.1) was assigned to the anatase phase of TiO_2[42] and the other at 16.5632 was characteristic of PLA.[43] No other peaks for TiO_2 could be detected due to its very low concentration.

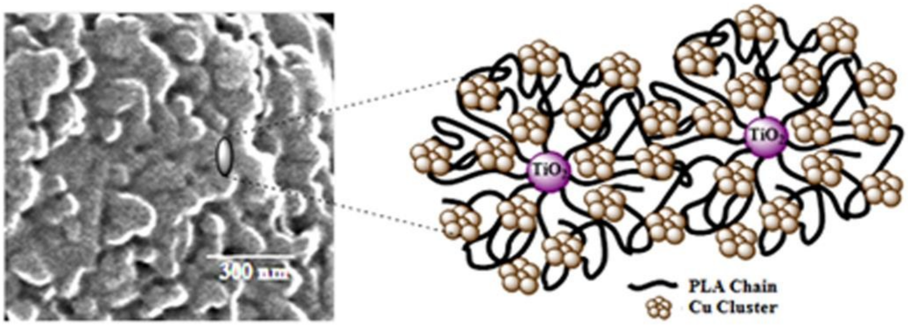

Fig. 5. SEM images of CuNPs @PLA-TiO_2

We tried to understand the morphology of the catalyst by Scanning electron microscopy (SEM). It showed spherical globules intertwined with each other. The reason became clear from particle size analysis (an average of three readings, see Figure S6, ESI) carried out on Malvern particles size analyzer. The average diameter of PLA-TiO_2 support when dispersed in water was found to be 55 to 85 nm whereas after impregnation with the CuNPs the average size of catalyst at half width was found to be 500 to 830 nm. This increase in the particle diameter was attributed to close association of PLA-TiO_2 brushes due to electrostatic interactions between the copper

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nanoparticles and the ester linkages of PLA chain of same or different brush. This resulted in a network (figure 5) in which copper nanoparticles were dispersed. Zeta potential is a measure of the magnitude of the electrostatic or charge repulsion/attraction between particles, and is one of the fundamental parameters known to estimate stability of colloidal dispersion. Zeta potential measurement showed a potential of -30.1 mV for water dispersion of PLA-TiO_2 (Fig. S4) which indicated very high stability of support. Whereas, for the copper loaded system (CuNPs@ PLA-TiO_2) zetapotential was found to be -70.3 mV (Fig. S5). These studies indicated that though some agglomeration of support (PLA-TiO_2) which itself was in nanometric scale has taken place, the overall stability of the catalytic system in water is good.

3.2.Sequential reductive *N*-arylation of nitroarenes

Preparation of secondary aryl amines is of great importance as they are widely used in agrochemicals, pharmaceuticals, conducting polymers, dyes, intermediates etc. Ullmann type C-N coupling of aryl halides with aryl amines is generally used to get the desired product using copper as catalyst. A number of reports of homogeneous and heterogeneous copper catalysts used for C-N coupling have been reported in literature.[44-46] Aromatic amines required for this step are themselves synthesized by reduction of nitroarenes. Separation and isolation of amines is always difficult and tedious as they are susceptible to oxidation under atmospheric conditions. As reduction of nitroarenes has been reported by copper nanoparticles by many workers, we decided to carry out the two steps viz. reduction of nitro arene and N-arylation of resulting aryl amine in sequential manner. But before proceeding to sequential studies, parameters for individual reactions were optimized.

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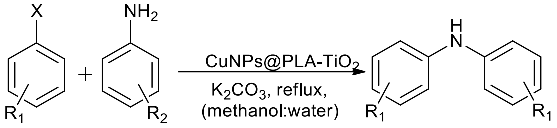
3.2.1 Reduction of nitroarenes



Scheme 1 Reduction of various nitroarenes catalyzed by CuNPs@PLA-TiO_2

A number of reducing agents have been reported for the reduction of nitroarenes usin CuNPs. We tried three reagents i. e. ammonium formate, hydrazine hydrate and sodium borohydride. No conversion was observed with ammonium formate whereas; hydrazine hydrate was effective under reflux conditions. However, complete conversion was observed with sodium borohydride at room temperature and the results are shown in table 1. Our earlier studies have shown that methanol/water is a good solvent for reduction of nitro compounds[48] as well as C-N coupling of aryl amines[47] hence, no other solvent was tried. However, we optimized the ratio of methanol/water for the best yield. From the results reported (Figure S10, ESI) it can be concluded that complete conversion of all nitroarenes can be obtained in 4:1 methanol:water. It has been observed that presence of a small amount of water promotes solubility of base as well as efficiency of the catalyst especially in coupling reactions.

Table 1 Reduction of nitroarenes under various conditions

Entry	Reducing agent	Temp. (°C)	time	Yield[a] (%)
1	$HCOONH_4$ (5 mmol)	reflux	24 h	trace
2	$N_2H_4.H_2O$ (3 mmol)	r.t.	24 h	trace
3	$N_2H_4.H_2O$ (3 mmol)	reflux	24 h	100
4	$NaBH_4$ (5 mmol)	r.t.	30 min	100

[a]Nitroarene (1 mmol), 0.1 g catalyst, 5 ml (methanol/water 4:1).

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The scope of the reaction was explored by reducing a number of substituted nitroarenes. Most reactants were reduced completely to corresponding amines within 30 minutes (Table 2) with high yield. Ortho substituted nitroarenes such as 2-nirto phenol and 2-nitro aniline were reduced at slower rate due to steric hindrance generating less effective resonance stabilization in comparison to para substituented (Table 2, entries 9, 10). In case of 4-nitro benzaldehyde, 4-amino benzyl alcohol was obtained showing reduction of both the functionalities.

To understand the kinetics of the reaction, reduction of 4-nitro phenol at two different concentrations was monitored by UV-visible spectrophotometric measurements at 35 °C. Aqueous solution of 4-nitrophenol in presence of sodium borohydride (pH 12) clearly showed a peak at 400 nm (λ_{max}) due to the formation of 4-nitro phenolate.[48] As the catalyst was added, reduction began immediately. Spectra measurement at regular time interval showed a gradual decrease in the λ_{max} (Fig. 8). Simultaneously, a new peak appeared at 300 nm which corresponded to the formation of 4-amino phenol. The reduction reaction was found to be pseudo first order as the sodium borohydride was taken in excess and rate of reduction would be independent of its concentration. The rate constant was calculated by plotting a graph of ln (At/Ao) against time t (min) (Fig. 6).[49] The calculated rate constants for the CuNP catalyzed reaction was found to be 3.44×10^{-2} sec^{-1} and 1.79×10^{-2} sec^{-1} respectively for I mmol and 2 mmol solutions. The value is close to the best reported in literature for copper catalyzed reduction of nitrobenzene.

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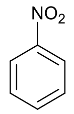
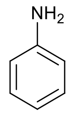
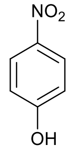
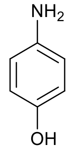
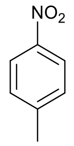
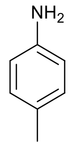
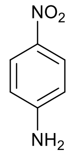
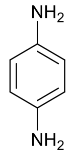
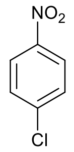
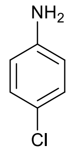
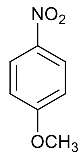
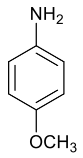
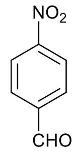
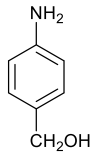
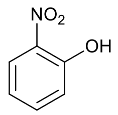
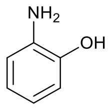
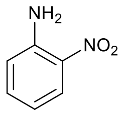
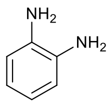
Table 2 Scope of the catalyst for reduction of various nitroarenes

Entry	Substrate	Product	T (min)	[a]Yield (%)
1			30	100
2			30	95
3			30	90
4			30	94
5			30	96
6			30	90
7			60	98
8			50	95
9			55	97

[a]Nitroarenes (1 mmol), $NaBH_4$ (5 mmol), 0.1 g catalyst,
5 ml $MeOH:H_2O$ (4:1), 40 °C, 30 min.

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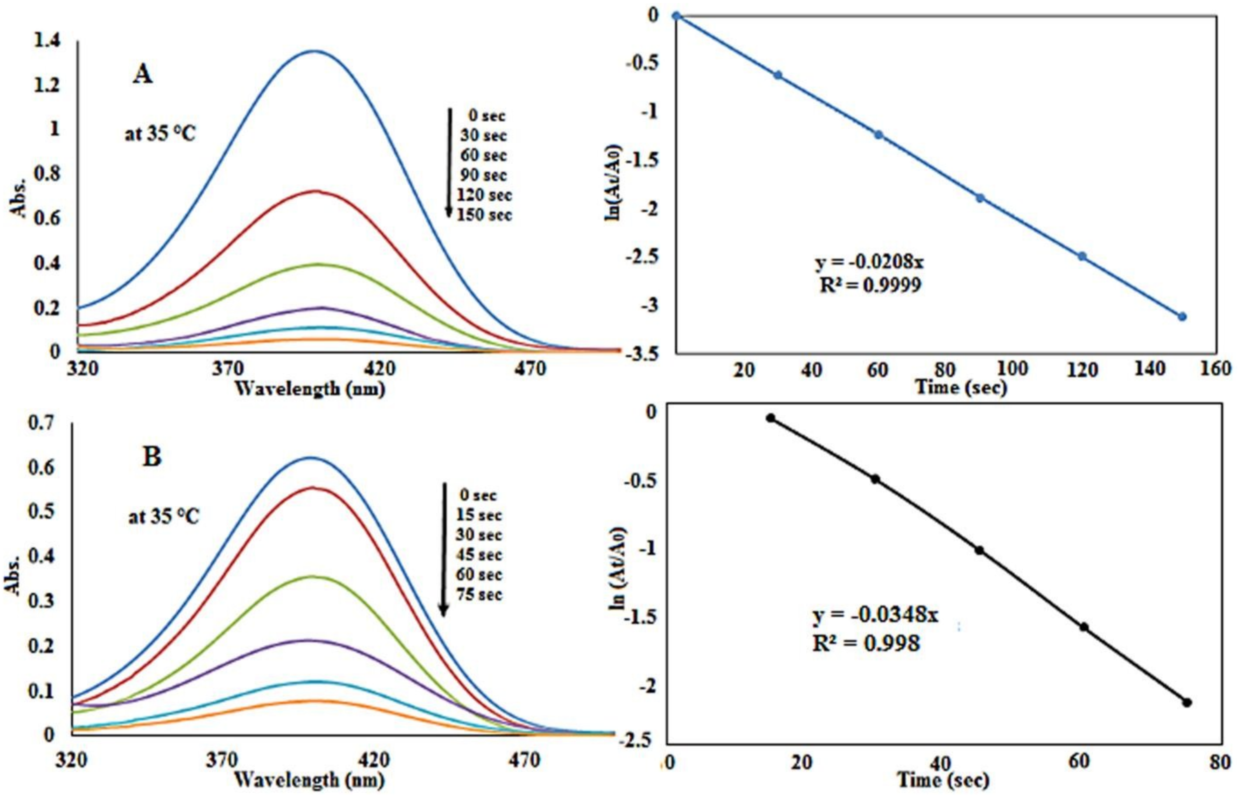
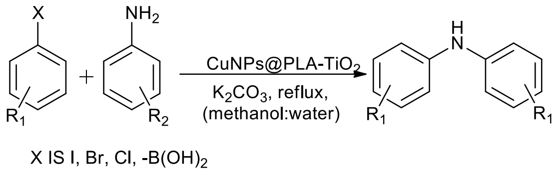


Fig. 6. Time dependent UV-Visible spectra and ln (At/A$_0$) versus t for reduction of 4-nitrophenol at different conc. A) 2 mmol. B) 1 mmol

3. Detailed study of C-N cross coupling reaction



Scheme 2 CuNPs@PLA-TiO$_2$ catalyzed C-N cross coupling reaction

N-arylation of aryl amines is widely used process in agrochemical, pharmaceutical, dye and polymer industry. Palladium catalysed Buchwald coupling is the most popular protocol to carry this process. However, of late development of environmentally benign methods for N-arylation or C-N coupling using copper nanoparticles in the absence of ligands have attracted the attention of various researchers.[50] N-arylation has of aryl amines have been reported with haloarenes as well as with arylboronic acids. In the present case, the reaction between aryl halides and aryl

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amine catalyzed by CuNPs@PLA-TiO_2 yielded diphenyl amine as the sole product whereas, N-arylation with phenylboronic acid gave substantial amount of biphenyl (20 %) due to homocoupling. Subsequently, all other reactions were tried with various aryl halides only. methanol-water mixture in 4:1 ratio was used as solvent and K_2CO_3 as base and it gave excellent results. The effect of catalyst concentration on N-arylation was examined in detail. The best yield for standard reaction between iodobenzene and aniline was obtained with 100 mg of catalyst quantity in 6 h under conventional heating and 30 min in closed vessel under microwave heating in good to high yields.

Table 3 Effect of catalyst conc. on N-arylation of aniline

Entry	Catalyst	Copper (mol %)	Base	Yield (%)
1	100 mg PLA-TiO_2	-	K_2CO_3	trace
2	25 mg catalyst	1.98	K_2CO_3	35
3	50 mg catalyst	4.0	K_2CO_3	60
4	100 mg catalyst	8.232	K_2CO_3	100

Iodobenzene (1 mmol), aniline (1.2 mmol), 0.1 g catalyst, K_2CO_3 (3 mmol), 5 ml (4:1) MeOH: H_2O, reflux temp., 6 h.

4. Sequential reductive N-arylation of nitroarenes

After optimizing the individual steps we carried out the two steps in sequential manner. First reduction was carried out at 40 °C and after completion of this step (30 – 60 min) aryl halides along with the base were added and the reaction continued under microwave (30 min) or conventional heating (6 h). The general applicability of the protocol was studied by taking a number of different aryl halides and their amination was carried out. The products were confirmed by their NMR and Electron spray mass ionization data (see ESI). The yield and the time required for various reactions is shown in table 5. The reaction with iodo and bromo

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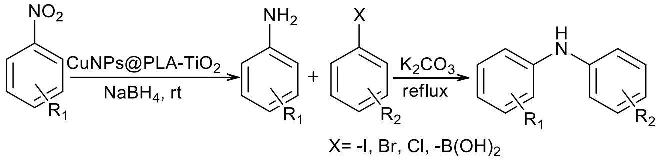
benzene went smoothly (Table 5, entry 1). However, chloro benzene required longer time. Compounds containing electron donating as well as electron withdrawing groups were tried and corresponding coupled products were obtained in good yield (Table 4, entries 2, 3). In case of 4-nitro aryl halides 4-nitroanisole was obtained as major product which indicates ring activation towards methoxylation rather than amination. Replacing methanol with DMSO as solvent gave the corresponding amine products (Table 4, entry 8).

Table 4 N-arylation of various aryl halides and various aryl amines



Entry	R_1	X	R_2	Micro wave	Conventional Yield (%)
1	H	I	H	80	98
2	4 $-CH_3$	I	H	75	92
3	4 $-OCH_3$	I	H	73	85
4	H	Br	H	75	94
5	4 $-CH_3$	Br	H	70	86
6	4 $-OCH_3$	Br	H	70	83
7	H	Cl	H	59	70
8	4 $-NO_2$	Cl	H	30^c	30
9	4 $-NO_2$, 2-OCH_3	Cl	H	65	70
10	H	I	2-aminopyrimidine	63	87

aryl halide(1 mmol), aryl amine(1 mmol), CuNPs@PLA-TiO_2(0.1g) K_2CO_3 (3 mmol), 5 ml (4:1) MeOH: H_2O

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3.5 Stability and reusability of the catalyst

In order to check the stability of CuNPs dispersed in water, the colloidal solution was analyzed by UV-Vis spectroscopy at regular interval of times over a period of 28 days and the results are shown in figure 7. It can be seen that there was no significant shift in the absorption maxima of the SPR band of CuNPs. The catalyst was found to be stable even after the reaction. Even FT-IR spectrum of fresh and used catalyst does not show any change. (Fig. S11, S12, ESI) indicating that the composition of catalyst is unchanged.

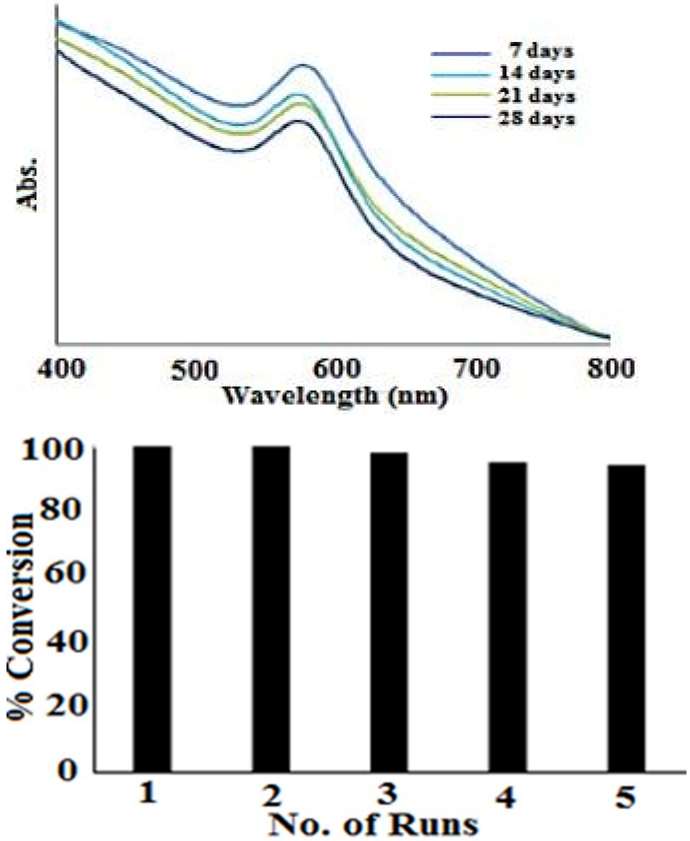

Fig. 7. UV-visible spectra of catalyst dispersion taken over a period of 28 days and its reusability

The recyclability of the catalyst was investigated for the N-arylation reaction of iodobenzene and aniline. After completion of reaction, the catalyst was removed from the reaction mixture by

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centrifugation washed with methanol and reused after adding fresh amount of reagents. The recovered catalyst was reused several times without any significant loss of activity (Fig. 7).

4. Conclusion

In summary, grafting of PLA on TiO_2 can provide a environmentally friendly support for synthesizing CuNPs with small size variation of 2 – 6 nm. The support enhanced the stability and dispersability of CuNPs in water. The synthesized nanoparticles showed excellent catalytic activity and recyclability for reductive amination of nitroarenes which was carried out in sequential manner under conventional and microwave heating in a benign mixed solvent system.

Acknowledgement

The authors are grateful to the DST nanomission for the financial support, UGC, New Delhi for the BSR fellowship to Nirav Barot and MANF to Tauhid Shaikh, CSMCRI, Bhavnagar, for the TEM-EDAX analysis, SAIF, Panjab University, Chandigarh, for SEM and ^{1}H NMR, Charotar University of Science and Technology, Changa, for XRD analysis.

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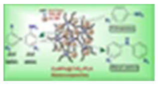

One pot synthesis of diarylamines from nitro arenes by sequential reduction and n-arylation

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