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# Copper nanoparticles grafted on carbon microspheres as novel heterogeneous catalysts and their application for the reduction of nitrophenol and one-pot multicomponent synthesis of hexahydroquinolines

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Novel carbon microspheres-supported metallic copper nanoparticles (Cu-NP/C) were synthesized using a low cost and facile method based on carbonising a styrene-based chelate-forming cation exchange resin loaded with Cu<sup>2+</sup> ions. The metal-organic framework served as both copper and carbon source. Cu-NP/C microspheres were characterized by XRD, Raman, SEM, TGA, EDAX, and BET surface area analyser, and employed as heterogeneous catalysts for the reduction of 4-nitrophenol to 4-aminophenol by NaBH<sub>4</sub> and for the synthesis of medicinally significant hexahydroquinoline derivatives based on the one pot multi-component reaction of aldehydes, dimedone, ethyl acetoacetate, and ammonium acetate. The sustainable and cheap starting material, the relatively easy synthetic procedure, the catalytic efficiency, and the easy separation and reusability of Cu-NP/C microspheres opened the door for their wide scale applications.

## Introduction

Catalysis is in the heart of chemical transformations, therefore there are continuous efforts to develop new catalysts and to increase catalytic performances for various applications. Metallic nanoparticles (NPs) have become essential tools for many chemical processes employed in the industry and academia during the last decades.<sup>1–5</sup> NPs possess high specific surface area, various shapes and sizes, high reactivity, and often exhibit activity different from that of the corresponding bulk materials due to distinctive quantum properties. Handling of NPs, however, is not easy, because NPs are often prone to self-aggregation and it is difficult to separate them from reaction media, because classical convenient filtration methods are not applicable. One economical way of overcoming or minimising these limitations is to anchor NPs on supports, which latter also serve as modifiers of catalytic properties. Nowadays, economic considerations and health issues are gaining more and more importance, and the development of catalytic NPs that are inexpensive, non- or

minimally-poisonous, highly active, selective, stable, robust, and easily separable from a reaction mixture is hardly desirable. Cu NPs provide a very promising alternative of heavy metal NP catalysis,<sup>1</sup> and the aim of the present work is to provide a novel route to carbon microsphere supported Cu NPs, and to test their catalytic activity in two selected reactions, namely the 4-nitrophenol (4NP) reduction and one-pot multicomponent synthesis of hexahydroquinolines. The combination of reactive NPs with micro-sized support is important for keeping the high activity of NPs while providing a possibility for easy catalyst handling and separation. We show in this paper that both Cu NPs and carbon support can be simultaneously and economically prepared by carbonising copper ion loaded styrene based cation exchange resins without using any additional reducing agent. Several carbon-supported Cu-based NPs were prepared previously using wet-chemical, photochemical, electrochemical, and microwave methods, as well as thermal treatments, and their synthesis is reviewed last year.<sup>1</sup>

The reduction of 4NP by NaBH<sub>4</sub> to 4-aminophenol (4AP) is an industrially important reaction<sup>6</sup> and a widely used model reaction to test catalytic performance of metal nanocatalysts due to the following reasons: 1) 4AP is the sole product of this reaction, 2) the reaction does not proceed at ambient temperature without a catalyst, 3) the reaction can be easily observed by a colour change from yellow (4NP) to colourless (4AP) and monitored by UV/Vis spectroscopy following the decrease of the absorption band of 4-nitrophenolate anion at 400 nm.<sup>6,7</sup> The reaction was shown to follow a pseudo-first-order kinetics at the presence of a large excess of NaBH<sub>4</sub>, and

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<sup>†</sup>Electronic Supplementary Information (ESI) available: figures containing results of TG, EDAX, Raman, SEM, sorption, NMR, MS, and UV measurements; plot of 4NP reduction kinetics; schemes for the synthesis of microspheres and mechanism of polyhydroquinoline formation; tables containing XRD and BET results, and melting points. See DOI: 10.1039/x0xx00000x

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the catalytic rate could be evaluated using first-order kinetics with respect to the 4-nitrophenolate concentration.<sup>6–9</sup>

Hexahydroquinolines (HHQs) are biologically active compounds and find applications in medicinal chemistry as anticancer, antimicrobial, antihypertensive, and antimalarial agents.<sup>10–14</sup> HHQs, in general, are synthesized by the four component Hantzsch's condensation reaction, involving various aldehydes, dimedone, ethyl acetoacetate, and ammonium acetate. Several homogeneous and heterogeneous catalysts such as inorganic salts, Bronsted and Lewis acids, ionic liquids, metal oxides, and zeolites were reported to be active in the condensation reaction.<sup>15–21</sup> Many of these methods, however, involve synthetic problems associated with difficult separation processes, expensive, hardly available, or non-recoverable catalysts, expensive reagents, or long reaction time. Considering the widespread applications of HHQ derivatives, there is a need to develop new and efficient catalysts for the green synthesis of these heterocyclic compounds. Therefore, our aim was to develop a facile and cheap catalyst system for Hantzsch's HHQ synthesis by selecting nanosized copper as the catalytically active metal and carbon microspheres as the catalyst support.

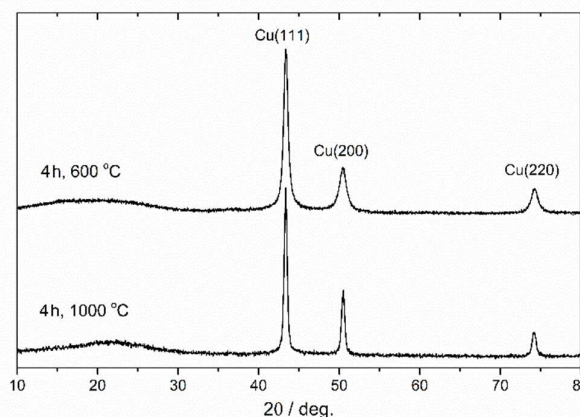
In this paper, we present a novel method for synthesizing copper NPs decorated carbon microspheres, their characterisation for the determination of their phase composition and morphology, and their application as heterogeneous catalysts in 4NP reduction and HHQ synthesis.

## Results and discussion

### Synthesis and characterization of Cu-NP/C microspheres

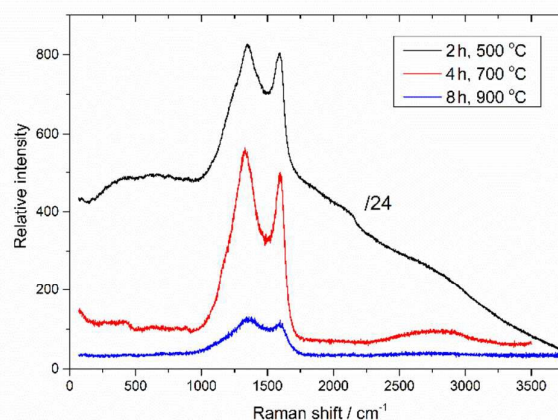
In order to synthesize Cu NP loaded carbon microspheres (Cu-NP/C), a commercial styrene-based chelate forming ion exchanger resin containing iminodiacetate ( $-\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2$ ) functional groups with a binding capacity of 1 mol divalent metal cation per  $1 \text{ dm}^3$  resin was selected as both the carbon source and Cu ion binder (see Experimental part). We expected that the carbonisation of copper ion loaded resin produces not only the carbon support but a reductive environment for the formation of metallic copper. Since copper ions were distributed in the resin according to iminodiacetate functional groups, the formation of only small Cu particles was expected due to diffusion at the carbonisation temperature. We note that iminodiacetate chelating functional groups selectively bind one equivalent of Cu(II) ions (see Scheme S1, ESI). To find information about the stability and decomposition of loaded resin, thermogravimetric (TG) analysis was carried out. This latter indicated resin decomposition between 180 and 450 °C and a complete weight loss of 68.2% up to 900 °C (see Fig. S1, ESI). Therefore, the carbonisation of the resin was investigated in the 500–1000 °C temperature range in 100 °C increments, and the effect of heating time was studied by performing experiments for 2, 4, and 8 hours. The Cu content of microspheres prepared by carbonisation at 600 °C for 4 hours was determined to be 8.1% using ICP-OES after digesting microspheres in hot chromic

acid. The Cu content on these microspheres' surfaces was measured to be 0.2% after dissolving surface Cu in 34% aqueous nitric acid.



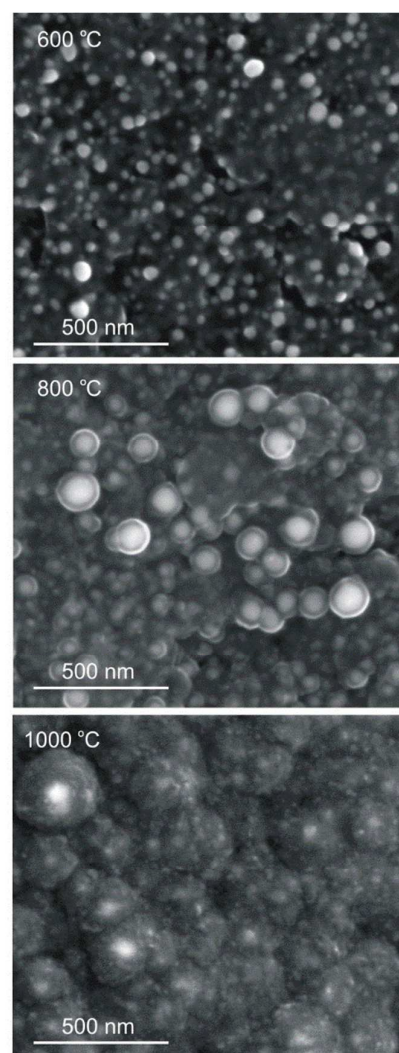
**Fig. 1.** Powder X-ray diffractogram of selected Cu-NP/C microspheres (carbonisation time and temperature is indicated).

The phase composition of synthesized Cu-NP/C microspheres was determined by powder X-ray diffraction (XRD). Representative XRD diffractograms are shown in Fig. 1. The XRD study unambiguously indicated that only metallic copper was formed as the sole crystalline phase during carbonisation between 600 and 1000 °C, and besides Cu a small amounts of  $\text{Cu}_2\text{O}$  appeared at 500 °C carbonisation (8, 6, and 3 at% of total Cu content applying a heating time of 2, 4, and 8 hours, respectively; see Table S1, ESI). The average crystallite size of copper particles was calculated to be 15 nm at 500 °C, using the Scherrer equation, and it increased gradually up to 35 nm by increasing the carbonisation temperature (see Table S1, ESI). EDAX investigations indicated the presence of copper on the surface or close to the surface of microspheres (see Fig. S2, ESI). No graphitisation was observed by XRD.



**Fig. 2.** Raman spectra of selected Cu-NP/C microspheres (carbonisation time and temperature is indicated, see also Figure S3, ESI).

Raman spectroscopy confirmed the carbonisation of the resin (Fig. S3, ESI), and selected spectra are shown in Fig. 2. The appearance of characteristic D, D', G, and 2D Raman bands at 1329–1347, 1162–1240 (shoulder), 1588–1599, and 2660–2700  $\text{cm}^{-1}$ , respectively, and the D/G band intensity ratio are characteristic of amorphous carbon.<sup>22</sup> The graphitisation of the carbonaceous material, according to Raman spectra, is very low, in agreement with XRD. Raman bands characteristic of amorphous carbon appear on top of a broad luminescence background at 500 °C carbonisation, what indicate imperfect carbonization at this temperature. This background, however, gradually decreases and disappears by increasing carbonisation time and temperature, respectively (Figs. 2 and S3, ESI). The measured Raman intensity, in general, decreases with increasing carbonisation temperature, which indicates gradual replacement of  $\text{sp}^3$  carbon atoms by  $\text{sp}^2$  carbon atoms. Raman spectra of microspheres obtained by carbonisation between 600 and 1000 °C for 4 and 8 hours is very similar at the given temperature, indicating similar structural organisation of carbon microsphere surfaces.



**Fig. 3.** SEM image of the Cu-NP/C microsphere surface obtained by carbonisation of the copper loaded ion exchange resin at 600, 800, and 1000 °C for 8h (see also Figure S5-7, ESI).

The shape and surface morphology of synthesized microspheres were studied by Scanning Electron Microscopy (SEM). Cu-NP/C microspheres inherited the spherical morphology of ion exchange resins (see Fig. S4, ESI), but their diameter decreased down to the half, to 300–500  $\mu\text{m}$ , due to shrinkage during the heat treatment. According to SEM Cu NPs were distributed all over the surface of carbon microspheres. After breaking some microspheres in a mortar, SEM confirmed the distribution of Cu NPs inside the microspheres, too. Tiny Cu NPs are clearly visible on the surface of microspheres obtained by carbonisation at 500 and 600 °C, but they tend to be embedded into the carbon matrix at higher temperatures. A carbon collar forms around Cu NPs at about 800 °C, and NPs disappear in a seemingly fluffy carbon matrix at higher temperatures (Figs. 3, S5, S6, and S7, ESI). SEM investigations thus suggest that Cu-NP/C microspheres prepared at around 600 °C are the most promising candidates for catalytic



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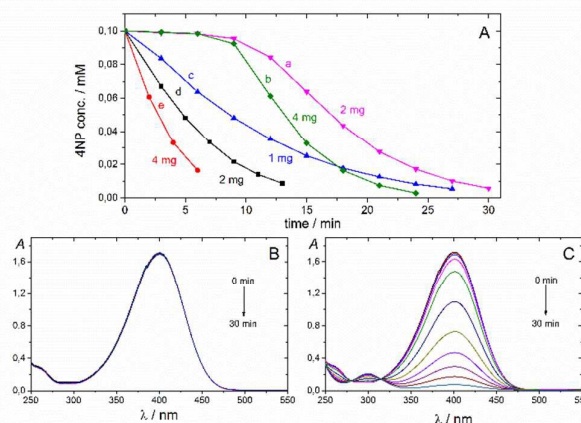
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applications. Cu NPs are known to be slowly oxidized by air oxygen,<sup>1</sup> and it was fortuitous for this study that microspheres synthesized two years ago and stored in a closed container but under air could be reinvestigated by XRD. The old samples prepared at 600 °C indicated the partial oxidation of copper (20 wt% of Cu was oxidized to Cu<sub>2</sub>O, possibly the surface content), but microspheres prepared at 1000 °C were practically unchanged (see Figs. S8 and S9, ESI). This confirmed that Cu NPs were embedded in the carbon matrix and protected from air in the case of high temperature synthesis. The specific surface areas of microspheres were determined using nitrogen adsorption measurements and found to be between 3 and 9 m<sup>2</sup>g<sup>-1</sup> (Table S1, ESI). The total pore volume for the sample prepared by carbonisation at 600 °C for 4 hours was measured to be only 0.0017 cm<sup>3</sup>g<sup>-1</sup>, and the average pore width was estimated to be 2.2 nm. The measured nitrogen sorption isotherms suggested poorly developed micro- and mesopores (see Fig. S10, ESI).

#### Catalytic activity of Cu-NP/C microspheres for the reduction of 4-nitrophenol

The Cu-NP/C sample prepared by carbonisation at 600 °C for 4 hours was selected for catalytic efficiency evaluation. 4NP was treated with large excess of NaBH<sub>4</sub> in water at the presence of various amounts of catalysts (initial concentrations of 4NP and NaBH<sub>4</sub> were 0.1 mM and 10 mM, respectively) at 20 °C, and the reaction was monitored by UV/Vis spectroscopy. The characteristic absorption band of nitrophenolate anion appeared at 400 nm. Upon addition of Cu-NP/C microspheres, the absorption band decreased with time and that of 4AP at 300 nm increased. The 4NP concentration decrease versus reaction time is shown in Fig. 4. No reaction between 4NP and NaBH<sub>4</sub> was observed at the absence of Cu-NP/C microspheres (Fig. 4). When 4NP and NaBH<sub>4</sub> solutions were mixed and the catalyst was added, an induction time of about 9 min was observed for the reaction. However, when the catalyst was added to the 4NP solution, stirred for 10 minutes, and NaBH<sub>4</sub> solution was consecutively added, the reaction proceeded without any induction time. The induction time of 4NP and NaBH<sub>4</sub> reaction was noted previously<sup>6,9</sup> and was explained by a slow nanoparticle surface reconstruction at the presence of 4NP.<sup>9</sup> Our observations are in line with this. At the presence of a large excess of NaBH<sub>4</sub>, the 4NP reduction reaction is ruled by a first order kinetics, indicated by the linear correlation of  $-\ln(c_t/c_0)$  versus time (min) plots, where  $c$  is the 4NP concentration at the given time (see Fig. S11, ESI). The apparent rate constant,  $k_{app}$ , can be determined from the slope of the fitted line. Increasing the amount of the catalyst used, the rate constant increased due to the increasing number of active sites for the reaction. The ratio of the rate constant over the total weight of the Cu-NP/C catalyst,  $k = k_{app}/m_{cat}$ , where  $m$  is the mass of catalyst used, was determined to be between 68 and 100 min<sup>-1</sup>g<sup>-1</sup>. In separate experiments Cu NPs were removed from the microsphere surface using 1:1 diluted nitric acid. These 'bare' carbon microspheres did not catalyse the 4NP reduction, what confirmed the importance and catalytic

activity of Cu NPs in 4NP reduction. Cu-NP/C microspheres prepared by carbonisation at 1000 °C for 4 hours were also investigated, but negligible catalytic activity was observed ( $k = 4 \text{ min}^{-1}\text{g}^{-1}$ ; Fig. S12, ESI), what is in line with SEM investigations indicating embedding of Cu NPs in the carbon matrix at high temperature.

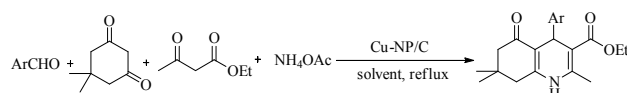


**Fig. 4.** Concentration of 4NP versus time for the 4NP reduction by NaBH<sub>4</sub> at the presence of Cu-NP/C microspheres (A) (amount of catalyst used is indicated; initial 4NP and NaBH<sub>4</sub> concentrations are 0.1 and 10 mM; catalyst was added to mixed solutions of 4NP and NaBH<sub>4</sub> (a and b); 4NP solution stirred with the catalyst for 10 min before adding NaBH<sub>4</sub> solution (c, d and e), temperature = 20 °C). Time dependent evolution of UV/Vis spectra of 4NP anion at the absence (B) and at the presence (C) of Cu-NP/C catalyst showing the reduction of 4NP by NaBH<sub>4</sub>.

#### Catalytic activity of Cu-NP/C microspheres in the one-pot multi-component synthesis of hexahydroquinolines

The catalytic activity of Cu-NP/C microspheres prepared by carbonisation at 600 °C for 4 hours were investigated for the synthesis of HHQs via the four component Hantzsch's condensation reaction (Scheme 1). The reaction was performed on a preparative scale, and thus was not monitored by spectroscopy. The reaction mixture was worked up using standard preparative methods and isolated yields were determined in all cases. Instead of varying, the reaction time was fixed to two hours and conclusion on catalytic activity was made on the basis of isolated product yields. For reactions with apparently smaller rate, reaction time was increased in selected cases. In order to study the effect of solvent and catalyst concentration on product yield, the reaction between benzaldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1.2 mmol) and ammonium acetate (1.5 mmol) was selected. The effect of solvent on the rate of reaction was studied in the presence of 5 mg Cu-NP/C catalyst (ca. 5 wt% of benzaldehyde used). Among various screened solvents, namely methanol, ethanol, isopropanol, 1,2-dichloroethane (DCE), THF, dioxane, and MeCN, ethanol was found to be the best in the studied model reaction concerning the yield of 2-amino-4-phenyl-3-cyano-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline (Table 1). Without catalyst the yield of the reaction was

very low, below 5% for each solvent. Using ethanol as the most appropriate solvent, the amount of catalyst was tested, and was found that 10 mg catalyst was sufficient to complete the Hantzsch's transformation within 2 hours (Table 1).



**Scheme 1.** Synthesis of hexahydroquinolines using Cu-NP/C catalyst.

**Table 1.** Solvent screening and optimisation of catalyst concentration

Entry <sup>a</sup>	Conditions	Catalyst (mg)	Isolated yield (%)
1	THF, reflux, 5h	5	38
2	Dioxane, reflux, 5h	5	58
3	DCE, reflux, 3h	5	63
4	MeCN, reflux, 5h	5	74
5	iPrOH, reflux, 3h	5	76
6	MeOH, reflux, 2h	5	82
7	EtOH, reflux, 2h	5	87
8	EtOH, reflux, 2h	10	92
9	EtOH, reflux, 2h	15	94
10	EtOH, reflux, 2h	20	94

<sup>a</sup> See Scheme 1; Ar= phenyl; Reagents: benzaldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1.2 mmol), ammonium acetate (1.5 mmol), and solvent (2 mL). See Fig. S13–15, ESI, for MS and NMR spectra.

**Table 2.** Yields of various hexahydroquinolines using the Cu-NP/C catalyst

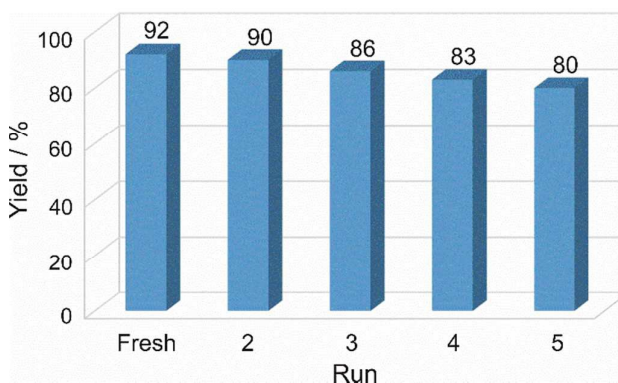
Entry <sup>a</sup>	Ar group	Isolated yield (%)
11	Phenyl	92
12	2,4-dichlorophenyl	88
13	2-chloro-4-fluorophenyl	86
14	4-chlorophenyl	94
15	2-fluorene	90
16	4-methoxyphenyl	89
17	2-hydroxyphenyl	87
18	3-hydroxyphenyl	89
19	3-nitrophenyl	91
20	4-nitrophenyl	88
21	4-bromophenyl	87
22	2-thiophenyl	82

<sup>a</sup> See Scheme 1 and Table S2, ESI; Conditions: reflux, 2h, ethanol, 20 mg catalyst, aldehyde (2 mmol), dimedone (2 mmol), ethyl acetoacetate (2.4 mmol) and ammonium acetate (3 mmol), solvent 5 mL. See Fig. S13–34, ESI, for MS and NMR spectra.

In order to test the general applicability of Cu-NP/C catalyst for HHQ synthesis, the reaction of various ortho, meta, and para substituted benzaldehydes, two of them synthesized for the first time, and thiophene-2-aldehyde with dimedone, ethyl acetoacetate, and ammonium acetate was studied under the optimized conditions (ethanol, reflux, 10 mg catalyst/1 mmol aldehyde). The catalyst was found to be efficient and provided excellent yields (82–94 %) for the investigated derivatives (Table 2). A plausible and stepwise mechanism for the four component reaction is suggested in Scheme S2, ESI, analogously to that in ref. [15]. It involves four possible steps: 1. the catalyst assists to enhance electrophilicity of carbonyl carbon of aldehyde which reacts with the enolic form of dimedone to form arylidene intermediate (I), 2. ethyl acetoacetate reacts with ammonium acetate to form β-

enaminoester (II), 3. the reaction of arylidene intermediate (I) with β-enaminoester (II), and 4. proton transfer and cyclization.

The reusability of the catalyst is important for practical applications, and it was studied by selecting the reaction between benzaldehyde, dimedone, ethyl acetoacetate and ammonium acetate, as well as the most favorable reaction conditions (ethanol, reflux, 10 mg catalyst/1 mmol aldehyde) and 2 hours reaction time. Experiments revealed that the Cu-NP/C catalyst could be consecutively reused four times without significant loss of catalytic activity (Fig. 5). The slight decrease in the yield of the corresponding product 2-amino-4-phenyl-3-cyano-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline can be attributed to a small catalyst loss during its recovery and deactivation. The efficiency of the Cu-NP/C catalyst is compared to those of a number of previously reported heterogeneous catalysts in Table S3, ESI.



**Fig. 5.** Graphical representation of the reusability of the Cu-NP/C catalyst.

## Experimental

### General information

Chemicals used were reagent grade from commercial sources and used without further purification. Identification of synthesized hexahydroquinolines was based on melting point and spectroscopic measurements. Melting points were measured in open capillaries using an Optics technology melting point apparatus and were uncorrected. <sup>1</sup>H NMR, <sup>13</sup>C NMR, and DEPT spectra were obtained on Bruker Avance 250 and 400 spectrometers and referenced to tetramethylsilane (TMS). Infrared (IR) spectra were recorded on a Shimadzu FTIR spectrometer (Prestige IR21) using neat samples. Samples were analyzed for exact mass on a mass analyzer (Waters-TQD).

### Synthesis of Cu-NP/C microspheres

A styrene-based VARION BIM-7 commercial chelate forming ion exchanger resin, containing 7% divinylbenzene crosslinker, 2% acrylonitrile modifier and iminodiacetate (-CH<sub>2</sub>N(CH<sub>2</sub>COOH)<sub>2</sub>) functional groups with a binding capacity of 1 mol divalent metal cation per 1 dm<sup>3</sup> resin was used as the

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starting material. The resin was saturated with  $\text{Cu}^{2+}$  ions using aqueous copper sulphate ( $\text{CuSO}_4$ ) solution according to the procedure described in our previous studies.<sup>22,23</sup> The exchanged resin was first dried in air and then in a drying box at 120 °C for 1 day. The dried resin was carbonized at 500, 600, 700, 800, 900, and 1000 °C for 2, 4, and 8 h in a high purity dry nitrogen stream using an electric furnace. The furnace was heated up to the desired temperature in 30 min, and cooled down to room temperature naturally after heat treatment.

### Catalyst characterization

X-ray powder diffraction measurements were done on a Model PW 3710 / PW 1050 Bragg-Brentano diffractometer using  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.541862 \text{ \AA}$ ). Raman spectra were recorded on a HORIBA JobinYvonLabRAM HR confocal Raman microscope using He-Ne excitation (632 nm) and a laser power of 0.1 mW. BET specific surface area was determined using the volumetric method and nitrogen gas at liquid nitrogen temperature, using an ASDI RXM-100 catalyst characterization instrument. Samples were pre-treated in vacuum at 300 °C for 2 hours. TG measurements were performed on a modified Perkin-Elmer TGS-2 thermo balance. Sample in a platinum sample pan was heated at 10 °C  $\text{min}^{-1}$  up to 900 °C in a nitrogen atmosphere. Scanning electron microscopy (SEM) and EDAX analysis were performed using an FEI Quanta 3D high-resolution microscope. Resolution of the instrument was  $\leq 1.2 \text{ nm}$  at 30 keV accelerating voltage and in high vacuum. Spectrophotometric measurements were done using a Perkin-Elmer UV/Vis Lambda 35 spectrometer applying a split width of 1 nm. Cu content was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Spectro Genesis instrument.

### Reduction of 4-nitrophenol (4NP)

Two stock solutions were prepared by dissolving 4NP and  $\text{NaBH}_4$  separately in distilled water. A quartz cuvette with an optical path length of 1 cm was consecutively charged with the catalyst (1, 2, or 4 mg), 1.5  $\text{cm}^3$  0.2 mM 4NP solution (stirred for 0 or 10 min before adding  $\text{NaBH}_4$ ), and 1.5  $\text{cm}^3$  20 mM  $\text{NaBH}_4$  solution. Concentrations of 4NP and  $\text{NaBH}_4$  in the initial solution were 0.1 mM and 10 mM, respectively. The reaction mixture was stirred and monitored by UV/Vis spectroscopy following the absorption band of 4NP anion at 400 nm. The stirring was stopped while recording the UV/Vis spectrum.

### General procedure for the synthesis of Hantzsch's hexahydroquinoline derivatives

A mixture of aldehyde (2 mmol), dimedone (2 mmol), ethyl acetoacetate (2.4 mmol), ammonium acetate (3 mmol) and Cu-NP/C catalyst (20 mg) in ethanol (5 mL) was refluxed for 2 h. The progress of the reaction was monitored by TLC (30% ethyl acetate: n-hexane). After completion of the reaction, the reaction mass was diluted with hot ethanol (10 mL) and filtered off to separate catalyst. The filtrate was concentrated on rotary evaporator to obtain the crude product which was purified by recrystallization from ethanol to afford the

corresponding pure hexahydroquinolines. The recovered catalyst was washed several times with hot ethanol, dried in an electric oven at 120 °C for about 30 minutes, and reused several times when it was required. Spectral data of newly synthesized compounds:

**Ethyl-4-(2-chloro-4-fluorophenyl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate (Table 2, Entry 13).** M.p.: 180-181 °C;  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ):  $\delta = 0.8$  (s, 3H), 1.19 (t, 3H), 1.9 (dd, 1H), 1.99 (s, 3H), 2.1 (dd, 1H), 2.2 (s, 3H), 2.3 (dd, 1H), 2.4 (dd, 1H), 3.9 (q, 2H), 5.12 (s, 1H), 7.05 (dd, 1H), 7.13 (dd, 1H), 7.25 (dd, 1H), 9.1 (s, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{DMSO-d}_6$ ):  $\delta = 14.1, 18.2, 26.4, 29.0, 31.9, 34.5, 50.2, 58.9, 103.0, 109.4, 113.8, 115.6, 132.5, 141.6, 145.2, 149.7, 158.6, 161.0, 166.6, 193.9$  ppm; IR (neat): 3270, 2902, 1780, 1670, 1604, 1060, 826, 890  $\text{cm}^{-1}$ ; Mass ( $m/z$ ): 392 ( $M+1$ )<sup>+</sup>.

**Ethyl-4-(9H-fluoren-2-yl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate (Table 2, Entry 15).** M.p.: 224-225 °C;  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ):  $\delta = 0.9$  (s, 3H), 1.0 (s, 3H), 1.19 (s, 3H), 1.98 (dd, 1H), 2.2 (dd, 1H), 2.3 (s, 3H), 2.5 (dd, 1H), 2.6 (dd, 1H), 3.8 (q, 2H), 4.0 (s, 2H), 4.9 (s, 1H), 7.19-7.35 (m, 4H), 7.5 (dd, 1H), 7.6-7.8 (dd, 2H), 9.1 (s, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{DMSO-d}_6$ ):  $\delta = 14.1, 18.3, 26.4, 29.1, 32.1, 36.1, 36.3, 50.3, 59.0, 103.8, 110.1, 119.3, 119.6, 124.3, 125.0, 126.2, 126.4, 126.6, 138.8, 141.0, 142.4, 142.8, 144.8, 146.8, 149.4, 166.9, 194.3$  ppm; IR (neat): 3279, 2957, 1703, 1649, 1210, 1072  $\text{cm}^{-1}$ ; Mass ( $m/z$ ): 428 ( $M+1$ )<sup>+</sup>.

## Conclusions

In conclusion, we have developed a pyrolytic method for the synthesis of novel copper nanoparticle/carbon microsphere (Cu-NP/C) composites from Cu-loaded iminodiacetate functionalized styrene-divinylbenzene copolymer (ion exchanger). The method is simple, cost-effective, and easy to scale-up for large scale production. Microspheres have been characterized for their phase composition and surface morphology using various methods. Based on these observations, microspheres obtained by carbonising the ion exchanger at 600 °C for 4 hours have been selected for catalytic evaluation. The selected Cu-NP/C microspheres have demonstrated excellent catalytic activities for the reduction of 4-nitrophenol and for the one pot four component synthesis of medicinally important hexahydroquinolines. Due to the facile and economical synthesis, reusability, activity, separability, and eco-friendliness, Cu-NP/C microspheres are expected to replace expensive noble metals in certain catalytic applications.

## Conflicts of interest

There are no conflicts to declare.

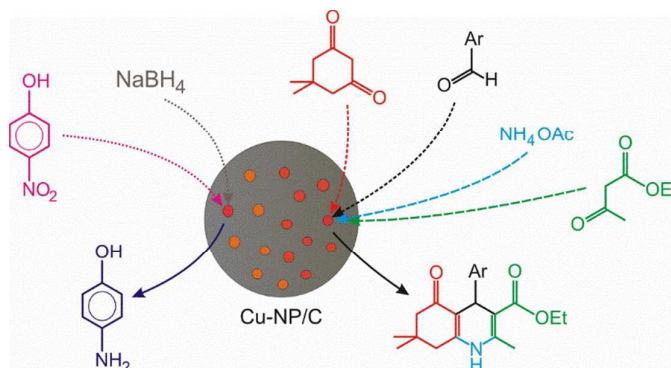
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## Notes and references

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**Table of content**

Carbon microspheres-supported copper nanoparticles were synthesized, characterized, and applied for the reduction of 4-nitrophenol and for the synthesis of hexahydroquinolines.