Copper micro/nanoparticles based catalytic conversion of 4-nitrobenzaldehyde to 4-nitrobenzoic acid

Rutuja Giri¹, Rachana Yadwade¹ and Balaprasad Ankamwar NanoBA

Bio-Inspired Materials Research Laboratory, Department of Chemistry, Savitribai Phule Pune University (Formerly University of Pune), Ganeshkhind, Pune-411007, India

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E-mail: nanoba.0000@gmail.com

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Abstract

Copper nanoparticles (CuNPs) have generated a great deal of interest in recent years, especially in catalysis are one of the promising materials in the advancement of copper-based technological applications. We synthesized copper nanoparticles through chemical reduction method using L-ascorbic acid at two different quantities and their spherical and flower like morphologies revealed by FE-SEM. This study also augmented with the catalytic conversion of 4-nitrobenzaldehyde to 4-nitrobenzoic acid using stated copper nanoparticles as a heterogeneous catalyst. Kinetic studies on the conversion of 4-nitrobenzaldehyde to 4-nitrobenzoic acid with time intervals of 30 min up to 180 min revealed the time required for the completion of the reaction.¹ ¹H NMR corroborated the product so obtained by the use of CuNPs as a catalyst, and ATR-IR analysis. A simple method of melting point exploited here to confirm the final product is a value-added. Thus, this simple analytical tool can boost the morale of researchers with limited resources in graduate and post-graduate laboratories.

Introduction

Synthesis protocol and catalytic activity of nanoparticles (NPs) are entitled with immense importance for chemical processes, exploited in the industry and academia [1, 2]. The alterations in the surface area modulates unique characteristics regarding electrons energy extent, electrons conversions, magnetism, temperature required for the phase transfer, melting points and the compatibility of copper nanoparticles with different polymers, organic and biological components. Because of these characters, copper nanoparticles are useful in catalysis, sensing, imaging [3]. There is a difference between properties of nanoparticles and the bulk materials because of the varied dimensions, shapes of nanoparticles which have distinctive quantum properties. Copper is present in a substantial amount in nature, economical, easy and workable ways of synthesis of copper nanoparticles making the copper nanoparticles attractive [4, 5]. The presence of high surface area makes copper nanoparticles catalytically very strong. The nanosized copper nanoparticles with high porosity helps to get the high yield in a short period [6]. Size and shape-controlled synthesis protocols play a very important role in copper-based catalysis [1, 2].

Few representative methods for the synthesis of copper nanoparticles include microemulsion techniques [7], sonochemical methods [8], metal vapour synthesis [9], laser ablation [10], radiation methods [11], vacuum vapour deposition [12], thermal decomposition [13] and chemical reduction [14, 15]. Amongst all these synthesis procedures most popular procedure is based on ‘chemical reduction’, since it is simple, economical and helpful in terms of size and shape selectivity. Many reactions are carried out in aqueous media because of its low-cost, eco-friendly, and support large-scale production. Nonetheless, the chemical reduction of Cu is challenging because it is less stable than copper oxides because of its surface oxidation during synthesis. Cu gets oxidized easily by dissolved oxygen in the reaction system, despite the use of strong reducing agents [16]. The prevention of oxidation during synthesis in an..
aqueous medium is essential. Many approaches were proposed during the last several years, including non-aqueous systems to replace aqueous systems. However, lower solubility of Cu precursors and other reagents in organic media limits this approach. The stabilizing agents such as oleic acid [17], gelatine [18] can resolve this issue up to a certain extent, if that provides complete coverage of the surface of particles. Different strategies are exploited to explore possible chemical and physical properties of copper nanoparticles, which have been creditable for the surge of interest in copper based nanoparticles and their catalytic utilization. Moreover, copper is a 3d transition metal which has phenomenon chemical and physical characteristics [19]. It has a broad range of oxidation states such as Cu$^0$, Cu$^{+}$, Cu$^{2+}$, Cu$^{3+}$ and thus can undergo a variety of reactions via one and two–electron pathways [3]. Copper-based nanocatalyst’s, unique characteristics and properties hold promising nanotechnologies such as catalytic organic transformations, electrocatalysis, and photocatalysis [20–26]. Among the popularly used metals for the catalytic activity such as palladium and platinum; copper is non-toxic and low-cost. Therefore, it is the most competitive material in catalytic reactions [17]. The control on the size and shape of copper micro/nanoparticles is a key reason in various synthesis protocols that depend on surface sensitivity towards the oxidation of copper [27]. Few researchers attempted earlier to keep control on size, shape, and surface properties which include the thiol capping agent [27], organic encapsulation in an aqueous phase [28]. Even so, limited monodispersity and susceptibility to oxidation stay intact [27].

Despite the above-listed limitations in the synthesis of Cu micro/nanoparticles, the key challenge would be to get benefit either as ready Cu and or Cu oxides in catalytic reactions. To overcome this kind of hindrance, we attempted to exploit as prepared Cu/Cu oxide micro/nanoparticles in the organic transformation of 4-nitrobenzaldehyde to 4-nitrobenzoic acid.

Copper nanoparticles are synthesized by chemical reduction method using L-ascorbic acid as a capping agent with two different volumes resulting in interesting shapes. We tested as prepared nanoparticles for catalytic conversion of 4-nitrobenzaldehyde to 4-nitrobenzoic acid. The stated copper micro/nanoparticles were effective in the organic transformation of 4-nitrobenzaldehyde to 4-nitrobenzoic acid. The product 4-nitrobenzoic acid is confirmed by melting points. This method of copper-based catalytic transformation of 4-nitrobenzaldehyde to 4-nitrobenzoic acid using a simple method of melting point has been value-added to boost the morale of researchers with limited resources.

Materials and methodology

Chemicals and Instruments

All high-quality analytical grade chemicals were used in the study with no further purification. Copper chloride dihydrate (CuCl$_2$.2H$_2$O) from Merck, L- Ascorbic acid (C$_6$H$_8$O$_2$), and Hydrazine Hydrate (H$_2$N$_2$.H$_2$O) from SDFCL, 4-nitrobenzaldehyde (C$_7$H$_5$O$_3$N) from Himedia, Hydrogen peroxide solution 30% (H$_2$O$_2$) from Merck, Ethanol from Merck were used as received. We prepared standard solutions in Milli-Q water.

UV–vis spectroscopy (Shimadzu dual-beam spectrophotometer; model UV-1800, 240 V), Powder x-ray diffraction (Bruker axs; model D8 Advance), Field emission scanning electron microscopy (JEOL model JSM–6360 A instrument) analysis were performed using models as stated. ATR-IR analysis was performed by Platinum ATR Tensor 37 instrument, $^1$H NMR studied using Bruker Ascend 400 MHz, TGA analysis was carried out from room temperature ~30 $^\circ$C to 1100 $^\circ$C with heating rate of 10 $^\circ$C per min in the nitrogen (N$_2$) atmosphere using TA-SDT 650 instrument (TA Instruments Trios V4.4.0.41128).

Synthesis of copper nanoparticles

We carried synthesis of CuNPs using chemical reduction method. Copper (II) chloride dihydrate used as a precursor salt, hydrazine hydrate as a mild reducing agent and L-ascorbic acid as a stabilizer. As we stated above, the control on the size and shape of copper micro/nanoparticles is the focused issue in various synthesis protocols that depends on the sensitivity of copper towards surface oxidation [27]. Here, we used L-Ascorbic acid in two different quantities as ascorbic acid, which can control the shape and size of CuNPs and acted mostly as capping/stabilizing agent; details are as subjoin below.

Method I (M1)

9 ml of 10mM L-Ascorbic acid solution added to 250 ml of 1 mM copper (II) chloride dihydrate solution as prepared using Milli-Q water followed by the addition of 150 ml of 8% hydrazine hydrate with stirring at the rate of 800 rpm on the magnetic stirrer. The colour of the solution changed from pale blue to brown. The stated solution kept undisturbed for 24 h. After 24 h, we observed the partially settled and partially suspended particles in the solution. This observation prompted us to test both; hence we separated supernatant by pipetting without disturbing settled particles. The supernatant was further centrifuged (12000 rpm, 30 min) to collect copper nanoparticles. We then dried the particles in vacuum desiccators (M1).
Method II (M2)
Here for M2, an 18 ml of 10mM L-Ascorbic acid solution added in the reaction mixture, instead of 9 ml, the rest of the procedure remains as described above for M1.

Characterization of copper nanoparticles
We divided the resulting solution into two portions, upper layer separated by pipetting and leaving settled particles undisturbed. Thus obtained upper layer of the solution was further separated into supernatant and pellet by centrifugation and tested by UV–vis spectroscopy on Shimadzu dual-beam spectrophotometer. The pellet was further characterized and exploited as a catalyst. X-ray diffraction (XRD) identified the crystalline nature of the pellet of copper nanoparticles (CuNPs). The multiple layered sample of copper nanoparticles was prepared by a drop coating on a glass slide and followed by air drying. We tested it for XRD on Bruker axs instrument operated at a radiation voltage of 40 kV and the current of 40 mA along with CuKα radiation (λ = 1.5406 Å). The morphological aspects of synthesized CuNPs revealed through Field emission scanning electron microscopy (FE-SEM) using a JEOL model JSM–6360 A instrument operating at an accelerating voltage of 20 kV. We identified the functional groups involved in the synthesis of CuNPs using Attenuated total reflection-infrared spectroscopy (ATR-IR) on the Platinum ATR Tensor 37 instrument.

Catalytic conversion of 4-nitrobenzaldehyde to 4-nitrobenzoic acid
Synthesis and characterization of copper nanoparticles
100 mg of 4- nitrobenzaldehyde was separately dissolved in two sets of 10 ml of ethanol, followed by additions of 0.01 mg of Cu nanoparticles and designated as M1 and M2. Then, 5 ml of 30% hydrogen peroxide added in each portion. We divided the resulting solution into two portions, upper layer separated by pipetting and leaving settled particles undisturbed. Thus obtained upper layer of the solution was further separated into supernatant and pellet by centrifugation and tested by UV–vis spectroscopy on Shimadzu dual-beam spectrophotometer. The pellet was further characterized and exploited as a catalyst. X-ray diffraction (XRD) identified the crystalline nature of the pellet of copper nanoparticles (CuNPs). The multiple layered sample of copper nanoparticles was prepared by a drop coating on a glass slide and followed by air drying. We tested it for XRD on Bruker axs instrument operated at a radiation voltage of 40 kV and the current of 40 mA along with CuKα, radiation (λ = 1.5406 Å). The morphological aspects of synthesized CuNPs revealed through Field emission scanning electron microscopy (FE-SEM) using a JEOL model JSM–6360 A instrument operating at an accelerating voltage of 20 kV. We identified the functional groups involved in the synthesis of CuNPs using Attenuated total reflection-infrared spectroscopy (ATR-IR) on the Platinum ATR Tensor 37 instrument.

Results and discussion
Synthesis and characterization of copper nanoparticles
We have already elaborated the outlined synthesis of CuNPs in aforementioned materials and methods. The principal feature signatures of CuNPs formation indicated due to change in color from pale blue to brown. The brown color appearance of CuNPs is mainly because of the free electrons present on the metal surface established resonance with the electromagnetic field. The synthesized CuNPs studied by optical measurements using UV–vis spectroscopy over the wavelength range of 200–1100 nm. Enhanced nonlinear optical property is a characteristic feature of copper nanoparticles with the absorbance in the visible region [29, 30]. Figure 1(a) shows the peaks around 585 nm and 581 nm for M1 pellet and M1 supernatant respectively, whereas figure 1(b) at around 584 nm for M2 pellet and 588 nm for M2 supernatant. The CuNPs shows the surface plasmon resonance (SPR) between 550–650 nm [31]. This supports and indicates the formation of copper nanoparticles.

XRD was used to study the crystalline nature of copper nanoparticles (M1 and M2) (figures 2 and 3). Figure 2 presents the powder XRD pattern of as-synthesized CuNPs. In figure 2(a) peaks observed at 2θ values of 43.28°, 50.32° and 74.1° which are consistent with Bragg’s reflections of (111), (200), and (220). We compared these peaks with the standard JCPDS File No. 03–1005 for the XRD of the pure fcc (face-centered cubic) metallic copper and matching with it.

In figure 2(b) peaks observed at 2θ values of 43.24°, 50.42°, and 74.2° relate to (111), (200), and (220) planes of metallic copper. These three peaks were also similar with those of the standard JCPDS File No. 03–1005 for the standard spectrum of the pure fcc (face-centered cubic) metallic copper. This confirms that the zero–valent CuNPs (Cu0) synthesized in the chemical reduction stage. The diffraction patterns of powder XRD confirm face-centered cubic (fcc) centered copper nanoparticles.

Figure 3 shows the typical surface morphology of CuNPs obtained by FESEM. The surface morphologies of the CuNPs were revealed by FESEM (figures 3 and 4). We observed the range of size for M1 nanoparticles as 780 to 3410 nm while it was 133–7045 nm for M2 nanoparticles. Moreover, they were about spherical and with a flower like morphology. Besides, we observed it these nanoparticles were overlapping with each other, thus forming aggregates in settled type.
ATR-IR was used to study the interactions between different chemical components and the variation in the chemical composition of the reaction mixture. ATR-IR spectra from pure CuCl₂, hydrazine hydrate, hydrogen peroxide, L- ascorbic acid, M₁ CuNPs, M₂ CuNPs recorded in figure 5. The peaks were observed at the 1601.75 cm⁻¹ and 1261.06 cm⁻¹ for the C=C double bond and an enol-hydroxyl group of L-ascorbic acid. The standard values of wavenumbers for the C=C double bond are between 1600 cm⁻¹–1680 cm⁻¹. The hydroxyl groups show the wavenumbers of 2500 cm⁻¹ to 3400 cm⁻¹. The main peaks observed for M₁ nanoparticles are 607.82 cm⁻¹, 807.70 cm⁻¹, 1362.53 cm⁻¹, 1461.72 cm⁻¹, 2121.90 cm⁻¹, 3231.03 cm⁻¹. The peaks observed at 1461.72 cm⁻¹, 2121.90 cm⁻¹ signify C-H deformation and C≡C stretching existing in alkynes. The peak at 3231.03 cm⁻¹ corresponds to primary N-H stretching while peaks at 607.82 cm⁻¹, 807 cm⁻¹, 1362.53 cm⁻¹ related to an aromatic ring, C-H stretching, –COO group of acids. In case of M₂ nanoparticles, ATR-IR peaks observed at 902.99 cm⁻¹, 1076.83 cm⁻¹, 3281.76 cm⁻¹, 1076.83 cm⁻¹, 2149.76 cm⁻¹, 3568.98 cm⁻¹. The peak at 902.99 cm⁻¹ confirms C=N stretching as occurs in amines and C–O stretching found in primary alcohols, vinyl, and aliphatic ethers. The peaks at 2149.76 cm⁻¹, 3568.98 cm⁻¹ depict C≡C stretching group and hydroxyl groups. These mentioned peaks compared with the prominent peaks observed in copper chloride, hydrazine

Figure 1. UV–vis absorption spectra recorded supernatant (a) (1) and pellet (2) of M₁ copper nanoparticles and (b) supernatant (1) and pellet (2) of M₂ copper nanoparticles.
hydrate, hydrogen peroxide, L-ascorbic acid. The Predominant peaks observed in ATR-IR of copper chloride are 915.81 cm$^{-1}$, 1479.27 cm$^{-1}$, and 2149.91 cm$^{-1}$. The prominent peaks of hydrazine hydrate noticed at 1077.17 cm$^{-1}$ and 3285.26 cm$^{-1}$. The predominant peaks which are depicted in ATR-IR of hydrogen peroxide are 1076.95 cm$^{-1}$ and 3249.45 cm$^{-1}$, whereas the peaks observed in pure L-ascorbic acid are 621.60 cm$^{-1}$, 818.62 cm$^{-1}$, 1314.30 cm$^{-1}$, 2159.84 cm$^{-1}$ and 3577.73 cm$^{-1}$. The shifts in the wavenumbers of these functional groups to the lower side indicate an association of these functional groups with copper nanoparticles [32, 33]. The L-ascorbic acid plays a vital role as stabilizer, and hence it reveals the interactions with the synthesized CuNPs. The peaks between 3100 cm$^{-1}$ to 3500 cm$^{-1}$ reveal the interactions of hydrazine hydrate with the CuNPs. The peaks at 1314.30 cm$^{-1}$ and 1601.75 cm$^{-1}$ represent the enol hydroxyl groups and C=C bond in ATR-IR of pure L-ascorbic acid (figure 5(d)).

After the reaction, ATR-IR of M1 and M2 CuNPs show hydroxyl, carbonyl groups and –COO groups of acids. From these results, we conclude it that ascorbic acid plays the vital role as a stabilizing agent. The ascorbic acid prevents Cu nanoparticles from oxidation, as ascorbic acid is an antioxidant. The capping of ascorbic acid over the copper nanoparticles offers stability to the nanoparticles. The hydroxyl groups in ascorbic acid are mainly responsible for the antioxidant nature of ascorbic acid. Thus, they protect the nanoparticles from the oxidation. There are few reports on the role of L-ascorbic acid as a reducing agent [1]. The intensity of peaks of functional groups of ascorbic acid is much more prominent than the peaks of functional groups of hydrazine hydrate. Thus, it concludes that hydrazine hydrate plays a vital role as a mild reducing agent and stabilizing agent.

Figure 2. XRD pattern of a solution–cast film of the (a) M1 pellet and (b) M2 pellet of copper nanoparticles.
The L-ascorbic acid plays a role of not only stabilizing agent but also acts as the source of protons and electrons for the synthesis of Cu\textsuperscript{0} nanoparticles\textsuperscript{[34–38]}.

Catalytic conversion of 4-nitrobenzaldehyde to 4-nitrobenzoic acid

Wide array of organic conversions can be catalytically carried out by copper nanoparticles. The nanoparticles are potentially useful because of conduction of reaction under green and sustainable manner. Oxidation is one of the vital processes in chemistry which is helpful in the designing and development of new useful products\textsuperscript{[39]}.

We used the copper nanoparticles in the organic transformation of 4-nitrobenzaldehyde to 4-nitrobenzoic acid as a catalyst. The analysis of product 4-nitrobenzoic acid carried out by \textsuperscript{1}H Nuclear magnetic resonance (NMR) spectroscopy (NMR) of 4-nitrobenzoic acid, ATR-IR, melting points of products at different time intervals.

The thermogravimetric (TGA) analysis results of M1 pellet and M2 pellet of copper nanoparticles are as shown in figures 6(a) and (b). This analysis helps to measure the changes in sample composition, thermal stability and purity of materials. The TGA helps in the study of materials' thermal behavior. Using TGA analysis of CuNPs confirmed the stability of nanoparticles up to the temperature 180 °C. Weight loss up to 180 °C was in the range from 5 to 10%, hence it is reasonably well stable up to 180 °C.

The product 4-nitrobenzoic acid formed, on 180 min of the reaction between M1 CuNPs, M2 CuNPs, and 4-nitrobenzaldehyde, was evaluated by \textsuperscript{1}H NMR since it is important for determination of structure of molecules\textsuperscript{[40]}. The chemical shift in \textsuperscript{1}H NMR data of M180, M2180, and (without nanoparticles) WNP180 appeared at 8.5. The chemical shift near 12 to 13 indicates a carboxylic group of acids. In the case of M2 copper nanoparticles, the chemical shift near 13,657 shows the carboxylic group. This signature supports the formation of 4-nitrobenzoic acid. Figures 7(b) and (c) indicate the \textsuperscript{1}H NMR spectrum of 4-nitrobenzoic acid with M1 and M2 CuNPs, respectively. Therefore, CuNPs can convert 4-nitrobenzaldehyde to 4-nitrobenzoic acid\textsuperscript{[32]}.

\textbf{Figure 3.} Representative FESEM images of copper nanoparticles from M1 pellet obtained from supernatant at (a) lower, (b) higher, (c) regular magnification.
The conversion of aldehyde to carboxylic acid is caused because of oxidation of aldehyde (–CHO) to acid (–COOH). The carbonyl group of carboxylic acids has an intense stretch from the range of 1760 cm\(^{-1}\) to 1655 cm\(^{-1}\). The band between 3100–2850 cm\(^{-1}\) is because of the C–H stretching. The band at 3567.03 cm\(^{-1}\) in M2180 is due to O–H stretching in carboxylic acid, which indicates the formation of 4-nitrobenzoic acid using M2 nanoparticles. A band of 1731.3 cm\(^{-1}\) express the presence of a carbonyl group of the carboxyl group of acids (figure 8(e)). The presence of the O–H stretch band at 3548.11 cm\(^{-1}\) was observed when the reaction was carried out by M1 CuNPs (figure 8(d)). The same with M1 nanoparticles in which O–H stretching is observed at 3548.11 cm\(^{-1}\) and for WNP we observed it at 3521.77 cm\(^{-1}\). The ATR-IR spectra of product, 4-nitrobenzoic acid formed by the use of CuNPs and compared with standard 4-nitrobenzoic acid, it confirms that CuNPs can convert 4-nitrobenzaldehyde to 4-nitrobenzoic acid as a suitable catalyst. The –CHO functional group of 4-nitrobenzaldehyde get oxidized to –COOH and formed 4-nitrobenzoic acid [32, 33] as revealed and supported by ATR-IR.

We measured the melting points of the products which formed at various time intervals to confirm the time required for formation of 4-nitrobenzoic acid. The complete conversion of 4-nitrobenzaldehyde to 4-nitrobenzoic acid was observed after 180 min in the presence of a catalyst. Conversely, the reaction in absence of CuNPs did not complete within 180 min. Therefore, the use of CuNPs enhances the conversion of 4-nitrobenzaldehyde to 4-nitrobenzoic acid. The melting point of pure 4-nitrobenzoic acid is 237°C [41]. Table 1 represents the melting points of final products in crude and on crystallization (4-nitrobenzoic acid)
Figure 5. ATR-IR spectra recorded from (a) pure CuCl₂, (b) hydrazine hydrate, (c) hydrogen peroxide, (d) L-ascorbic acid, (e) M1 CuNPs, (f) M2 CuNPs.

Figure 6. TGA-DTA pattern of a) M1 pellet and b) M2 pellet of copper nanoparticles.
which are formed through the conversion of 4-nitrobenzaldehyde to 4-nitrobenzoic acid with copper nanoparticles both (M1 and M2). Therefore, it can be concluded that the CuNPs can efficiently convert 4-nitrobenzaldehyde to 4-nitrobenzoic acid. Therefore, CuNPs could be the best measures as catalysts for organic conversions at the laboratory level without the use of high-end instruments.

**Conclusions**

We used the chemical reduction method for the synthesis of copper nanoparticles. FESEM revealed particle sizes for M1 between 780 nm to 1670 nm, and 2045 nm to 3410 nm and for M2 in the range from 7045 nm to 8410 nm and 133 nm to 166 nm. The copper nanocomposites are spherical and flower-like shaped. UV–visible spectrum affirms the preliminary signatures of copper nanoparticles formation. The synthesized nanoparticles
Figure 8. ATR-IR spectra of (a) 4-nitrobenzaldehyde, (b) 4-nitrobenzoic acid, (c) without nanoparticles, (d) M1180 4-nitrobenzoic acid and (e) M2180 4-nitrobenzoic acid.
M1 and M2 efficiently used for conversion of 4-nitrobenzaldehyde to 4-nitrobenzoic acid and confirmed by the amenable technique of melting point, that can be performed in any undergraduate and postgraduate laboratories. The conversion of 4-nitrobenzaldehyde to 4-nitrobenzoic acid achieved within 3 h, which has been confirmed by melting point determination corroborated by ATR-IR and $^1$H NMR.

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**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

**Notes**

The authors declare no competing financial interest.

**ORCID iDs**

Balaprasad Ankanwara NanoBA https://orcid.org/0000-0002-9986-6298

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