

Fabrication and Corroboration of Cupric Chloride Nanoparticles with Tetrabutylammonium Bromide (TBAB) – Itaconic Acid Based Deep Eutectic Solvent (DES)

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Abstract: Deep Eutectic Solvents (DES), as a new class of green solvents, have achieved attentiveness in the last twenty years because of their stupendous applicability in technological processes, their preparation simplicity, and their high bioadsorbability and benign nature towards environment. Recently, DESs have been found as a multipurpose media to synthesize a wide range of inorganic nanomaterials. This present work summarizes the application of tetrabutylammonium bromide (TBAB)-itaconic acid based DES as environmentally benign medium to synthesize cupric chloride nanoparticles at low cost and in easy steps. The upgrade reaction conditions to prepare cupric chloride nanoparticles were mixing copper chloride, (5R)-[(1S)-1,2-Dihydroxyethyl]-3,4-dihydroxyfuran-2(5H)-one, and TBAB-itaconic acid based DES for 1 hour and 30 minutes at ambient temperature in the accompany of polyvinylpyrrolidone (PVP). Characterization of prepared samples using FE-SEM - field emission scanning electron microscopy, EDX - energy dispersive x-ray analysis, and TEM- transmission electron microscopy showed that cupric chloride nanoparticles obtained are of size in the range of 11 nm to 29 nm.

Keywords: Cupric chloride nanoparticles, FE-SEM, TEM, EDX, TBAB-itaconic acid based deep eutectic solvent (DES)

I. INTRODUCTION

Nanomaterials that are purposely synthesized are of four genres such as carbon-based, metal-based, arborols, and nanocomposites. In the present century, metal nanoparticles especially copper nanoparticles (CuNPs) have been intensively prepared and characterized for their extensive applications in various fields such as photochemical catalysis, electrochemical sensing, even in dentistry and solar/photovoltaic energy conversion [1-5].

The fabrication of CuNPs has been carried out by using various techniques such as radiolysis, sono-chemistry, photochemistry, direct chemical reduction, reversed micelles, seeding growth, and micro-emulsion [6–8] or even via the liquid phase plasma method [9]. In CuNPssynthesis, the utmost importance is on control of their particle shape, and distribution of its size. Templating agents can be used to handle the shape and proportion of particles. Use of templating agents such as Trihydroxidoboron, 2-Hydroxypropane-1,2,3-tricarboxylic acid, and (5R)-[(1S)-1,2-Dihydroxyethyl]-3,4-dihydroxyfuran-2(5H)-one, cholesteric liquid crystals, and different types of surfactants as was reported [10, 11, 12].

Therefore, in our research work, a unique solvent called deep eutectic solvents (DES) which were developed 15 years ago by Abbott [13] due to their unique properties that are budget-friendly, easy to synthesize, and have better biocompatibility has been applied. DES have twin role as a reaction forum and a structure-directing agent (SDA). DESs usually consist of a hydrogen bond acceptor (HBA) and hydrogen-bond donor (HBD) which form a homogenous liquid when heated and remain liquid at room temperature, having melting point lower than starting material used [14] [15]. Various nanomaterials, such as zeolite analogs can be synthesize by DES [16], silver nanoparticles of narrow size 4.5 nm [17], gold– palladium core–shell nanoparticles [18], platinum–cobalt nanocrystallites [19], magnetic nanoparticles of Fe₃O₄ [20], multi-walled carbon nanotube [21] [22], nanostructured semiconductors [23] [24] [25], and DNA

nanostructures [26]. Deep eutectic solvents shows various application in the field of nanotechnology which has been reviewed in [27] [28]. In various fields, cupric chloride is widely used as the catalyst for organic and inorganic reactions [29] [30] [31]. We have synthesized the CuNPs by using cupric chloride, ascorbic acid, and TBAB-itaconic acid based DES in presence of polyvinylpyrrolidone (PVP) at ambient temperature.

II. EXPERIMENTAL SECTION

Materials:

Tetrabutylammonium bromide (TBAB), with 98% purity, was purchased from Amrutlal Bhurabhai CO. PVT Limited Mumbai, Maharashtra. Itaconic acid with 98% purity, cupric chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), and (5R)-[(1S)-1,2-Dihydroxyethyl]-3,4-dihydroxyfuran-2(5H)-one was purchased from K.J Enterprises Mumbai, Maharashtra

Synthesis of CuNPs:

By selecting tetrabutylammonium bromide (TBAB) and itaconic acid as HBA and HBD in a 1:1 molar ratio and blending the two components at 86°C for 30 mins on a heating mantle with magnetic stirrer until a unvarying monotonous colorless liquid was formed as TBAB-itaconic acid based DES [32]. It remained in liquid state at room temperature after 24 hours. To 7 cm^3 DES, 1.1116 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.6877 g vitamin C were added in presence of PVP. We have selected the presence of PVP in DES [33] since it controls growth rate of nanoparticles and balances the superficial of particles. The concoction was stirred mildly using a magnetic stirrer at ambient temperature for 1 h 30 minutes. To this, 25 cm^3 diluted muriatic acid (0.1 mol. dm^{-3}) was added. After standing it for a 30 minutes a white insoluble solid strained out. The white solid sample was washed with ethyl alcohol and then dried to form dry solid to carry out its further analysis.

Characterization of the synthesized samples:

The primary inspection of the framework of composed cupric chloride nanoparticles were depicted by Field emission scanning electron microscopy (FE-SEM) of FEI QUANTA 200 F furnish with an Energy dispersive x-ray spectroscopy (EDX). The proportion of crystal sizes were carried out on TECNAI 12 G2 TEM Transmission electron microscope (TEM) at an accelerating voltage of 200 KV.

FE-SEM - Field emission scanning electron microscopy :

In Figures 1, 2, 3 and 4, the arranged samples were well-defined and display a in proportion spherical shape. Furthermore, the outcome confirm that the morphology and an assemblage of cupric chloride particles can be dominant by PVP more productively.

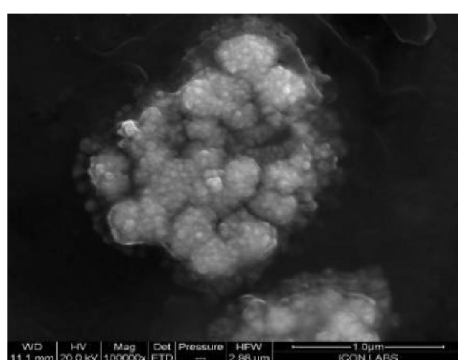


Figure 1.

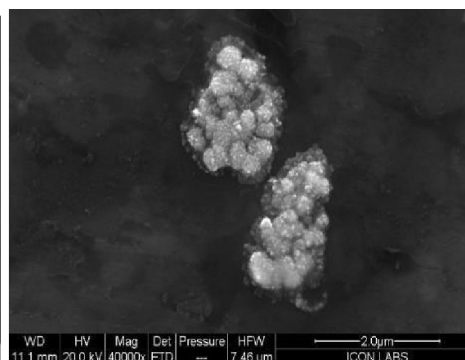


Figure 2

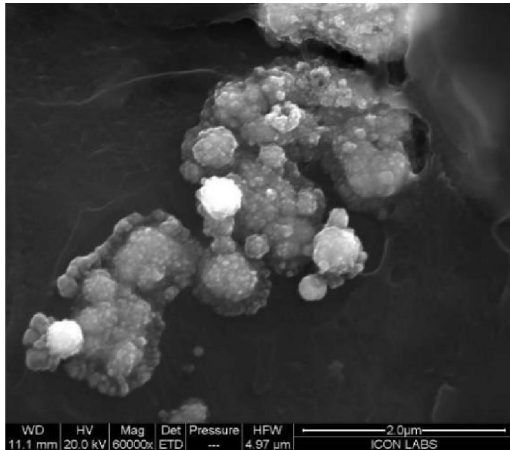


Figure 3.

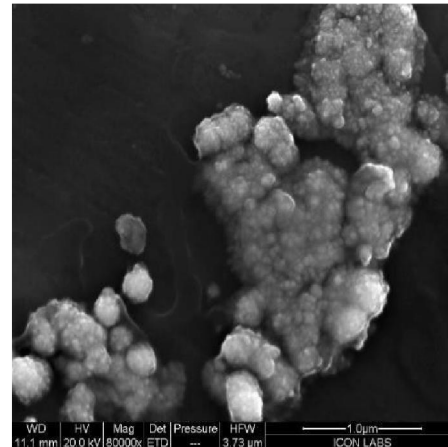


Figure 4.

Figure 1, 2, 3, & 4 illustrate sketch of FE-SEM of the as-prepared CuNPs.

TEM - Transmission Electron Microscopy :

Figure 5, and Figure 6 illustrate the typical TEM sketch of cupric chloride nanoparticles which are spherical and rod-shaped having particle sizes in the range of 11nm to 29 nm. Besides this, it can be committed that PVP could effectively combat the cupric chloride particle growth, making the size of cupric chloride nanoparticles much smaller.

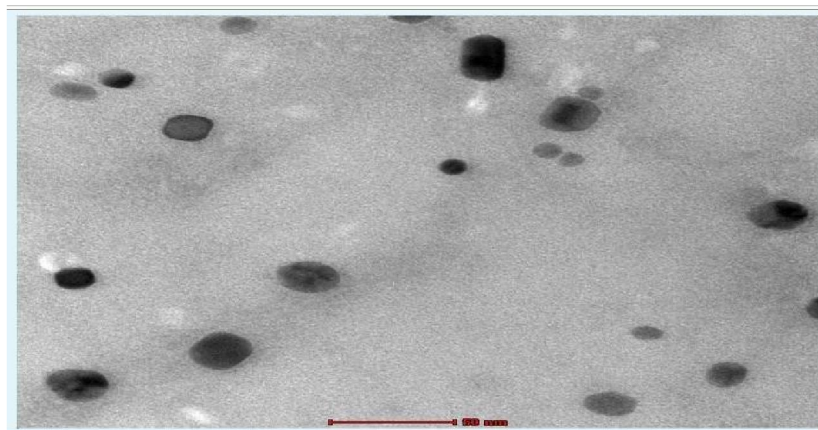


Figure 5. Illustrate the TEM sketch of spherical and rod-shaped CuNPs

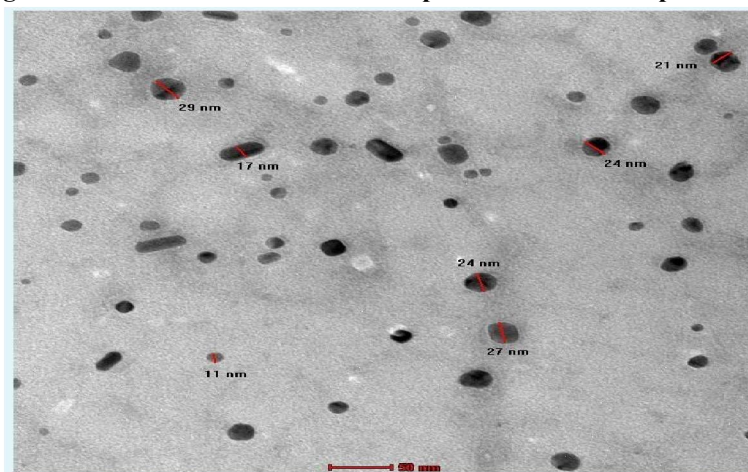


Figure 6. Illustrate the TEM sketch of 11 nm, 17 nm, and 21 nm – 29 nm CuNPs

EDX- Energy Dispersive X-Ray Analysis:

Figure 7. Illustrate the EDX spectrum of the assembled cupric chloride nanoparticles. Spectra manifest the peaks from Cu, Cl, O, and C. Table No. 1 declare that the Net. Int of cupric is 411.1 with high purity and lowest 3.3 % error. The carbon peaks which are visible in EDX spectrum are from carbon conductive tape used for fixing the sample and carrying out its analysis

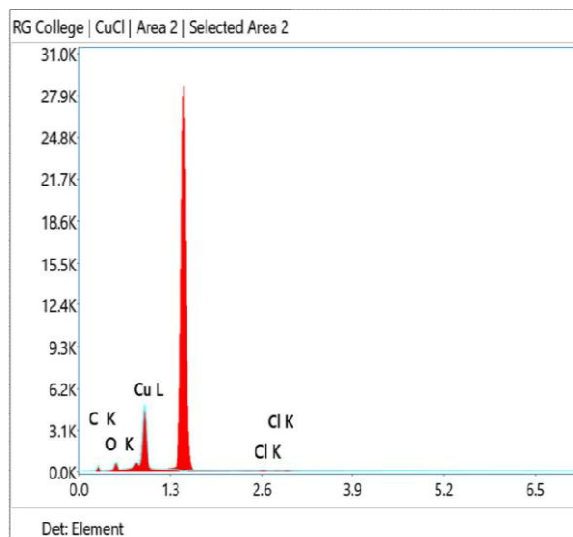


Figure 7. EDX spectrum of the as-prepared CuNPs

| Element | Weight% | MDL | Atomic% | Net Int. | Error% | R | A | F |
|---------|---------|------|---------|----------|--------|--------|--------|--------|
| C K | 36.6 | 1.67 | 64.3 | 71.1 | 13.1 | 0.8602 | 0.0736 | 1.0000 |
| O K | 14.8 | 0.88 | 19.5 | 110.0 | 12.9 | 0.8736 | 0.1087 | 1.0000 |
| Cl K | 0.5 | 0.24 | 0.3 | 15.9 | 37.2 | 0.9151 | 0.7439 | 1.0227 |
| Cu K | 48.1 | 0.94 | 16.0 | 411.1 | 3.3 | 0.9568 | 0.9889 | 1.0466 |

Table No. 1

III. CONCLUSION

The SEM, EDX, and TEM analysis results obtained showed that cupric chloride nanoparticles are formed successfully in presence of TBAB-itaconic acid based DES at comparatively lower temperatures and without the use of hazardous solvents. According to SEM, EDX, and TEM; CuNPs exhibited an approximately spherical shape and rod shape with an average size of about 11nm, 17 nm, and 21 nm to 29 nm range under the optimized reaction conditions. DESs provide a very simplified process that is easily manageable, innocuous, and sustainable. The reported procedure does not require the preparation of precursors or the use of highly corrosive acids and harmful reagents, which may be an advantage over other methods. Further investigation into the applications of these newly synthesized CuNPs is underway in our laboratory.

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