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RESEARCH PAPER

# Fabrication of oxides of copper-nickel bimetallic nano particle using *Zingiber officnale* extract: an eco-friendly approach for electrochemical application of glucose detection

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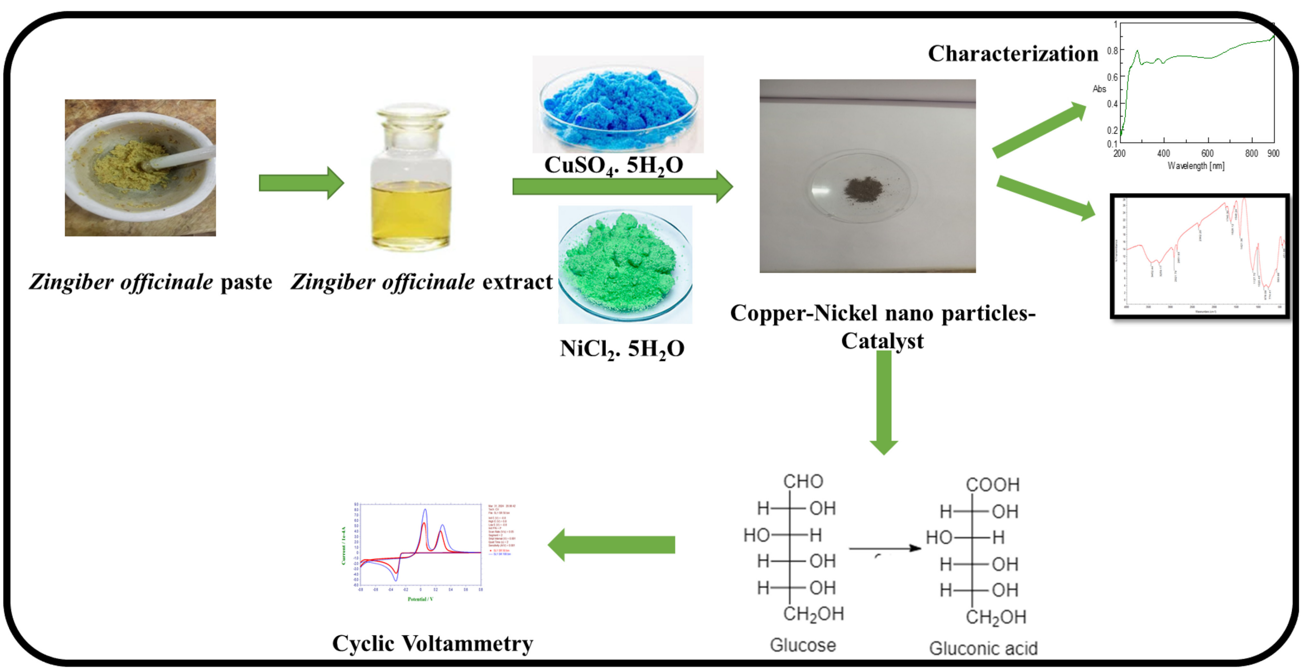
## Abstract

The oxidation of glucose's C1 position is more facile than the oxidation of its main or secondary alcohol functionalities when supported metal catalysts like Au, Pd, and Pt are present. Hence an efficient and economic green methodology of conversion of glucose to gluconic acid using copper-nickel bimetallic catalyst is carried out. *Zingiber officinale* extract is prepared which is used for the green synthesis of bimetallic copper-nickel catalyst. The bimetallic catalyst is used for the conversion of glucose to gluconic acid. The bimetallic nano particles are characterized using UV–Visible spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR). The peak in UV–Visible spectroscopy at 380 nm resulted as the plant molecules acted as reducing and capping agent for the conversion of copper and nickel oxides to nano composites. FTIR peaks are observed at 583 $cm^{-1}$ and 2362 $cm^{-1}$ which corresponds to CuO and NiO composites along with hydroxyl groups. The conversion of glucose to gluconic acid is confirmed by Cyclic Voltammetry which shows electrochemical activity between − 0.8 and + 0.8 V with current increase. The process can be utilized to develop biosensors for glucose detection.


### Graphical abstract




**Keywords** Green synthesis · Gluconic acid · Fourier transform infrared spectroscopy · Cyclic voltammetry · Biosensors

Extended author information available on the last page of the article

## Introduction

The unique geometrical architecture and mixing patterns of bimetallic nanoparticles (BMNPs) improve their functioning (Stamenkovic et al. 2007; Tao et al. 2008). They have increased catalytic activity, stability and selectivity over monometallic nanoparticles (Lim et al. 2009; Omori et al. 2011; Chen et al. 2005; Kyriakou et al. 2012). Certain chemical transformations that were not demonstrated by monometallic nanoparticles as catalysts can be carried out by bimetallic nanoparticles as catalysts. Due to the fact that bimetallic nanoparticles possess a particular fusion of two metals, each of which has a specific role to execute the overall response mechanism.

Gluconic acid can be produced biochemically by photochemical, electrochemical, or catalytic processes carried out in the presence of heterogeneous materials based on noble metals. Other metals, such as Cu, Ce, Ti, Mn, Fe, Ag, and Cr, have also been shown to be active for the oxidation of glucose to gluconic acid, in addition to Au, Pd, and Pt. Bimetallic catalysts are preferable to monometallic catalysts due to the synergistic effects of the chosen metals. Au-based catalyst, carbon supported Au-catalysts, Metal-oxide supported Au catalyst, bimetallic catalysts such as Pt–Pd bimetallic catalysts for the oxidation of glucose into gluconic acid is studied by Yan et al. (2020).

Zhang et al. (2021) discussed the base free glucose oxidation over structure-tailored heterogenous catalysts. He further discussed about the emerging oxidation method such as the ultrasound-assisted oxidation, microwave-assisted oxidation. Wenkin et al. (1996) have done the preparation of carbon-supported Bi-Pd catalysts for the selective oxidation of glucose into gluconic acid and discussed the major role played by the bismuth in this oxidation process.

Sandu et al. (2021) studied the relation between bismuth and Pd/Bi on supported Alumina in the glucose oxidation process. They confirm that the higher bismuth content for the conversion leads particle aggregation and enlargement which causes weaker bonding and results in particles washout. Further, they acclaim that higher bismuth content for the oxidation process leads low catalytic activity than Pd/Bi on supported alumina. The catalytic activity of trimetallic nanoparticles is studied Jagajjanani by Rao et al. (2015) and confirms that it would be an excellent catalyst for the glucose conversion process.

Liu et al. (2020) have experimented the one-pot aqueous oxidation of glucose and gluconic acid into tartaric acid using bimetallic Au/Pt catalysts in the presence of molecular oxygen. Further proved that, the structural and electronic reconfiguration leads C–C and C–H bond cleavage occur on bimetallic catalysts. Karski et al. (2003) have studied the catalytic properties of bimetallic Pd–Bi, Pd–Ti, Pd–Sn, Pd–Co catalysts supported on carbon and $SiO_2$ for the oxidation of glucose to gluconic acid. Further, the comparison of the catalysts has been discussed and proved that intermetallic compounds Bi-Pd increased the selectivity of catalysts.

Although various catalysts are used for the conversion of glucose to gluconic acid, the bimetallic catalyst using gold proved to be effective. Considering the cost and efficiency of the conversion, an economically feasible and efficient method is required for the process. The present work aims at achieving the fore mentioned facts for the conversion of glucose to gluconic acid.

## Materials and methods

The copper-nickel bimetallic nano particles are green synthesized using *Zingiber officinale* extract and it is used for the economically feasible conversion of glucose to gluconic acid.

### Preparation of *Zingiber officinale* extract

*Zingiber officinale* is washed throughly with deionized water. It is chopped and grinded with mortar pestle until it is made in to a paste. 200 ml of deionized water is added to the paste and it is boiled for 2 min at 60 °C. The boiled extract is centrifuged at 5000 rpm for 15 min. The supernatant is collected and filtered thrice. The resultant extract is maintained at 4 °C in refrigerator for the preparation of nanoparticles.

### Green synthesis of bimetallic Cu–Ni hybrid nanoparticles

5 gm of $CuSO_4$. $5H_2O$ and 5 gm of $NiCl_2.6H_2O$ are mixed and added to 100 ml of *Zingiber officinale* extract and the pH is maintained at 5.7. The mixture is now stirred in magnetic stirrer at 60 °C for 2 h. The color changes from green to dark brown which confirms the hybrid nanoparticles. It is centrifuged at 10,000 rpm for 20 min. The nanoparticles are washed with ethanol thrice and the product is kept in muffle furnace for 2 h at 500 °C to remove the volatile particles (Fig. 1). Thus, the nano particles are purified using centrifugation and solvent extraction method. The nanoparticles are characterized using UV–Visible spectrophotometry and Fourier-Transform Infrared Spectroscopy.

### Oxidation of glucose to gluconic acid

36 gm of Glucose is weighed and 100 mL water and the mixture is heated to 50 °C. Once the temperature is stabilized, the catalyst is added to the solution. The mixture

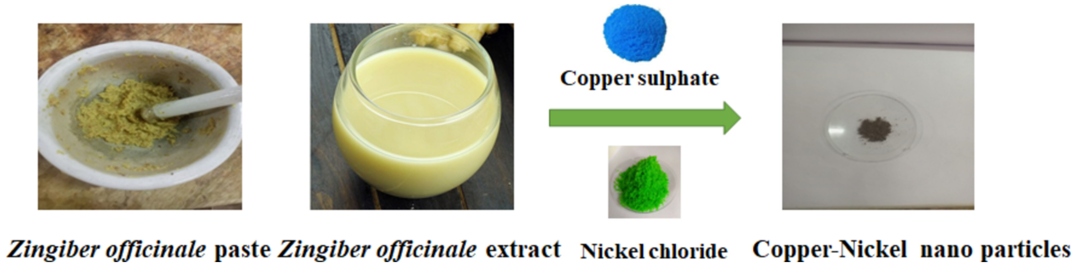



**Fig. 1** Green synthesis of bimetallic Cu–Ni hybrid nanoparticles

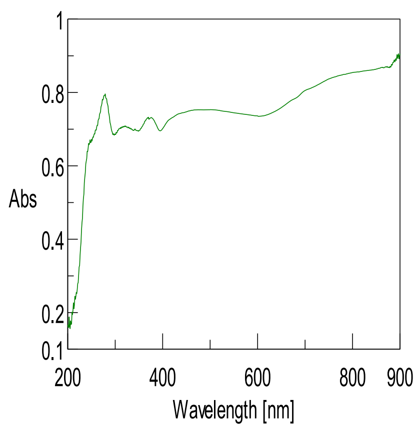



**Fig. 2** UV–Visible Spectrum of copper-nickel nano particles

is kept in the magnetic stirrer. The oxygen is introduced slowly for 2 h. The mixture is taken in vials one hours once for the Cyclic Voltammetry characterization. The mixture is kept in magnetic stirrer for 5 h.

### Cyclic voltammetry

Cyclic Voltammetry is done using Cyclic Voltammeter Instrument Model: CHI650C. The analysis is done after every hour of the reaction and also for the supernatant liquid produced at the end of the reaction.

## Results and discussion

In the present work, copper-nickel nanoparticles have been prepared by green synthesis and used for the conversion of glucose to gluconic acid. The characterization of copper-nickel nanoparticles is done using UV–Visible spectrophotometry and Fourier-Transform Infrared Spectroscopy.

### UV–visible spectroscopic analysis

The UV–Visible spectrum for the copper-nickel nanoparticles is shown in Fig. 2. In UV–Visible spectroscopy, a sample absorbs a certain wavelength and produces a characteristic absorption peak. This process requires UV–visible light with sufficient activation energy to stimulate electron migration to higher shells and subshells. UV–vis spectroscopy is frequently used to estimate the concentration of the seen sample, although it can only be used to identify a tiny part of chemical compounds.

Copper oxide and nickel oxide nano particles exhibit peaks at 340 and 320 nm respectively. Bimetallic nanoparticle synthesis exhibited a characteristic 380 nm peak. The peak below 300 nm proves the formation of bimetallic nano particle as reported by Parveen et al. (2022). Compounds like gingerols and their derivatives, which are found in the rhizome extract of *Zingiber officinale*, can aid in the stabilization and reduction of nanoparticles. The absorbance peaks are influenced by the plant extract and nanoparticle concentrations. It is evident that there is a direct relationship between absorbance peaks and the concentrations of $CuSO_4 \cdot 5H_2O$ and $NiCl_2 \cdot 6H_2O$ throughout the nanoparticle formation process.

### Fourier transform infrared spectroscopy (FTIR) analysis

Fourier Transform Infrared Spectroscopy plays the potential role in analyzing the functional groups of the plant extract in the reduction process of copper and nickel ions to nanoparticles (Fig. 3), FTIR spectroscopy is conducted in the spectrum region of 400 $cm^{-1}$ to 4000 $cm^{-1}$.

Stretching vibration peaks corresponding to O–H functional group is found at 3452 $cm^{-1}$, C–O, C=O and N–H functional groups are found at 1127 $cm^{-1}$, 1628 $cm^{-1}$ and 2921 $cm^{-1}$ respectively. The stretching vibrations of C–H is obtained at 1421 $cm^{-1}$and 2851 $cm^{-1}$ respectively. Peaks at 450 to 700 $cm^{-1}$ corresponds to CuO and NiO composites along with hydroxyl groups as reported by Parveen et al. (2022). The amine, hydroxyl, and carboxyl groups found in

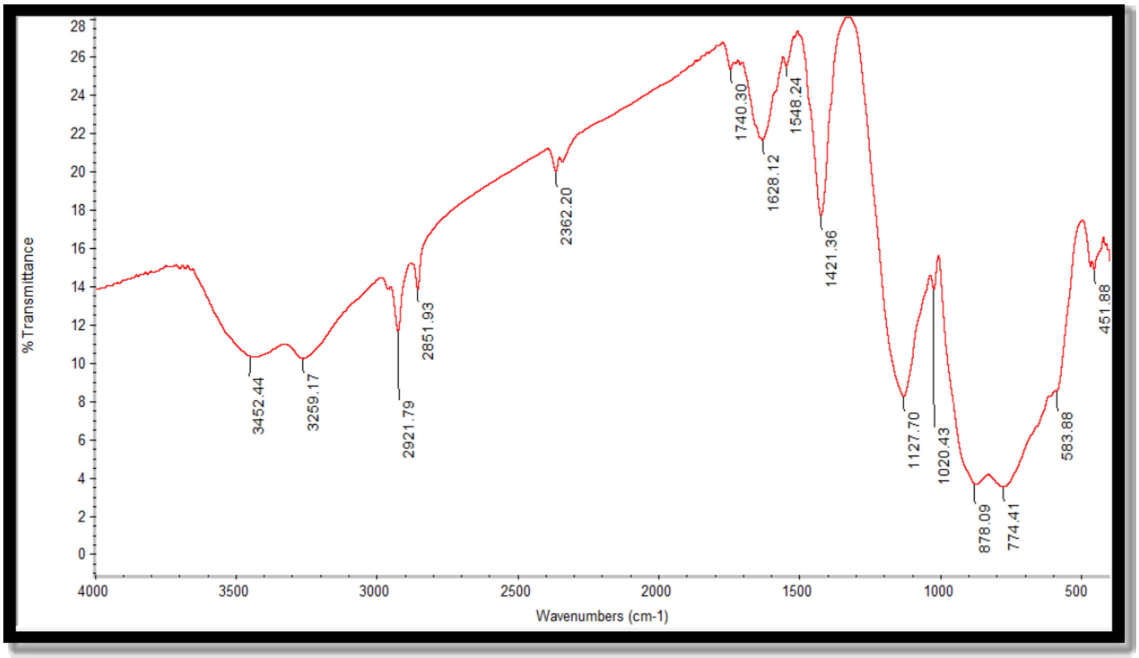



**Fig. 3** FTIR spectrum of copper-nickel nano particles

*Zingiber officinale* extract may contribute to the production of nanoparticles. When *Zingiber officinale* extract is used as a capping and reducing agent, the functional groups attached to these polymers and the proteinaceous components might be implicated in the reduction of metal ions to nanoparticles.

Our research indicates that functional groups such amides, carboxylic acid, amino acids, and hydroxyls contributed to the reduction of copper-nickel ions to Cu–Ni hybrid nanoparticles (Abdullah et al. 2022). These findings are in agreement with the results of Faisal et al. (2021), Usman et al. (2020) and Vaseghi et al. (2019).

## Cyclic voltammetry (CV) analysis

Cyclic voltammograms of copper-nickel catalyzed glucose at different hours of stirring and also for supernatant liquid acquired at low (50 mV $s^{-1}$) and high (100 mV $s^{-1}$) scan rate are shown in the Figs. 4, 5 and 6 respectively. G1 to

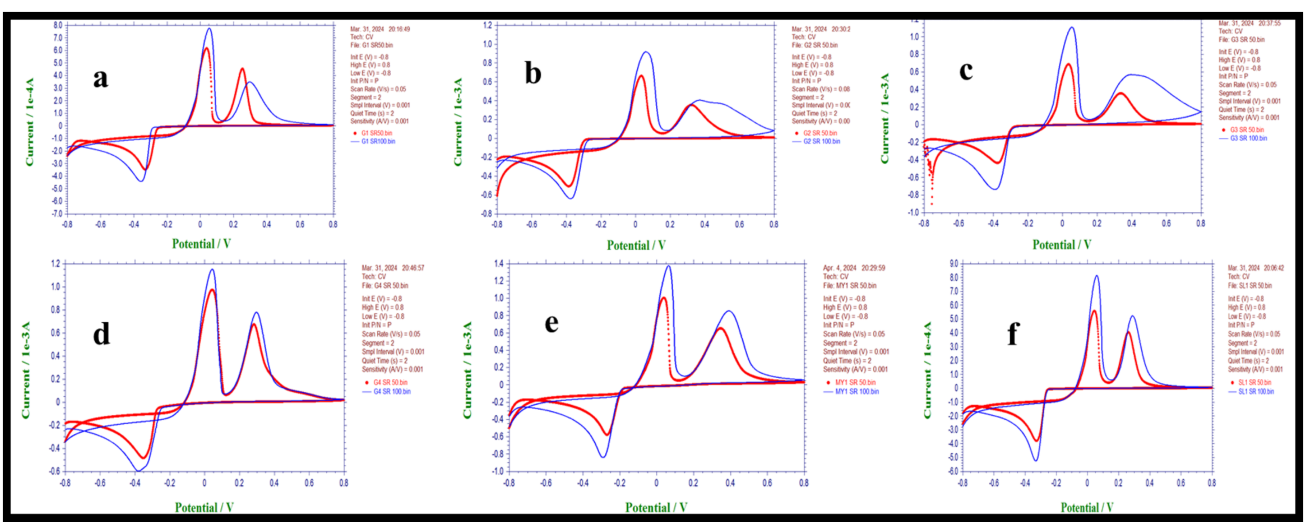



**Fig. 4** Cyclic Voltammograms for the conversion of glucose to gluconic acid: **A** after one hour, **B** after two hours, **C** after three hours, **D** after four hours **E** after five hours, **F** for supernatant liquids

G4 shows the cyclic voltammograms taken after 1, 2, 3 and 4 h of stirring. The electrochemical activity between − 0.8 and + 0.8 V with current increase implies the oxidation of glucose. All the voltammograms show an increase in potential from negative value to positive. The curves prove that the reaction is quasi reversible since the ΔEp values is not the same for anodic and cathodic curves.

The oxidation process involves two steps. The first step of oxidation occurs nearly at 0.1 V and further increase of potential results in the product in the second step. The first step may be the formation of intermediate on the surface of copper-nickel catalyst which on increasing potential produces the product. The second step occurs at more positive potential of 0.4–0.6 V with current of 0.6–0.7 mA at G4 that is after 4 h of stirring. The results are in agreement with the studies of formation of gluconic acid from glucose by Faverge et al. (2023). The specific capacitance after 2 h of stirring is found to be maximum with a value of 2.2647 F/g which insisted that the catalyst can be used as composite electrode with better power characteristics (Fig. 4).

The oxidation voltage is 0.4 V which shows the good catalytic activity of oxides of copper and nickel bimetallic nano particles. Copper oxide nano particles are electrochemically oxidized in alkaline condition to copper (III) which oxidizes glucose to gluconolactone and itself gets reduced to copper hydroxide. Gluconolactone is oxidized to stable gluconic acid by hydrolyzation process. The oxidation of Cu (II) to Cu (III) requires a voltage of 0.7 V whereas this conversion is produced at 0.4 V in the present work which aids in the conversion of glucose to gluconic acid in the presence of nickel oxide nano particles. The present study is in accordance with the study of glucose conversion using gold and CuO nano particles reported by Ali et al. (2024).

## Conclusion

The present work aims at producing efficient and cost-effective method for the conversion of glucose to gluconic acid using bimetallic catalyst copper-nickel hybrid nano composites. The bimetallic catalyst is prepared using green synthesis with the aid of *Zingiber officinale* extract which acts both as reducing and capping agent. The formation of hybrid nano composite is confirmed using UV–Visible spectrum with maximum absorbance at 380 nm and FTIR with corresponding peaks at 583 $cm^{-1}$ and 2362 $cm^{-1}$ respectively. The Cyclic Voltammetry studies confirm the reaction with increasing potential from negative to positive.

**Author contributions** Dr. M. A. Sabitha has contributed to the project administration and writing of the manuscript, Dr. A. Syed Mohamed has contributed to the planning of the project.

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## Declarations

**Competing interest** The authors declare no competing interests.

**Ethical approval** The paper accurately and thoroughly reflects the authors' own research and analysis. We certify that this paper is unique, hasn't been published anywhere else, and isn't being considered for publication anywhere else.

**Consent to participate** Informed consent was obtained from all individual participants included in the study.

**Consent for publication** The participant has consented to the submission of the work to the journal.

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