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Green Route Fabricated Electro-active CuO Nano Clusters from Natural Product for Multiplexed Applications

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Herein, a green synthesis methodology for making copper oxide (CuO) nanoparticle clusters in a cost-effective and simple way is reported. While cuprous sulfate pentahydrate is used as a source of copper, the outer layer of green peas (*Pisum Sativum*) is used as a source of phenol. Extracting the phenol from pea peels is a simple process that uses water as a solvent. Copper salt is reduced by the phenolic content that is so produced. Both physicochemical and microscopic characterization Scanning Electron Microscope (SEM), and Energy-dispersive X-ray (EDX) analysis were performed on the particles. A variety of pea-peeling samples were used during the procedure's several executions to ensure reproducibility. The preparation process was appropriate, as the outcomes were identical. Analyses were also conducted on the produced particles' electrochemical activity as an application. A well-defined and organized redox reaction was seen at $E' = +0.25$ V against Ag/AgCl which were also shown to be highly electro-active. With the benchmarked redox mediator (5 mM ferricyanide), the particles also produced an outstanding redox peak at $E^{1/2} = -0.01$ V vs. Ag/AgCl. In a common reducing organic reaction, such as the reduction of p-nitro phenol to p-amino phenol, they were also found to be effective catalysts. Additionally, tests were conducted on the produced particles for their anti-bacterial and antifungal properties. Overall, a simple method for the formation of commercially viable CuO nanoparticle clusters is developed with the potential for diverse applications.

Keywords: CuO, Nanoclusters, Electroactive, Peas peel, Green synthesis, Anti-microbial

INTRODUCTION

Publications on the manufacture and use of nanoparticles (NPs) have proliferated in the last few decades. The use of nanomaterials has increased dramatically because of their chemical, mechanical, physical, electrical, thermal, magnetic, and biological capabilities [1]. Consequently, nanoparticles are assigned as the base for the upcoming generation of nanotechnology. It is also estimated that the supremacy of nanoparticles will be retained in the future due to their vast applications [2]. The synthesis process is crucial in determining the morphology of nanoparticles.

Consequently, there is a widespread effort to create new synthesis pathways in order to achieve the desired form and size [3]. Researchers' interest in environmentally acceptable and economically viable green synthesis methods using plant extracts is growing. The use of dangerous chemicals, additives, catalysts, solvents, and other materials is eliminated, making them superior to traditional chemical methods [4]. The chief benefit is the economic cost as using the green route is cheaper and can be employed for bulk synthesis.

NPs are of several types, for example, carbon-based like carbon nanotubes [5], nanofibers, nanorods, porous, and metal-based. Currently, varied metallic nanoparticles are fabricated using metals like Silver, Copper, Gold, Zinc, Titanium, *etc.* [6]. Transition metal oxide NPs, among many

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other NPs, are widely used in a variety of biological, chemical, electrical, mechanical, and other fields [3]. Transition metal oxides are important semiconductors used in solar energy harvesting, catalysis, electrical conductivity, mechanical stability, and sensing [2]. Amidst various metal oxides NPs, copper oxide (CuO) NPs have gained noteworthy attention owing to their cost effectiveness and multiple applications for example, thermal transfer [7], organic catalysis [8], anti-microbial activity [9], electrochemical sensing [10], solar cell [11], supercapacitor [12], fuel cell [13], *etc.* In this regard, many procedures are reported using chemical [14], hydrothermal [15], pyrolytic [16], solution combustion [17], *etc.* wherein, toxic chemicals are exploited. Given the current ecological concern, green synthesis is becoming increasingly popular, and the creation of Cu nanoparticles from physiological plant extracts is being employed extensively. For instance, magnolia leaf extract of *Euphorbia nivulia* [18], gum karaya [9], brown alga [1], *punicagranatum* [19], *Malva sylvestris*, *Abutilon indicum* [20], Aloe vera [3], coffee powder [2], tea leaf [21], *Citrus medica* Linn [22], soybeans [23], *Ginkgo biloba* [24], Magnolia Kobus [25], *Ziziphus spina-christi* [26], *Cassia Auriculata* [27], *Rubiocardifolia* [28] *etc.* Usually, the polyphenolic content in the plant extracts is used as a natural reducing agent for the NPs formation. Table 1 below depicts a comparison between the

CuO nanoparticles prepared using plant extract.

Although there are many papers reported in the literature utilizing the broad-spectrum plant and fruit extract-based green synthesis of Cu/CuO nano particles, to the best of our knowledge, there is no report available regarding the use of green pea peelings as the reducing agent. Furthermore, the reported works have majorly focused on antibacterial activity with scanty reports on dye degradation and catalytic activity. The novelty of the present work is mainly about using the waste peelings, and the particles prepared are electroactive in nature. Further, catalytic reactions and anti-fungal and anti-bacterial are also reported.

The present work describes a novel methodology wherein, the waste product, after consumption of green peas (peelings) extract is used for green synthesis of CuO nanoclusters. An article published in Business Today on December 18, 2019, states that India consumes over 30 lakh tonnes of peas a year. Peas rank as the fourth most important type of legume, after soybean and ground nuts. Owing to their abundant vitamin content, peas are regarded as a valuable food that may fulfill the nutritional needs of around 800,000 people worldwide [29]. Peas are considered an economic, easily obtainable, protein, minerals, carbohydrates, and multivitamin source [29]. Based on published research, the crude extract made from green pea peelings contains a considerable amount of flavonoids and polyphenols [30]. In

Table 1. Comparison of CuO Nanoparticles Prepared *via* the Green Route

S.No.	Plant Used	Application	Ref.
1	Euphorbia Nivulia	Anti-bacterial activity	[18]
2	Gum karaya	Anti-bacterial activity	[9]
3	Brown Alga	Anti-microbial activity	[1]
4	Punicagranatum	Anti-peach Aphid activity	[19]
5	Abutilon Indicum	Antimicrobial, photocatalytic dye degradation and antioxidant activity	[20]
6	Coffee powder	-	[2]
7	Tea leaf	Anti-bacterial activity	[21]
8	Citrus medica Linn	Antimicrobial activity	[22]
9	Soybeans	-	[23]
10	Ginkgo biloba	Catalytic activity for cycloaddition	[24]
11	Magnolia kobus	Antibacterial activity	[25]
12	Ziziphus spina-christi	Antibacterial and dye adsorption	[26]
13	Cassia Auriculata	Antimicrobial activity	[27]
14	Rubiocardifolia	Antibacterial activity	[28]
15	Pea Peel	Electroactive, catalytic activity, antibacterial and antifungal	This work

the present work, the Phenolic content of pea is used as a natural green reducing agent to form CuO nanoparticles. Furthermore, the prepared particles are examined for diverse applications like electro-activity, catalyst for chemical synthesis, and anti-bacterial activity.

Recently, there has been a lot of interest in the use of green route-based particles as catalysts in chemical synthesis. In order to produce ecologically benign chemistry, it is necessary to look for greener chemical reactions using non-toxic chemicals and green solvents. This is from the perspective of sustainable and environmentally friendly chemistry. Nitrogen compound reduction to amine is one such frequent reaction. This has been extensively researched in a variety of settings using different catalysts, solvents, and reagents. There is still a need to investigate a novel approach that is economical, increases yield, and is ecologically benign [31,32].

In the present work, we have come up with a novel application to the synthetic reaction using greenly prepared CuO for the reduction of aromatic nitro to aromatic amines. Further, the antibacterial activity of the prepared particles against *E. coli* and *S. Aureus* and Antifungal growth activity was also examined. Overall, the prepared nanoparticles showed great potential in various applications and can be prepared in an extremely cost-effective way.

EXPERIMENTAL

Chemicals

Pisum Sativum (Fresh green peas) was purchased from a local D-mart. Copper sulfate pentahydrate, anhydrous sodium phosphate monobasic, sodium phosphate dibasic dehydrate, p-nitro phenol in MeOH:H₂O (1:2), (Methanol) NaBH₄ (Sodium Borohydride) NaCl (Sodium Chloride) Peptone and agar powder was procured from Sigma-Aldrich. (MERCK, United States) Potassium ferricyanide, potassium chloride was purchased from Sisco Research Laboratories Pvt. Ltd. (SRL) - India. All other basic chemicals used were of quality and analytical grade/purity obtained from Sisco Research Laboratories Pvt. Ltd. (SRL)-India.

Apparatus

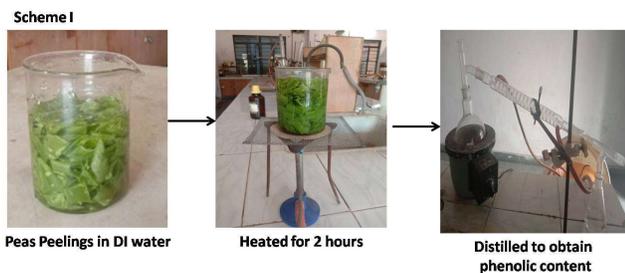
Distillation glass unit, CHI 660 potentiostat purchased from Sinsil, India, magnetic stirrer, Whatman filter paper,

HB pencil graphite, platinum wire, Ag/AgCl electrode, electrochemical cell, water bath, beakers, round bottom (RB) flask, Funnel, Petri plates, and other common glass wares were used purchased from vendor Hychem Laboratories Pvt. Ltd., India.

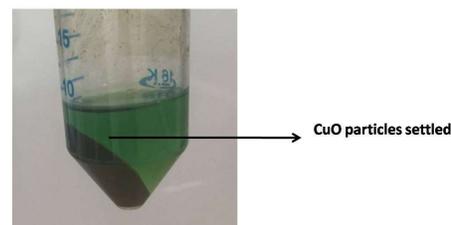
Methodology

Extraction of Phenolic content from Pea Peel. A straightforward distillation technique was used to remove the pea peel's phenolic content. We purchased fresh peas grown organically at a nearby big market. 500 g of pea peelings were gathered, cleaned with acetone and 90% ethanol to get rid of undesired contaminants, and then rinsed with distilled water to get rid of any remaining debris. The peelings were coarsely chopped into tiny bits and transferred to a spotless 500 ml beaker. Adequate De-ionized water (around 400 ml) was added until the pea peelings were completely submerged. For a duration of two hours, the beaker was placed over a Bunsen flame. Utilizing a Whatman filter paper, the mixture was filtered following heating. Simple distillation was used to extract the pure phenolic component from the green-colored filtrate that was obtained. For purity assurance, TLC was examined. A step-by-step pictorial depiction of the process is shown in Scheme I. A measurement of 1.2-1 g μmol^{-1} of phenolic content was made in the pea [33].

Preparation of reaction mixture with the phenolic compound. In a 250 ml amber glass volumetric flask, the distilled water and the phenolic content that had been collected were combined. This was mixed with 0.1995 g of copper sulfate pentahydrate salt (5 mM). The flask was wrapped in aluminum foil and sealed with a stopper. The bottle was kept in the dimly lit room for a whole day. A precipitate with a brown color was obtained. The mixture was put into a sterile, clean centrifuge tube, and it was centrifuged for 20 min at 3500 rpm in batches. Following the decants separation, the precipitate was repeatedly cleaned with distilled water and 90% ethanol before being baked for an entire night at 700 °C. Following two hours of calcination at 4000 °C in a muffle furnace, the dry particles were kept and used for characterization and application. Following centrifugation, Scheme II displays the settled particle. The protocol was followed to manufacture copper nanoparticles using the phenolic content of pea-hydrated copper sulfate (CuSO₄.5H₂O).



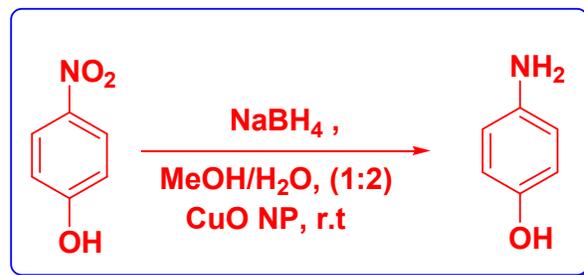
Scheme I



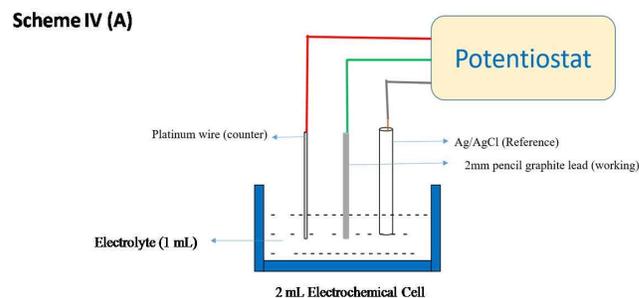
Scheme II: The real image of CuO nanoparticles formed post-centrifugation

Chemical reduction reaction. A solution of 4-nitro phenol (0.67 ml, 0.1 mmol in MeOH:H₂O (1:2) with NaBH₄ (0.54 g, 0.2 mmol) and CuO Nanoparticles (0.011 g, 0.02 mmol) was stirred constantly for 10 min under ice. The resulting mixture was allowed to stir at an ambient temperature until the color changed from yellow to brown. Scheme III shows the reaction involved.

Electrochemical analysis. A 2 ml volume of an electrochemical cell with a conventional three-electrode system [34,35] was used to study the electrochemical behavior of the synthesized copper oxide nanoclusters. In this, a commercial HB pencil, 2B, 2 mm in diameter was used as the working electrode, (silver-silver chloride) Ag/AgCl as the reference electrode, and platinum as a counter electrode. The potential window was set in the range of -1 to +1 V vs. Ag/AgCl for n = 10 segments at a potential scan rate of 50 mV s⁻¹. Scheme IV (A) shows the cartoon representation of the experimental setup and Scheme IV (B) shows a real image of the pencil electrode used. 1 ml of the supporting electrolyte, pH 7, 0.5 M phosphate buffer solution was used (PBS). The supporting electrolyte was prepared by mono and dibasic sodium hydrogen phosphate. In addition, 5 mM potassium ferricyanide solution in 1 mM of (potassium chloride) KCl was used as a redox mediator benchmark



Scheme III. 4-Nitro phenol reduction reaction



Scheme IV (B)



Scheme IV. (A) Cartoon representation of the three-electrode electrochemical experimental set-up. (B) Real images of HB pencil used as working electrode

system. The cyclic voltammetry (CV) experiments were carried out on CHI 660 C. All the basic chemicals used were of analytical grade.

Anti-bacterial activity. 5 g each of peptone, sodium chloride, and beef extract Peptone was taken in a sterile conical flask containing 1000 ml of pH 7.2 deionized water. This was then filled with 1.5-2% nutritional agar, sealed with a cotton plug, and autoclaved for 15 min at 121 °C and 15 pounds of pressure. Under laminar airflow, the media is put into a petri dish and left to harden. The ATCC provided the gram-positive *S. aureus* (ATCC25923) and gram-negative *E. Coli* (ATCC25922) bacterial strains used in the investigation.

Anti-Fungal activity. *Aspergillus terreus* spores were used as fungal strains. The peptone media prepared was used in petri dishes for demonstration of anti-fungal activity.

RESULTS AND DISCUSSION

SEM Characterization/Energy Dispersive X-ray (EDX) Analysis

The obtained nanoclusters were examined using a SEM. The SEM characterization of several preparation batches at different magnifications is displayed in Fig. 1. It was discovered that tiny, spherically-shaped particles with an average size of about 430 nm are produced. Additionally, a strong propensity for these nanoparticles to group and form clusters has been observed. It was discovered that this cluster of nanoparticles had an average diameter of about 1.5 μm . Furthermore, the elemental analysis using EDX demonstrated the existence of oxygen and copper. Carbon, sulfur, and minuscule amounts of silica were also likely

identified because of the silicon wafer used to take the photos and the pea extract (Fig. 2).

Application for Electrochemical Activity

The produced clusters were characterized by electrochemical CV techniques in order to investigate their nature. The findings of the CV are shown in Fig. 3. The CV response of a bare pencil lead used as an electrode is shown in Fig. 3A. Here, the wooden covering was removed, the interior graphite lead was extracted, and a commercial Apsara 2B pencil was used. The obtained lead was trimmed to a 7 mm length. Using a bio-analytical system polishing kit (BASi, USA), the pencil leads were first mechanically cleaned to get rid of any undesired contaminants like clay, glue, etc. In addition, it underwent chemical treatment using diluted HCl, 90% ethanol, and distilled water following the described protocol [33]. Additionally, they were dried in the hot air oven, overnight for 100 $^{\circ}\text{C}$. The resulting pencils were used as electrodes for electrochemical activity [34,35].

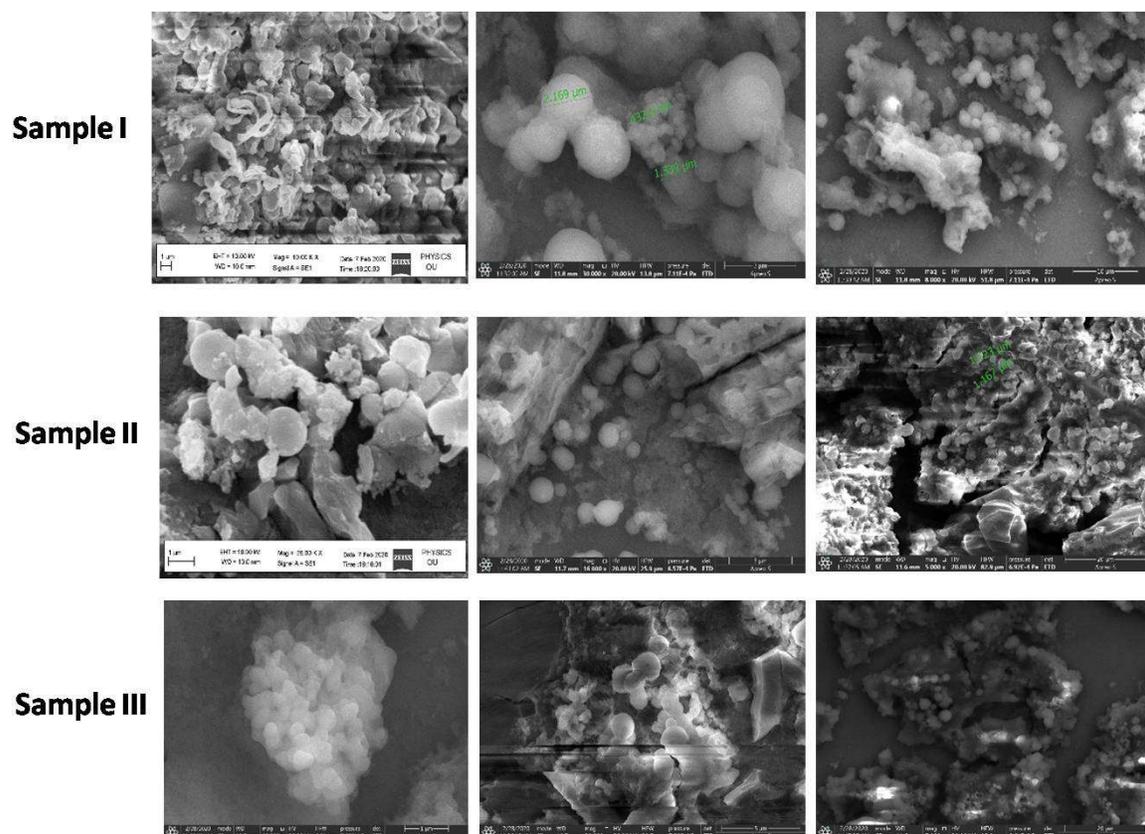


Fig. 1. SEM images of various batches of CuO nanoclusters formed using different batches of pea peelings.

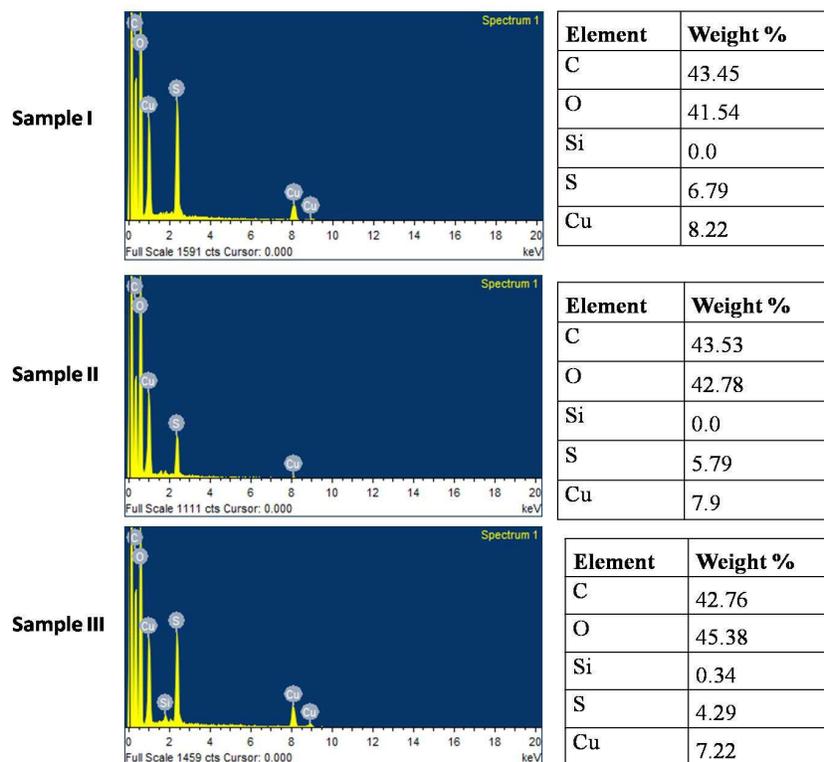


Fig. 2. EDAX spectrum of various batches of CuO nanoclusters formed using different batches of pea peelings.

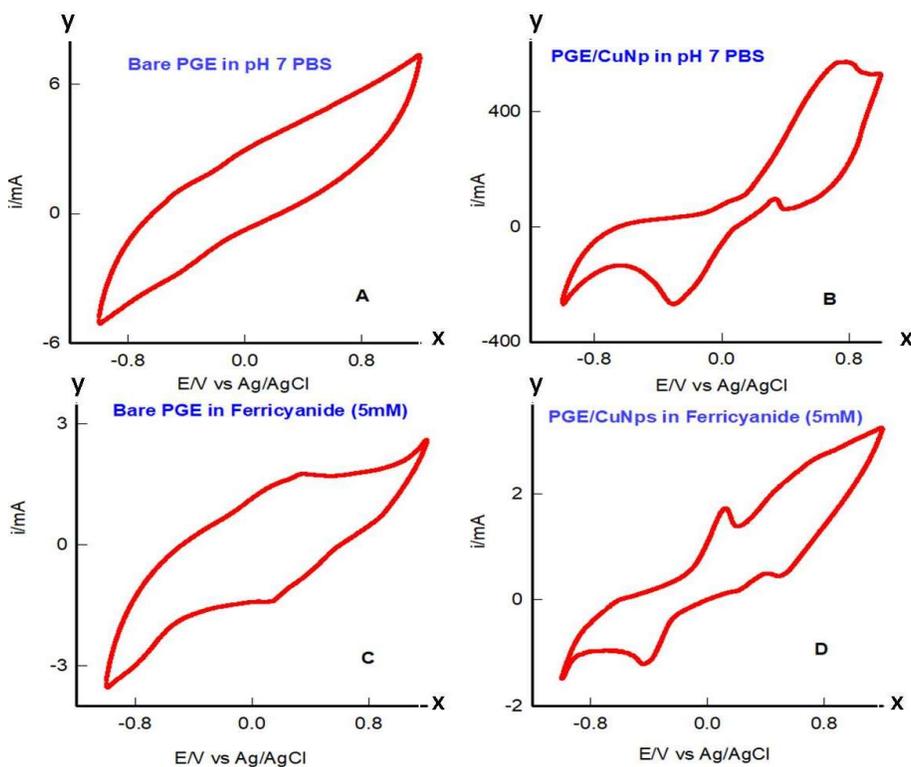


Fig. 3. (A) CV of bare pencil (B) Cv of pencil/CuO in pH 7 PBS solution. (C) CV of bare pencil in 5 mM ferricyanide and (D) CV of pencil/CuO in 5 mM ferricyanide-KCl at 50 mV s^{-1} .

In order to prevent undesirable electrochemical reactions from occurring anywhere other than the active surface area, the sides of the pencil leads were covered with a paraffin layer before use, just leaving the surface area exposed to the electrolyte. For easier understanding, Scheme 4 provides an image of a pencil electrode covered in paraffin film. The pencil surface was pre-anodized in accordance with a documented method, which involved potentiostatic polarization in pH 7 PBS for 180 seconds at an applied potential of 2V *versus* Ag/AgCl [36,37]. This activated surface was used as a working electrode. As can be seen, in Fig. 3A, wherein, bare treated pencil lead is used for performing CV experiments, in the potential window of -1 to +1 V *vs.* Ag/AgCl, at 50 mV s⁻¹, for n = 20 segments, no redox response is observed. Whereas, in Fig. 3B, it can be clearly realized that, after the chemical modification of the pencil with prepared CuO nanoclusters, a well-defined redox peak at an over potential E' = +0.25 V *vs.* Ag/AgCl was witnessed. The pencil surface was modified by drop casting 5 µl of CuO nanoparticle cluster (2 mg dispersed in 500 µl of 90% ethanol). Then, the surface was air-dried for 3 ± 1 min. CV was performed within specified parameters. Consequently, it may be said that the clusters improved the bare pencil graphite's electron transfer mechanism, making it electrochemically viable. The redox peaks acquired confirm that the produced particles are electro-active in nature and have the capacity to undergo oxidation and reduction upon application of a certain voltage.

The CV of the CuO-modified pencil electrode was examined in a KCl solution containing 5 mM ferricyanide in order to confirm the electron transport behavior. As shown in Fig. 3C, a small ferricyanide-related redox peak is visible when a pencil graphite electrode in a 5 mM ferricyanide-KCl solution is exposed to CV. However after adding synthetic particles to the electrode by drop coating, a well-organized redox peak was seen at E' = -0.01 V *versus* Ag/AgCl. These studies amply illustrated the CuO clusters' suitability for redox electrochemical sensing, and as a result, they can be applied to a wide range of sensing tasks by improving electron transfer through increased mechanism viability.

Application for CuO as a Catalyst in Organic Reaction

A typical reaction was carried out employing a cluster of

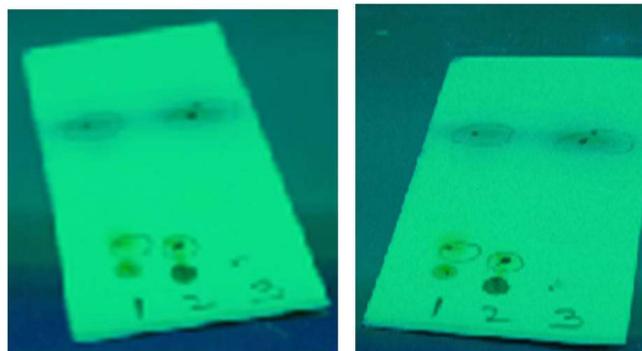


Fig. 4. TLC-solvent system (EtOAc/Hexane 1:9), 1: represents reaction without catalyst 15% Conversion. 2 represents reaction with catalyst (80-85% conversion). 3 represents the starting material (para nitro phenol).

CuO nanoparticles to reduce p-nitro phenol to p-amino phenol. Thin layer chromatography (TLC) was used to track the reaction's progress and demonstrate the reactant's full conversion to product [31,32]. Figure 4 is the TLC of the product obtained.

Anti-bacterial Activity

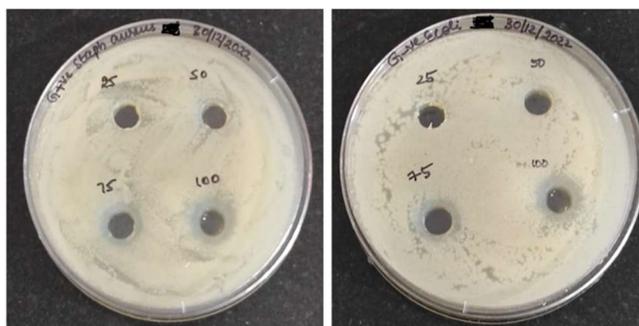
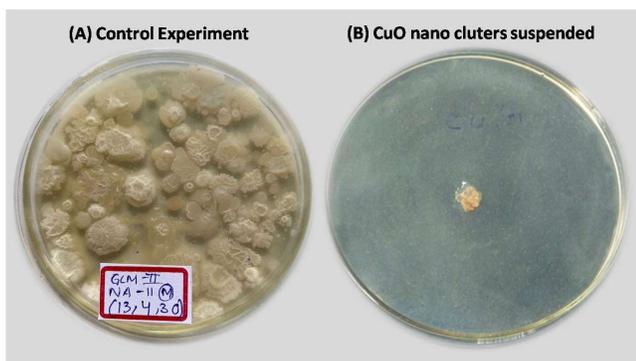
E. Coli and *S. Aureus* were used to analyze CuO's antibacterial properties. The well diffusion assay used to illustrate CuO's antibacterial action is shown in Fig. 5. CuO exhibits antibacterial action, according to the result. Whereas the resistant strain has less zone of inhibition, the strain vulnerable to CuO exhibits more. Zone of inhibition indicates that *E. coli* is more susceptible to clusters of CuO nanoparticles. Different nanoparticle concentrations affect the zone of inhibition. A zone of inhibition is absent at 25 µg and 50 µg, but present at 75 µg and 100 µg, respectively, are 1 mm and 2 mm. Similar to this, *S. Aureus* has zones of inhibition at 75 µg, 100 µg, and 1 mm and 1.5 mm. Figure 5 shows the real image of the zone of inhibition in petri plates and Table 2 shows the calculations [38,39].

Anti-fungal Activity

Sterile peptone agar medium with 100 µg ml⁻¹ of the minimal inhibitory concentration of CuO was added and then transferred into a sterile petri dish. The same procedure was used to prepare a second petri dish without CuO as a control.

Table 2. Zone of Inhibition Calculation

No	Strain	Concentration (μg)/Zone of Inhibition (mm)			
		25	50	75	100
1	<i>Staphylococcus aureus</i>	0	0	1	1.5
2	<i>E coli</i>	0	0	1	2

**Fig. 5.** Anti-Bacterial Activity of CuO (A) *S. Aureus* (B) *E. coli*.**Fig. 6.** (A) Control experiment with fungal spores and no CuO. (B) CuO suspended dish showing no growth.

They were both allowed to harden. *Aspergillus terreus* spores were suspended on the solidified media in the Petri dish's center using a cork borer. For 72 h, these dishes were incubated at 37 °C [40]. The control petri dish (A) as seen in Fig. 6, shows extensive growth whereas, (B) with the CuO particles shows no growth. Hence, CuO clusters exhibited anti-fungal properties as well.

CONCLUSION

This research reports on a green synthesis method for copper oxide (CuO) nanoparticle clusters that is easy to use and reasonably priced. The phenol came from the outer layer of green peas (*Pisum sativum*), whereas cuprous sulfate penta hydrate was the source of copper. A straightforward technique employing water as a solvent was used to extract phenol from pea peels. The resultant filtrate was obtained by a simple distillation process. Thus, produced phenolic content was used as a natural product-reducing agent for copper salt. Overnight, the desired particles with a noticeable yield were achieved. The particles were subjected to physicochemical characterization, microscopic characterization using SEM, and EDAX analysis with numerous batches in order to analyze the morphology (shape and size). It was appropriate to confirm that the preparation process was repeatable because the results were the same. Another application that was looked at was the generated particles' electro-chemical activity. The produced particles were discovered to have a defined redox response at $E' = +0.25$ V against Ag/AgCl and to be extremely electro-active in nature. Additionally, the particles produced a remarkable redox peak at $E^{1/2} = -0.01$ V vs. Ag/AgCl when using the benchmarked redox mediator, 5 mM ferricyanide. Consequently, it was found that because the particles are electro-active, they might be used for electro-catalysis over an underlying electrode. They also turned out to be useful as catalysts in a typical chemical reaction that converts p-nitro phenol to p-amino phenol. Additionally, there were notable outcomes from the produced particles' antifungal and antibacterial qualities. Therefore, to produce commercially viable CuO nanoparticle clusters with multiplexed application, a straightforward green technique synthesizes particles from waste.

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