Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(2):139-144
(http://derpharmachemica.com/archive.html)

Electrochemical synthesis, characterization and antimicrobial screening of copper oxide nanoclusters

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ABSTRACT

The present study describes synthesis of copper oxide nanoclusters by electrochemical reduction method wherein copper metal sheet was used as a sacrificial anode while platinum was used as an inert cathode. The electrolysis was carried out at varied current density for 2 hrs in aqueous solutions using tetrabutyl phosphonium bromide (TBPB) as a capping agent. The nanostructure of the synthesized nanoclusters have been analyzed using X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectrometer (FT-IR) and UV–Vis spectro-photometer. The copper oxide nanoclusters were screened for their antimicrobial activity.

Keywords: Electrochemical reduction, copper oxide, nanoclusters, tetrabutyl phosphonium bromide, antimicrobial activity.

INTRODUTION

Nanocluslers received considerable attention due to their unique properties entirely differing from bulk material [1]. The nanomaterials are known for their unique mechanical, chemical, physical, thermal, electrical, optical, magnetic, biological and also specific surface area properties, which in turn define them as nanostructures, nanoelectronics, nanophotonics, nanobiomaterials, nanobioactivators and nanobiolabels. In the last one decade, a large variety of nanomaterials and devices with new capabilities have been generated by employing nanoparticles based on metals, metal oxides, ceramics (both oxide and non-oxide), silicates, organics and polymers [2].

There are several methods reported in the literature for the synthesis of copper nanoparticles including radiation method [3], microemuslion method [4], thermal decomposition method [5], laser ablation method [6], and aqueous chemical reduction method [7].

The present work aims at synthesis of copper oxide (CuO) nanoclusters by electrochemical reduction method, the analysis of synthesized nanoclusters by and screening X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectrometer (FT-IR) and UV–Vis spectro-photometer and antimicrobial activity screening.

MATERIALS AND METHODS

Electrochemical synthesis

In the preparation of copper oxide nanoclusters, electrolysis cell vessel of volume capacity 20-50 ml and two electrode systems consisting of the bulk copper sheet (1 x 1 cm) and the same inert cathode (1 x 1 cm platinum sheet). Both electrodes were immersed in 0.01N aqueous solution of tetrabutyl phosphonium bromide. The tetrabutyl phosphonium bromide serves not only as the supporting electrolyte but also as the stabilizer for nanoparticles to prevent their further growth. During the synthesis, the bulk copper metal is oxidized into copper ion which reduced at inert cathode to form copper oxide nanoparticles most probably at the interfacial region of the cathodic surface and within the electrolytic solution. A controlled current electrolysis was carried out for 2 hrs and current density of 5, 10, 15 and 20 mA/cm^2. During the course of electrolysis, the solution became light blue to dirty green and dark brown precipitate formed. After two hours electrolysis was stopped. The solution was transformed into bottle and after some time the solid particles were separated from solution by simple decantation process and washed for 3 to 4 times with water to remove unreacted tetrabutyl phosphonium bromide.

Characterization of copper oxide nanoclusters

The copper oxide nanoclusters were characterized by high end X-ray diffractometer, thermogravimetric analysis (TGA 50 Thermoanalyzer Shimadzu), Fourier transform infrared spectrometer (IR Affinity 1 Shimadzu) and UV-Visbile spectrophotometer (UV 1800 Shimadzu).

Antimicrobial studies

In vitro antibacterial activity of copper oxide nanoclusters synthesized were tested against gram positive and gram negative bacterial strains of *Staphylococcus aureus* (NCIM-2079) and *Escherichia coli* (NCIM-2109) using the agar well diffusion assay method [8]. Approximately, 25.0 ml of molten and cooled nutrient agar media were poured in the sterilized petri dishes. The plates were left over night at room temperature to check for any contamination to appear. The bacterial test organisms were grown in nutrient broth for 24 hours at 37 °C. A 100 µl nutrient broth culture of each bacterial organism was used to prepare bacterial lawns. Agar wells were prepared with the help of a sterilized stainless steel cork borer. The wells in each plate were loaded with 50 and100 µl of 100 µg/ml of copper oxide nanoclusters and zone of inhibitions were measured in comparison with standard antibiotic ampicillin.

RESULTS AND DISCUSSION

Electrochemical synthesis

The compounds **K1** to **K4** were synthesized by electrochemical method with appreciable yields. Samples were withdrawn after 15 mins of electrolysis for UV-Visbile spectral analysis to check the growth of particle size.

UV-visible studies

The compounds **K1** to **K4** were scanned from 200 nm to 800 nm using double beam UV-Visible spectrophotometer. The absorption maxima were observed to be in the UV region hence all the compounds were scanned from 200 nm to 400 nm. The overlain spectra with absorption maxima and absorbance of compounds **K1** to **K4** after 15 min and 2 hrs of electrolysis are shown in Figure 1 and 2 respectively. From the UV-Visible spectral analysis blue shift is observed in the copper oxide nanoclusters when current density is increased during electrochemical synthesis. Similarly it has been observed that at 15 min the absorbance is higher as compare to 2 hrs electrolysis which indicates that particle size is smaller at 15 min of electrolysis than that of 2 hrs.

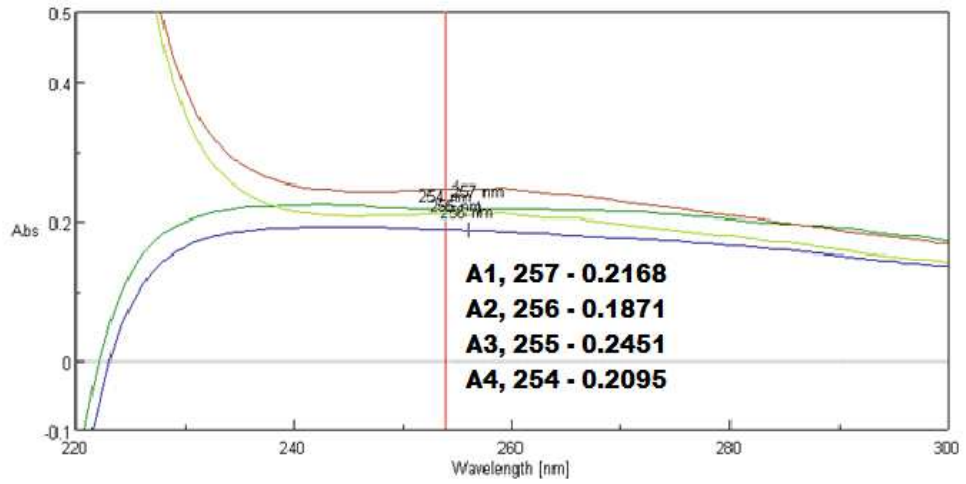

Figure 1. **Overlain UV spectra of K1 to K4 after 15 minutes**

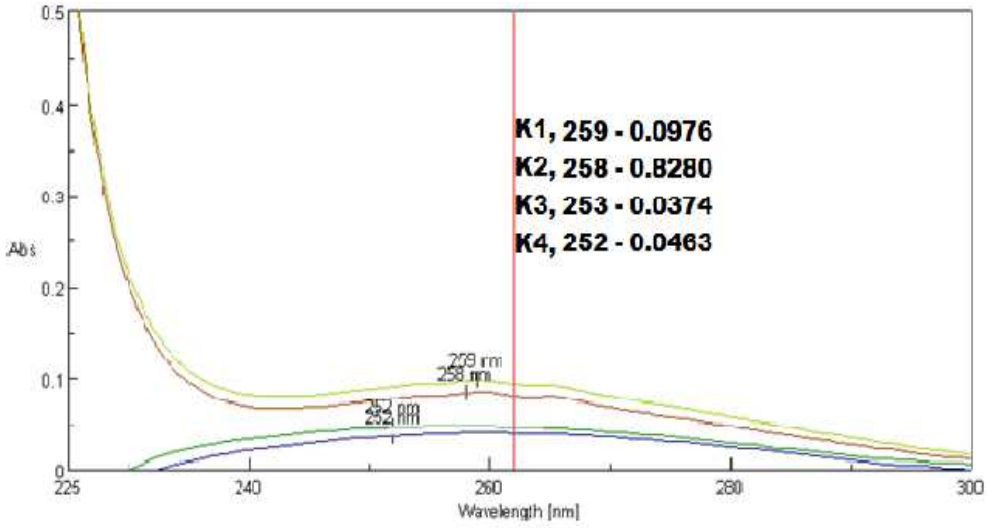

Figure 2. **Overlain UV spectra of K1 to K4 after 2 hrs**

FT-IR studies

The compounds **K1** to **K4** were calcinated by heating at 750°C in muffle furnace. The FTIR spectra of copper oxide nanoclusters (compound **K1** to **K4)** before and after calcination were recorded. The FTIR spectral analysis reveals that after calcination the capping agent tetrabutyl phosphonium bromide has been completely removed from the copper oxide nanoclusters. The absence of band at 3256.35 and 3583.70 cm^{-1} after calcination which was appeared in the FTIR spectra of **K1** before calcination (Figure 3, 4) confirms that tetrabutyl phosphonium bromide has been completely removed during calcination. Similar changes are observed in the FTIR spectra of compound **K2**, **K3** and **K4** also.

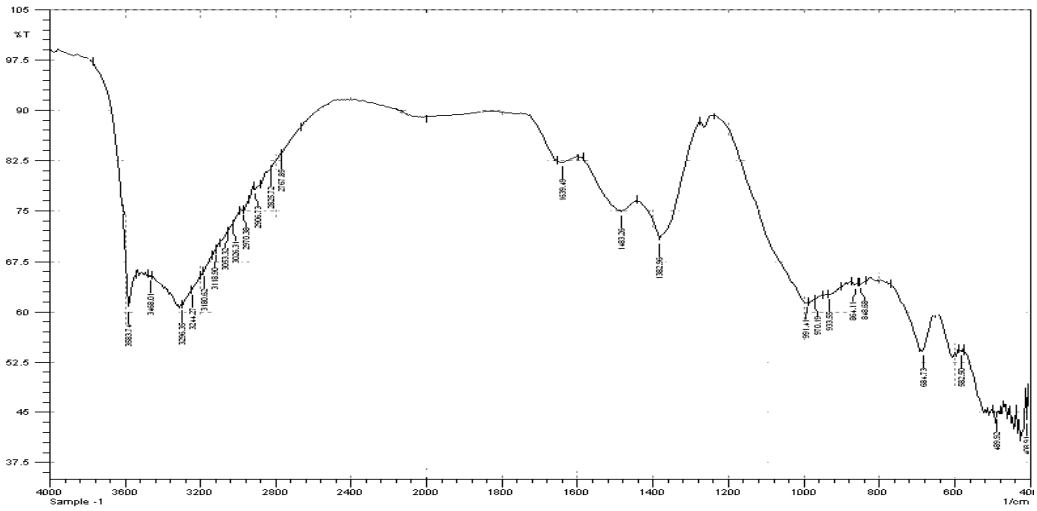

Figure 3. **FTIR spectra of K1**

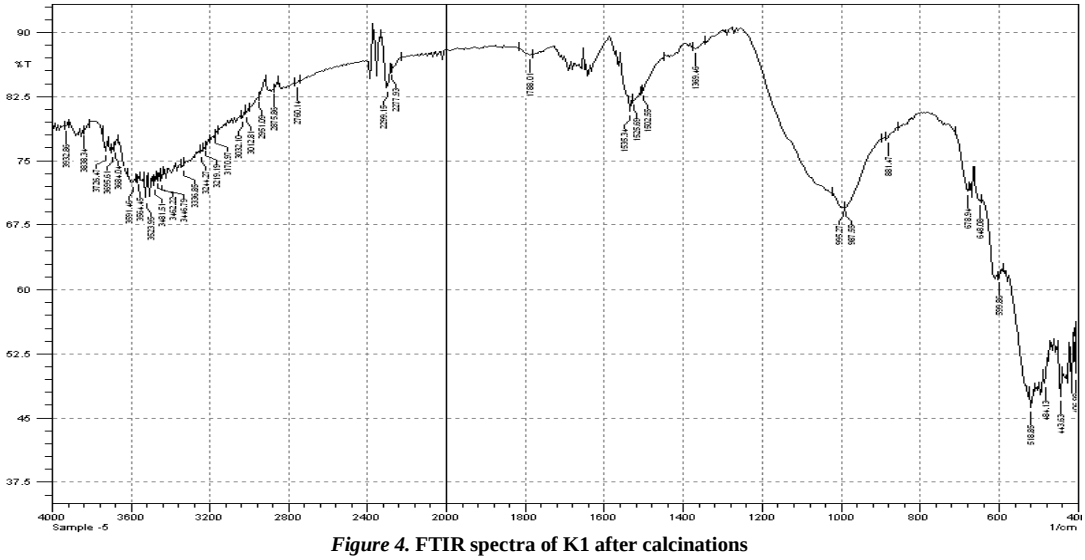

Figure 4. **FTIR spectra of K1 after calcinations**

Thermal studies

The synthesized copper oxide nanoclusters were subjected for thermogravimetric analysis (TGA) which shows that weight of copper oxide nanoclusters is constant above 200°C (Figure 5). The TGA data reveals that capping agent tetrabutyl phosphonium bromide no longer persist with the copper oxide nanoclusters above 200°C.

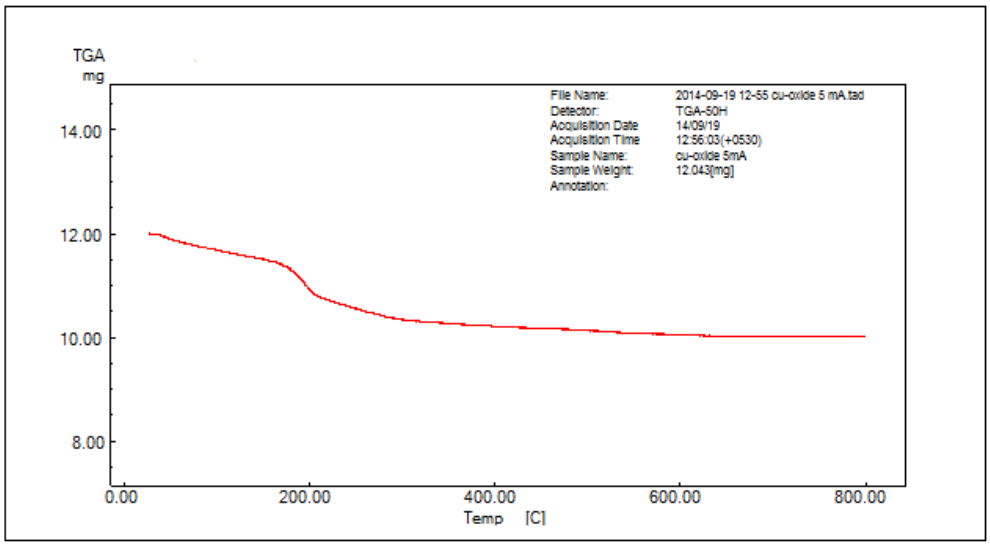

Figure 5. **TGA data of copper oxide nanoclusters**

XRD studies

The XRD studies of synthesized copper oxide nanoclusters to know the particle size (Figure 6 and Table 1). The ten peaks were observed at 35.77, 38.89, 49.01, 53.74, 58.29, 61.87, 66.44, 68.41, 72.63 and 75.66 showing particle size of 2.785, 2.595, 3.426, 3.508, 3.582, 3.648, 3.740, 3.783, 3.883 and 3.962 nm respectively. The average particle size of copper oxide nanoclusters synthesized by electrochemical reduction method is 3.491 nm.

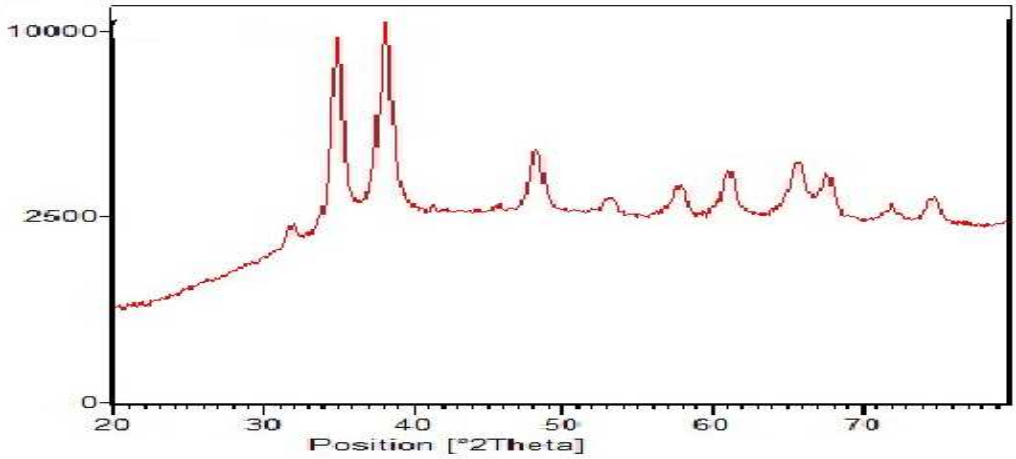

Figure 6. **XRD pattern of copper oxide nanoclusters**

Table 1. XRD data of copper oxide nanoclusters

Peak	2θ	θ	h k l	d (Å)	D value(Å)	D value (nm)
1.	35.77	17.88	2 1 0	2.50	27.85	2.785
2.	38.89	19.44	1 2 2	2.31	25.95	2.595
3.	49.01	24.05	2 2 2	1.85	34.26	3.426
4.	53.74	26.87	2 2 4	1.70	35.08	3.508
5.	58.29	29.14	0 2 5	1.58	35.82	3.582
6.	61.87	30.93	1 0 6	1.49	36.48	3.648
7.	66.44	33.22	3 1 4	1.40	37.40	3.740
8.	68.41	34.20	2 2 3	1.37	37.83	3.783
9.	72.63	36.31	0 1 7	1.30	38.83	3.883
10.	75.66	37.83	4 0 3	1.25	39.62	3.962
Average particle size						3.491

Antimicrobial studies

The antibacterial activity of synthesized copper oxide nanoclusters in terms of zone of inhibition against gram positive and gram negative bacterial strains of *Staphylococcus aureus* and *Escherichia coli* is shown in Table 2. The antibacterial activity data reveals that copper oxide nanoclusters shows comparable antibacterial potential as that of ampicillin. The copper oxide nanoclusters are more active against gram positive than gram negative bacterial strains.

Table 2. *In vitro* antibacterial activity of synthesized copper oxide nanoclusters

Compound	Quantity	Antibacterial activity(zone of inhibition in mm)	
		Staphylococcus aureus	*Escherichia coli*
CuO nanoclusters	50 µl	18	13
	100 µl	23	17
Ampicillin	50 µl	19	15
	100 µl	25	18

CONCLUSION

The copper oxide nanoclusters were successfully synthesized with appreciable yields by electrochemical method using tetrabutyl phosphonium bromide as capping agent. The characterization studies confirmed formation of nanoclusters. The copper oxide nanoclusters show broad spectrum antimicrobial activity.

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