

Nanomaterial Based Electrochemical Sensors for Endocrine Disrupting Compounds

Gaurav Bhanjana, Ganga Ram Chaudhary, Sandeep Kumar, Neeraj Dilbaghi

Abstract—Main sources of endocrine disrupting compounds in the ecosystem are hormones, pesticides, phthalates, flame retardants, dioxins, personal-care products, coplanar polychlorinated biphenyls (PCBs), bisphenol A, and parabens. These endocrine disrupting compounds are responsible for learning disabilities, brain development problems, deformations of the body, cancer, reproductive abnormalities in females and decreased sperm count in human males. Although discharge of these chemical compounds into the environment cannot be stopped, yet their amount can be retarded through proper evaluation and detection techniques. The available techniques for determination of these endocrine disrupting compounds mainly include high performance liquid chromatography (HPLC), mass spectroscopy (MS) and gas chromatography-mass spectrometry (GC-MS). These techniques are accurate and reliable but have certain limitations like need of skilled personnel, time consuming, interference and requirement of pretreatment steps. Moreover, these techniques are laboratory bound and sample is required in large amount for analysis. In view of above facts, new methods for detection of endocrine disrupting compounds should be devised that promise high specificity, ultra sensitivity, cost effective, efficient and easy-to-operate procedure. Nowadays, electrochemical sensors/biosensors modified with nanomaterials are gaining high attention among researchers. Bioelement present in this system makes the developed sensors selective towards analyte of interest. Nanomaterials provide large surface area, high electron communication feature, enhanced catalytic activity and possibilities of chemical modifications. In most of the cases, nanomaterials also serve as an electron mediator or electrocatalyst for some analytes.

Keywords—Sensors, endocrine disruptors, nanoparticles, electrochemical, microscopy.

I. INTRODUCTION

DOCUSATE or dioctyl sulfosuccinate is a compound used to treat the constipation. It works as stimulant laxative. It is very cheap and available as its sodium, potassium or calcium salts [1]. Docusate has several applications as dispersant, food additive, wetting specialist, disinfectant, surface active agent and emulsifier [1], [2]. Although dioctyl sulfosuccinate has several uses in medication yet it has shown carcinogenicity, mutagenicity, and teratogenicity in humans above a minimum concentration level [3]. It may be used in small quantity as a drug to cure common problems like constipation and bowel dysfunction but possesses serious

problem as side effects and water contamination if not disposed properly. The common side effects caused by docusate are stomach or intestinal cramping diarrhea, skin rash, throat irritation and irritation of skin. Docusate is not given to the individuals who have an infected appendix, sickness, stomach torment, side effects of a ruptured appendix, etc. It is also not prescribed to those patients which are seeping from the rectum, undiscovered dying, congestive heart disappointment, hypertension, faecal impaction, or intestinal check [4]. Abusing of docusate sodium for drawn out stretches of time may make guts end up plainly subject to the solution. Due to widespread applications and toxicity issues, it is necessary to determine qualitatively and quantitatively the concentration of docusate in various food and beverage samples. Conventional techniques like HPLC, MS, and GC-MS used for estimation of docusate are associated with certain limitations like complex procedure, heavy and costly equipment, laboratory bound procedure, large sample volume and soaring cost per sample [4]-[6]. These limitations associated with the conventional methods can be easily overcome with the help of electrochemical analysis. On-site detection can be performed with the assistance of hand held devices. Ultra-sensitivity, selectivity, and required detection limit can be achieved with the help of Nanoengineering of the working electrodes [5]-[8]. Various types of nanomaterials are gaining enormous attention among scientific and research community for nanoengineering. Out of various nanomaterials, carbon based nanomaterials and metal based nanoparticles have shown great potential in the field of sensing. Carbon nanotubes, graphene, and carbon dots have been applied for electrochemical sensing of pesticides, explosives, pharmaceutical drugs and other biological fluids. Nanoparticles of silver, gold, copper, zinc, and their oxides have been explored for direct redox sensing of environmental contaminants. Among different metal oxide nanomaterials, copper oxide nanoparticles are the best material in terms of surface area, electronic communications, band gap and ease of synthesis [9]-[11]. In view of these facts, novel electrochemical technique has been proposed for analytical determination of docusate in real as well as laboratory samples. Cyclic voltammetry method has been applied as an efficient electrochemical tool for direct redox determination of docusate. Sensitivity and required detection limit has been attained with the help of copper oxide nanoparticles. Copper oxide (CuO) nanoparticles have been used as electrocatalyst for fabrication of gold electrode. CuO nanoparticles have been synthesized using chemical method and have been characterized well with the assistance of spectroscopic and

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microscopic techniques. Synthesized and characterized CuO nanoparticles were coated on gold electrode surface with the help of nafion as binding agent. Fabricated CuO/Nafion/Au electrode was evaluated electrochemically for determination of docusate.

II. MATERIALS AND METHODS

All chemical used were purchased from Sigma Aldrich and used as such without any further purification. CuO nanoparticles were prepared using chemical method. Aqueous copper sulphate (0.01 M, 100 mL) and urea (0.025 M, 100 mL) were mixed under continuous stirring for 1h. Consequently, drops of ammonia were added to maintain the solution pH till 9. Stirring was given for 1h, the resultant mixture was moved to Teflon bottles and kept at 150 °C for 2 h. After completing the desired reaction time, the bottles were cooled to room-temperature and brown precipitates were which were washed with distilled water and ethanol. Dried powder was characterized and used further for electrode modification. Field emission scanning electron microscope (FESEM), transmission electron microscope (TEM), PSA particle size analysis (PSA), Fourier-transform infrared (FTIR) and X-ray powder diffraction (XRD) analyses were performed to elucidate the morphological, topological, structural and elemental characteristics of the synthesized copper oxide nanoparticles. Morphological and topological features of the synthesized nanoparticles were confirmed with the help of FESEM and TEM micrographs. Stability of the synthesized copper oxide nanoparticles was evaluated with the help of particle size analyzer results. Particle size of the synthesized nanoparticles was obtained at regular intervals of time. Change in particle size was noticed after every 2h. Elemental composition and percentage purity of the synthesized nanoparticles was attained with the help of FTIR spectrum. Structural composition of the synthesized nanoparticles was elucidated with the help of XRD plot. Conventional three-electrode system was used to take the electrochemical measurements. Platinum wire was used as counter electrode with reference to Ag/AgCl as reference one. Fabricated CuO/Nafion/Au electrode was utilized as working electrode for direct determination of docusate in aqueous samples.

III. RESULTS AND DISCUSSION

CuO nanoparticles were synthesized using chemical method and characterized with the help of FESEM, TEM, particle size analyzer, and FTIR. Aqueous slurry of synthesized nanoparticles was subjected to microscopic analysis. An aqueous drop of copper oxide nanoparticles was placed on stub with the help of double sided tape and dried under table lamp. Gold coating was done and the sample was analyzed using FESEM. FESEM images of synthesized copper oxide nanoparticles are shown in Fig. 1, and TEM image is given in Fig. 2. FTIR spectrum of copper oxide nanoparticles is portrayed in Fig. 3. It is confirmed from Fig. 1 that the nanoparticles are in size range 80-100 nm and characteristic peaks of Cu-O bond can be seen in FTIR spectrum [9]-[11].

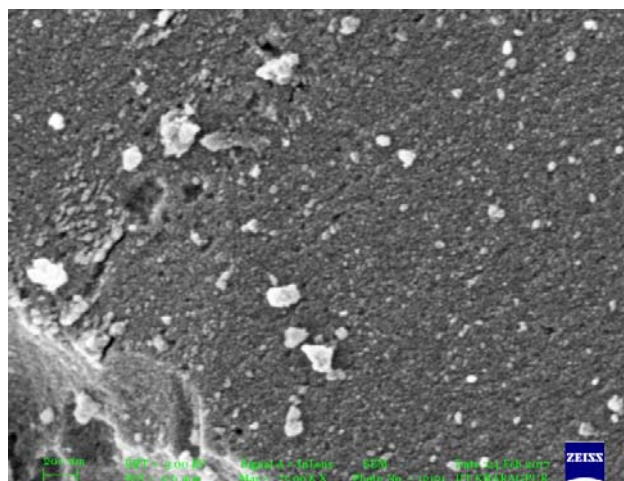


Fig. 1 FESEM image of CuO nanoparticles

It can be seen in Fig. 1 that the nanoparticles are spherical in shape as well as segregated in nature.

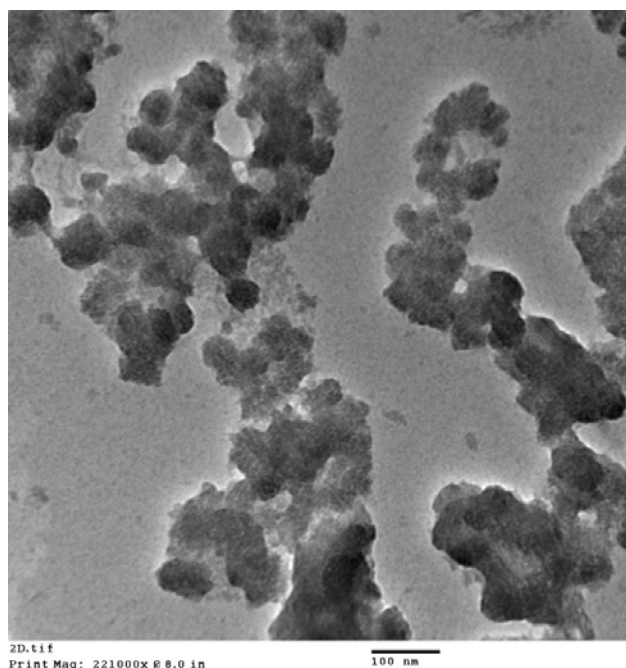


Fig. 2 TEM image of the CuO nanoparticles

Particle size of the synthesized copper oxide nanoparticles was also confirmed with the help of TEM, and TEM images also prove that the synthesized nanoparticles are in range of 80-100 nm.

Peak at 628 cm^{-1} in FTIR spectrum can be attributed to CuO bond. On the other hand, broad peak at 3422 cm^{-1} is due to the presence of adsorbed water molecules. Stability of synthesized CuO nanoparticles was determined with the help of particle size analyzer results. Particle size of synthesized nanoparticles was evaluated with the passage of time and change in particle size was observed. Aqueous suspension of CuO nanoparticles was made with the help of water bath sonicator and subjected to evaluation for change in particle size. Effect on particle size

was seen after every two hours. Four readings were taken and are reflected in Figs. 4-7.

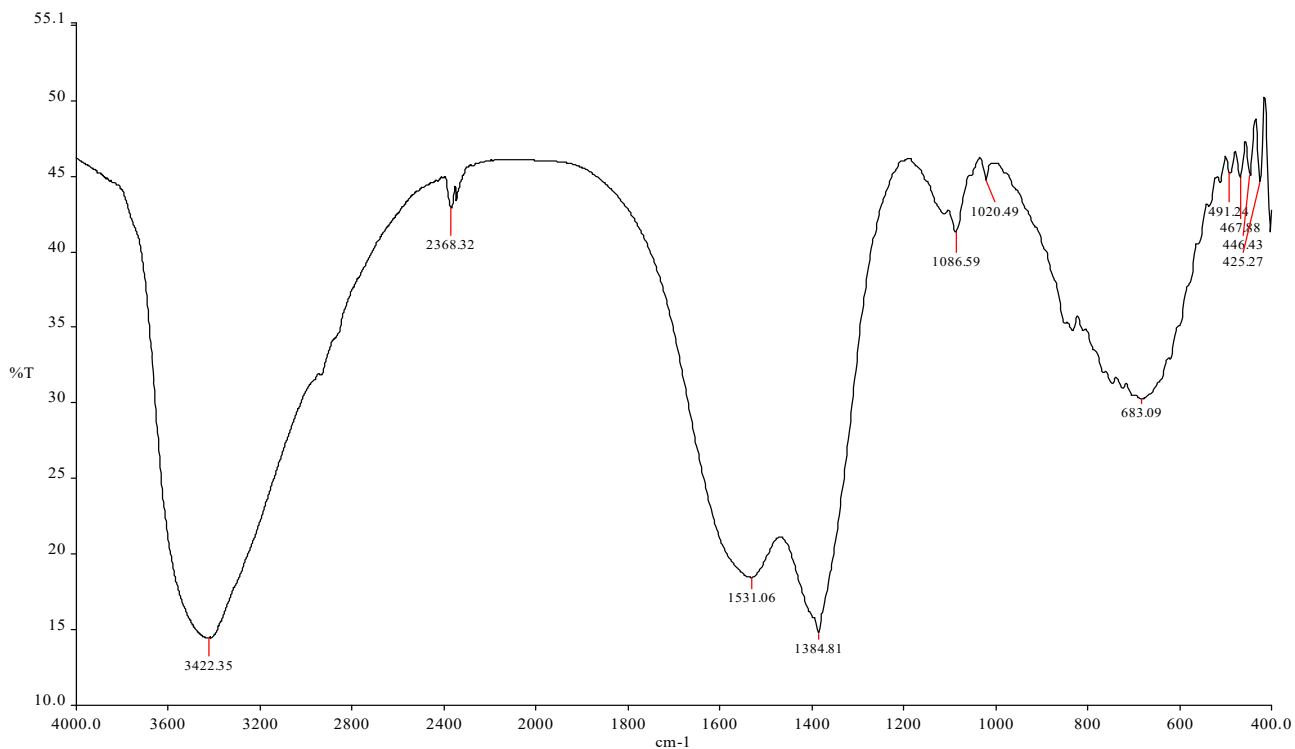


Fig. 3 FTIR image of CuO nanoparticles.

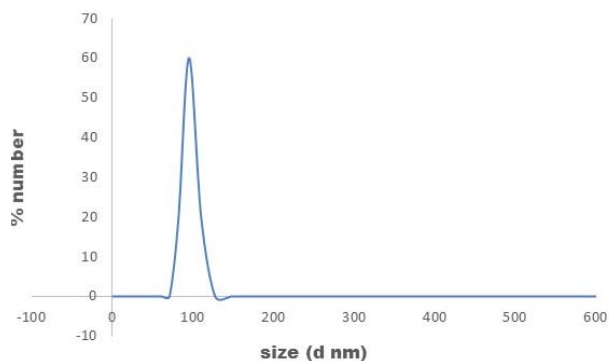


Fig. 4 Particle size analyzer result after 0h

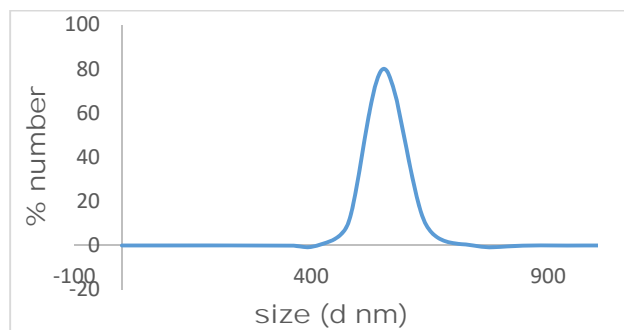


Fig. 6 Particle size analyzer result after 4h

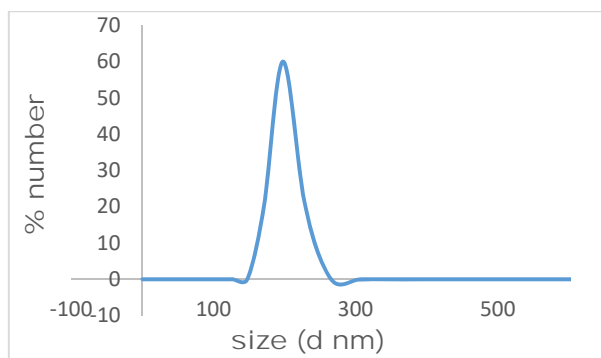


Fig. 5 Particle size analyzer result after 2h

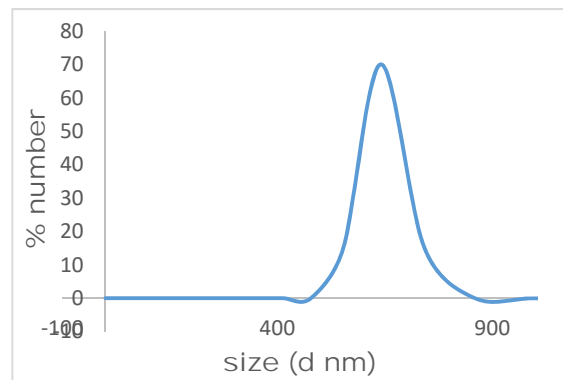


Fig. 7 Particle size analyzer result after 6h

It can be seen clearly from Figs. 4-7 that there is an increase

in particle size with the passage of time. This trend can be easily understood by the fact that aggregation is taking place with the passage of time. At 0h, there was segregation among the nanoparticles due to sonication; hence the particle size was least. On the other hand, with passage of time, aggregation is taking place among the particles. Due to aggregation, particle size is continuously increasing with time. XRD image of the copper oxide nanoparticles is given in Fig. 8. It is clear from Fig. 8 that the synthesized copper oxide nanoparticles have shown all characteristic reflections of the pure copper oxide. Moreover, there is no appearance of any other significant peak for the impurity in the obtained graph. It can be confirmed with the help of FTIR and XRD spectra that the synthesized nanoparticles are pure copper oxide with no impurity in them. After elucidation, it was confirmed that the synthesized copper oxide nanoparticles belong to monoclinic crystal structure. These all performed characterizations clearly reflect that the synthesized material is pure copper oxide having no impurities in them. From application point of view, these synthesized and well characterized copper oxide nanoparticles were utilized as efficient electrocatalytic material for direct redox sensing of docusate. Due to wide band gap, enhanced electron communication feature and high surface to volume ratio copper oxide nanoparticles can work as effective mediator between the electrode and the analyte for direct transfer of electrons. This property has been explored in this research work with the help of cyclic voltammetry technique. CV technique is the most powerful technique used in electrochemistry for those analytes which are redox active. As docusate also has charge on it, it can be easily detected with the help of electrochemical analysis. During CV cycle, it can lose or gain the electrons at certain specific potentials.

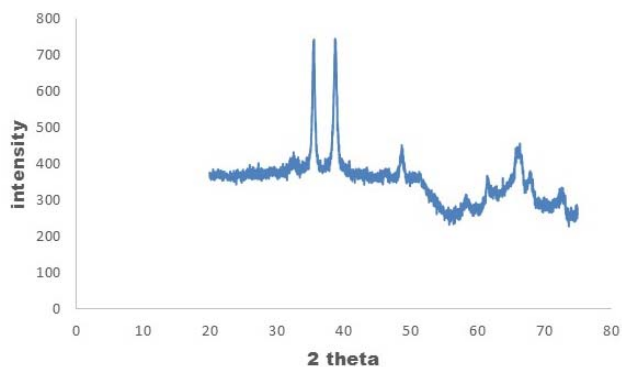


Fig. 8 XRD spectrum of the synthesized CuO nanoparticles

These CuO nanoparticles were coated to fabricate CuO/Nafion/Au electrode which was used for determination of docusate using cyclic voltammetry (CV) technique. Nafion was used as binding agent to tightly hold the nanoparticles on electrode surface. It is used to prevent the leaching of nanoparticles from electrode surface. CV plots of fabricated electrode in presence and absence of docusate is shown in Fig. 10. It is clear from Fig. 10 that significant oxidation and reduction peak (blue plot) is obtained in presence of docusate with the help of fabricated electrode. It can also be elucidated

from the figure that the oxidation peak is much significant as compared to the reduction peak in CV plot. This effect can be proved by looking the formula of the docusate as shown in Fig. 9.

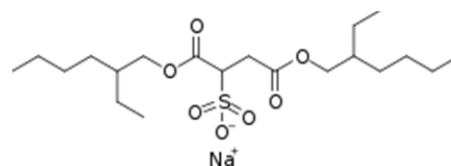


Fig. 9 Structure of docusate sodium

It can be seen clearly from the structure of docusate that it has negative charge on sulphonic group. Due to presence of negative charge, it will lose the electron at specific potential. Hence oxidation peak is very clear and significant in CV plots. There is no appearance of peak in CV plot with fabricated electrode in absence of docusate. This result clearly proves that the copper oxide nanoparticles are working as efficient electro-catalytic material in direct redox sensing of docusate. Fabricated electrode was found to be responsive even after one month of safe storage.

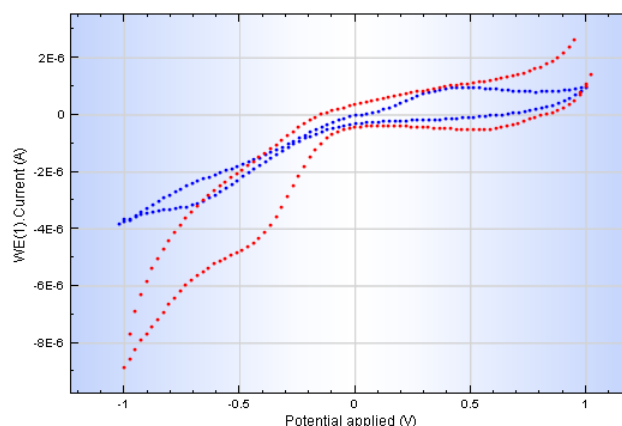


Fig. 10 CV plots of fabricated electrode in presence (blue) and absence (red) of docusate

Effect of docusate concentration on peak current was also optimized and is given in Fig. 11.

It can be proved from Fig. 11 that there is an increase in peak current with increase in docusate concentration. As docusate concentration is increasing, peak current is also increasing linearly. CV technique is the simplest technique in electrochemistry which is user friendly and results can be obtained within a minute. Another advantage of the CV technique is the requirement of less sample volume. It is pertinent to mention here that a sample volume of few microliters is sufficient to analyze the sample with the help of electrochemical detection. In this way, it is quite clear from the above experiments that docusate can be easily determined with the of CV technique. Screen printed electrodes can be applied for on-site detection of real water and food samples. Other electro active analytes can also be determined with the help of proposed technique. Pesticides, explosives,

environmental contaminants, and other important biological fluids can be easily determined with the help of optimization using proposed method.

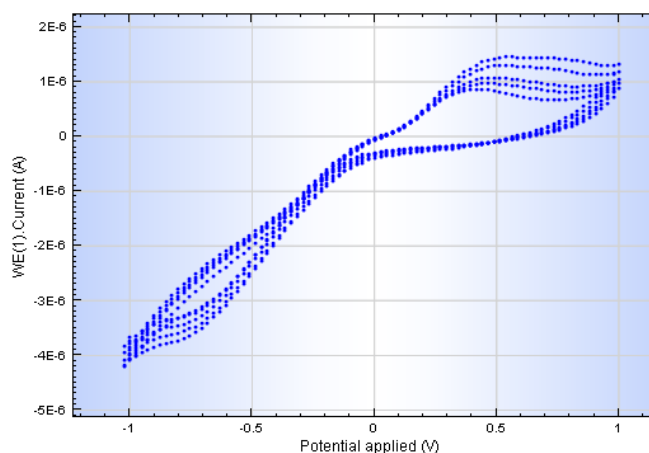


Fig. 11 Effect of docusate concentration on CV plots

IV. CONCLUSION

It is quite clear from the obtained results that fabricated electrode can be used for direct determination of docusate using CV technique and CuO nanoparticles are working as electrocatalyst in direct determination of docusate. Cyclic voltammetry characterizes the detection of Docusate at different concentration ranging from 25 ppm to 50 ppm.

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