PURE AND FLUORINE DOPED CDO NANOPARTICLES FOR ANTIMICROBIAL ACTIVITIES

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Abstract

Fluorine doped CdO nanoparticles (F-CdOnps) were obtained by chemical reaction method. Optical, structural, vibrational and morphological properties of F-CdOnps were examined by UV-vis optical absorption spectroscopic, X-ray diffraction, Fourier transform infrared spectroscopic and Transmission electron microscopic techniques. These prepared F-CdOnps show face centred cubic (FCC) crystalline structure, lesser size, and higher band gap, strain and dislocation density with respect to pure CdOnps. Formation of nanoparticles was confirmed from TEM and SEM images. The consequences of the antibacterial studies confirm the superior aptitude of F-CdOnps with respect to pure CdOnps to inhibit the growth of both bacteria namely Pseudomonas *aeruginosa (gram negative) and Bacillus cereus (gram positive).*

Keywords: *CdO; Nanoparticles; X-ray techniques; Structural; Antibacterial activity.*

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1. INTRODUCTION

In recent years, microorganisms have developed to become drug resistant by the alterations in their chromosomes/genetic materials. Emergence of the antibiotic resistance pathogens has become a severe healthiness problem and thus, many studies have been reported to develop the present antimicrobial treatments. It is known that over 70% of bacterial infections are resistant to one or more of the antibiotics that are usually used to eliminate the infection. These troubles require the growth of new effectual antibacterial agents against new generation bacteria. The nanoparticle contact with biological materials guides to the creation of novel nanomaterial with control precise characteristics such as size, distribution, morphology and surface chemistry. A well-organized method to estimate nanotoxicity is to examine the reaction of bacteria exposed to nanoparticles. So it will be helpful, if an easy mechanism can be intended to inhibit the development of various pathogenic bacteria. Currently, metal oxide nanomaterials are among the vastly created nanomaterials and have established to be efficient in treating dangerous materials such as chlorinated solvents, microorganisms, pesticides and mustards. Among all semiconductor materials, Cadmium Oxide (CdO) is a II-VI n-type semiconductor, harmless and chemically stable. It has attractive properties such as big band gap, small electrical resistivity and high transmission in the visible region which presents potential applications in the optoelectric fields such as photovoltaic cells, photo-diodes, photo-transistors, gas sensors, and transparent electrodes [1-5]. When compared to bulk, CdOnps exhibit novel, tunable, particular features and properties due to the increase in surface to volume ratio, high reactivity, and new quantum effects which result from reduction in their particle size to nanoscale. CdOnps with different shapes have been prepared by using different techniques [6-10]. Many studies are contributing to know the original characteristics of metal oxide nanoparticles using various nonmetal dopants like fluorine [11-14]. In the present study, we have prepared fluorine doped CdOnps, to improve their typical properties and antimicrobial applications.

2. EXPERIMENTAL METHODS

Chemicals in this study were of analytical grade and employed with no more purification. CdO and F-CdOnps were prepared by wet chemical method. 0.9M ethanol solution of Sodium hydroxide was added drop wise with 0.5M ethanolic solution of cadmium nitrate and stirred for complete dissolution of contents and permitted to settle for during the night at room temperature to prepare cadmium hydroxide. The supernatant liquid was then removed cautiously and the remaining solution was centrifuged (10,000rpm) for 30minutes. The centrifugate was cleaned sometimes with distilled water and ethanol, and then dried at 100˚C for 5hrs. Then the sample was calcined at 400ºC for 3hrs to get pure CdOnps. F-doping was attained by the addition of proper quantity of Ammonium fluoride to the primary solution. Lastly, the powder was calcinated at 400ºC for 3hrs to obtain F-CdOnps. The phase of the powders were studied by XRD using X'Per PRO (PANalytical) X-ray Diffractometer with CuKα radiation (λ =1.5406A˚). Optical studies were characterized by using Double Beam UV-vis Spectrophotometer (LMSP UV 1900). Size and shape of the samples were made using a JEOL TEM 2010 HRTEM with an accelerating voltage of 200 kV. The antimicrobial activity of CdO and F-CdOnps against bacteria namely Pseudomonas aeruginosa and Bacillus cereus was made by disc diffusion method.

3. RESULTS AND DISCUSSION

3.1 Structural Studies

XRD pattern of pure and F-CdOnps was shown Fig. 1. Four diffraction peaks detected at 33.07º, 38.42º, 55.48º and 65.85º can be indexed to the (111), (200), (220) and (311) reflections of FCC structure of pure and doped CdO nanopowders (JCPDS file no. 75-0592). The broad diffraction peak in the F-CdOnps was attributed to smaller particle size which indicates that Fluorine doping inhibits the development of particles. Here fluorine atoms endorse one free electron when it holds in position of oxygen due to the hybrid orbital configuration of fluorine ($2S^2 2P^5$) and oxygen ($2S^2 2P^4$). Due to the comparable radius of fluorine (1.36Å) and oxygen (1.40Å) atoms, there was no alteration in peak points in F-CdOnps with respect to pure CdOnps [14]. The average particle size of the pure and F-CdOnps computed using Scherrer formula was 25.14nm and 13.81nm respectively. The strain for pure and F-CdOnps was 0.13 $x10^{-2}$ and 0.25 $x10^{-2}$ respectively. The dislocation density was found as $17.54x10^{14}$ m^{-2} and $57.86x10^{14}$ m^{-2} for pure and F-CdOnps respectively.

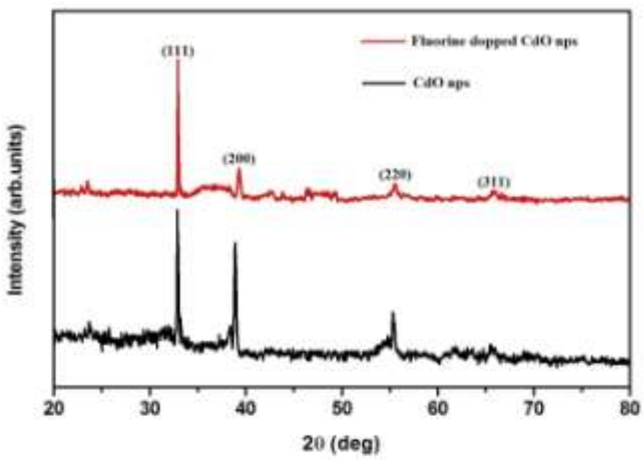


Fig 1. XRD pattern of pure and fluorine doped CdOnps.

3.2 Optical Studies

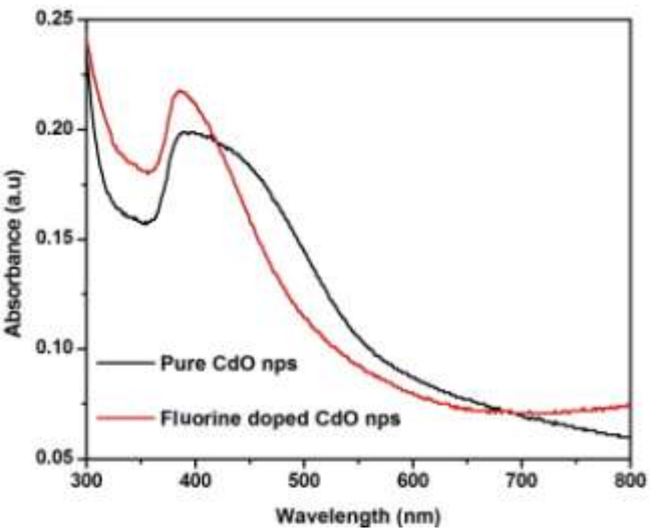


Fig 2 UV-vis absorption spectrum of pure and fluorine doped CdOnps.

Fig. 2 shows the UV–vis spectra of CdOnps and F-CdOnps. CdO exhibits absorption at 387 nm. Due to the introduction of tiny quantity of Fluorine in the reaction medium, the absorption (382 nm) moves in the direction of blue end and the Full Width Half Maximum value decreased from 178nm to 150nm which is caused by the donation of electrons (fluorine atoms) into the substitutional places of the CdO crystal structure. This point out that fluorine doping could faintly restrain the growth of CdO crystallite and forms huge number of small nanoparticles provides pointed and strong SPR. The spectrum is able to demonstrate a shift in the direction of blue or red end depends on the particle size, shape, aggregation and the neighboring dielectric medium. This specifies the quantum confinement of the nanoparticles. Here formation of small sized F-CdOnps depend on fluorine since it helps to bind to the surface of the CdOnps, hence performing as stabilizer and tuning the growth of particles to attain a high degree of similarity.

3.3 Vibrational Studies

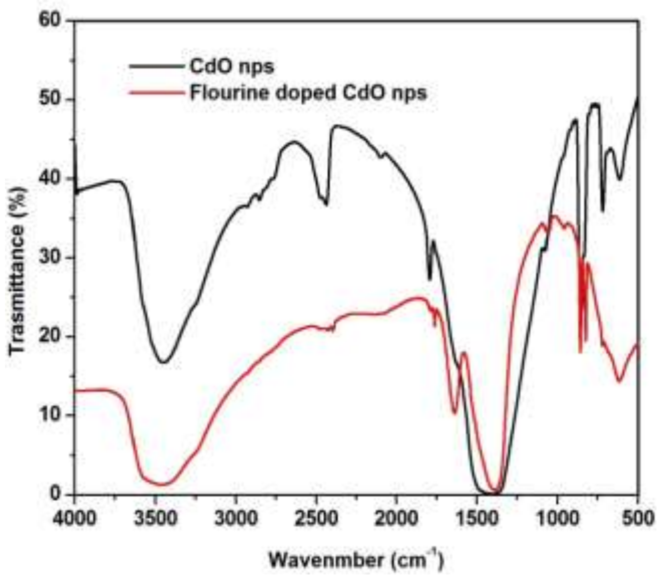


Fig 3. FTIR spectrum of pure and fluorine doped CdOnps.

Fig.3 shows that the FTIR spectrum of pure and doped CdOnps. The strong peak at 1384cm^{-1} related to the C-N stretching vibration group. The peak at 1050-1080cm^{-1} conformed the binding of $–OCH_3$ group. The peak at 600-800cm^{-1} can be assigned to the CdO nanoparticles. The peak positioned at 611cm^{-1} credited to CdO that were downshifted and more symmetric at 621cm^{-1}in the F-CdOnps spectrum [15]. The peaks at 2396-2800cm^{-1} are confirmed that the amines and C-H stretching vibration modes in the hydrocarbon (CH aliphatic). F-CdOnps show that the high absorbance bands around 3466cm^{-1} and 1654cm^{-1} assigned to OH stretching and OH vibration. The peak at 1654cm^{-1} also belongs to Cd-O. The spectrum of F-CdOnps was sharper than that of CdOnps, which may be accredited to the altering of particle shape and size.

3.4 Morphological Studies

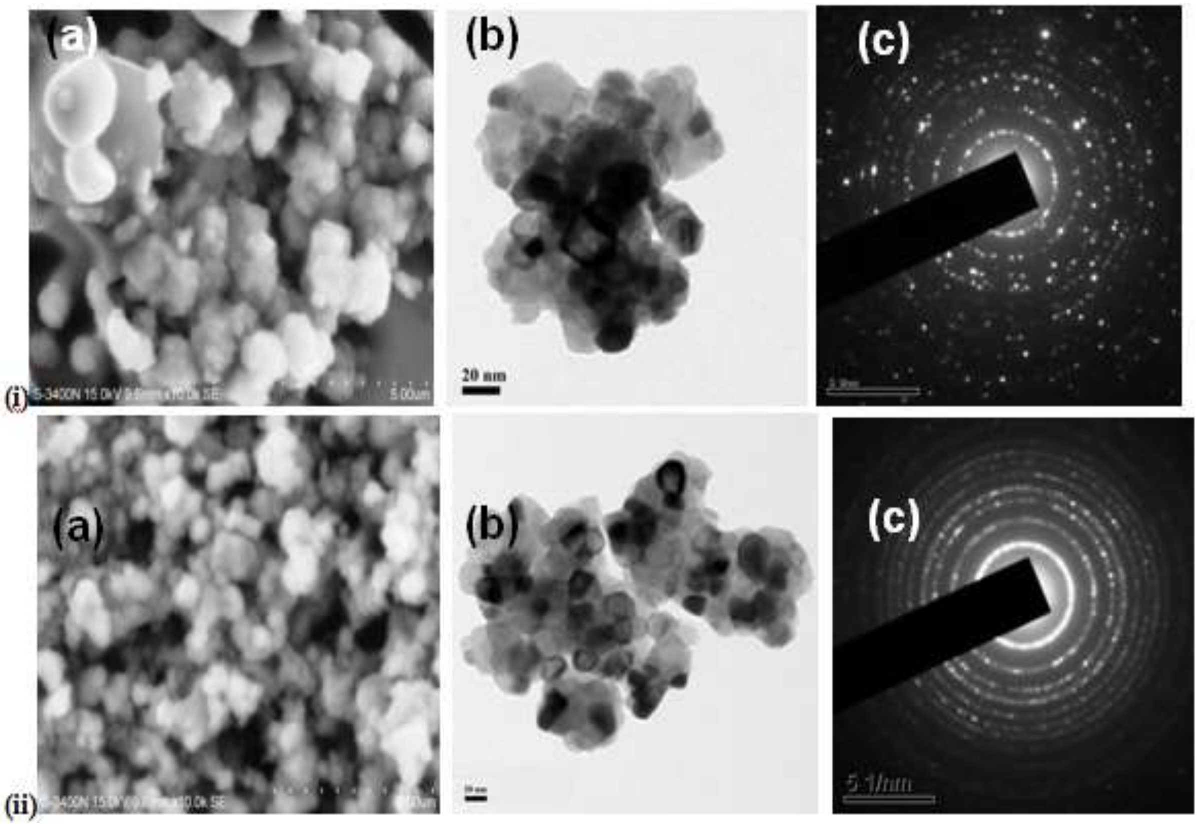
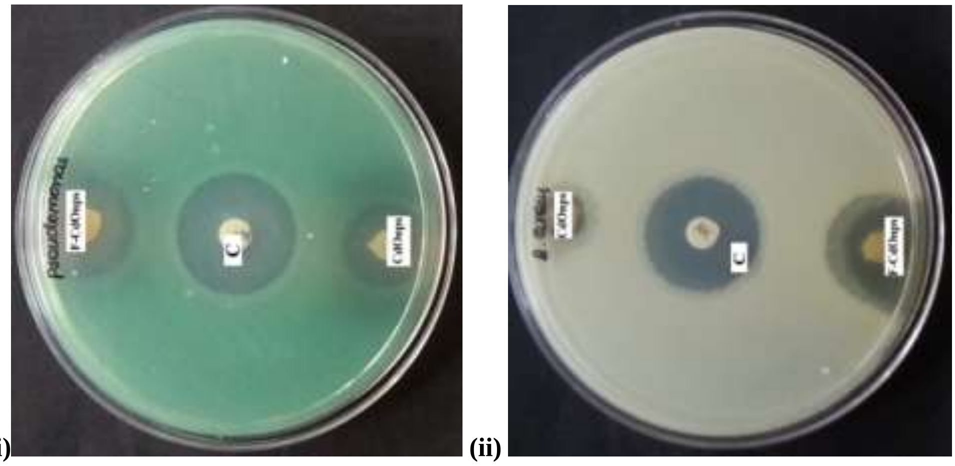


Fig. 4. (a) SEM and (b) TEM images, and (c) SAED patterns of (i) CdOnps and (ii) F-CdOnps.

SEM and TEM images, and SAED patterns of CdO and F-CdOnps were shown in Fig. 4(i) and (ii), respectively. It can be seen from Fig.4 (i) that particles are of irregular agglomeration, truncated cubes with different shaped as aggregates with sizes ranging from 11 to 46nm with an average size of 24nm. F-CdOnps showed more regular arrangement, and clear formation of nanoparticles. It established the size of the nanoparticles controlled by fluorine doping and demonstrated the particle distribution ranging from 10 nm to 35 nm with average size of 14nm. The sizes got from TEM images concur almost fit with the XRD and SEM results. In evaluation to the number of larger sized particles, smaller sized particles were created more in number. This may possibly due to the confinement of nanoparticles by fluorine. The bigger particles present here were owing to the overlapping of tiny particles. This showed fluorine plays a vital function in the formation of CdOnps with some agglomeration and obviously monitored in Fig. 4. SAED pattern of the crystalline areas of bright circular rings indicating high crystallinity in the F-CdOnps with respect to pure CdOnps.

3.5 Antimicrobial Activities of Prepared Nanoparticles

Fig.5 shows the antibacterial activity of CdO and F-CdOnps against (Gram negative pathogen) *P.*aeruginosa and (Gram positive pathogen) B.cereus.



(i) (ii)

Fig. 5. Zone of inhibition of CdOnps and F-CdOnps for (i) *P.aeruginosa* and (ii) B.cereus respectively.

The antibacterial activity shows that the gram positive bacterial strain is less affected than gram negative. F-CdOnps exhibit greatest activity in *P*.aeruginosa (20mm) and the lowest in B.cereus (13mm). Similarly CdOnps display best ctivity in *P*.aeruginosa (15mm) than B.cereus (9mm). F-CdOnps show more action with respect to CdOnps because fluorine can influence bacterial metabolism (enzyme inhibitor), and also metal fluoride complexes are accountable for fluoride inhibition of proton translocating F-ATPases and mimicking phosphate to form complexes with ADP at the reaction centers of the enzymes [16]. Based on Fig.5, the antibacterial activity of F-CdOnps was more because smaller particles having bigger surface area, which can enhance the capability to go through cell membrane and provide more bactericidal effect.

4. CONCLUSION

In present study, CdO and F-CdOnps were obtained by wet chemical method and characterized by XRD, FT-IR, UV-vis, SEM and TEM. XRD pattern showed that the fine created nanoparticles and has FCC structure. SEM and TEM proved the creation of 14nm sized nanoparticles. UV–vis spectra of CdO and F-CdOnps specify the quantum confinement result with blue shift. The band gap energy increases with decreasing particle size owing to fluorine replacement. Fluorine remarkably doped with CdOnps and decreased the surface defects. The prepared nanoparticles revealed size dependent antibacterial activity. This approach will be extremely useful for the synthesis of nanostructures in various valuable industrial applications for inhibiting the growth of bacteria.

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