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Research Article

STRUCTURAL, OPTICAL AND ANTIBACTERIAL ACTIVITY OF UNDOPED AND La DOPED CdO NANOPARTICLES SYNTHESIZED BY SIMPLE PRECIPITATION METHOD

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ABSTRACT

Nanoparticles of undoped and La doped CdO have been obtained by simple precipitation method with different La concentrations (3, 5, 10 and 15 at. %). Influence of La dopant on crystal structure, microstructure, optical properties and antibacterial efficiency of the nanoparticles was investigated by means of X-ray diffractometer, field emission scanning electron microscope, photoluminescence spectrometer and antibacterial examination. Crystal structure analysis reveals that La doping appreciably increases the crystalline size and also it shows the polycrystalline nature of the samples. Microstructural investigation shows that the samples contain nanoparticles. The optical property has determined by the PL spectral analysis. It has also been found that La dopant with CdO increases the zone of inhibition for both gram positive and gram negative bacterial strains.

INTRODUCTION

Recently researchers have much attention on the synthesis of nano sized semiconductor metal oxides because of their fundamental importance and wide range of potential technological applications (Saito *et al*., 2004; Srivatsava *et al*., 2006). It's known that II-VI semiconductor have attracted much attention due to their unique properties for their applications in optoelectronics (Wageh *et al*., 2011). Semiconductor nanoparticles belong to state of matter in the transition region between molecules and solids (Guozlong Cao, 2004). There has been a keen interest in the study of Transparent Conductive Oxide materials such as ZnO, CdO, SnO_2, In_2O_3, and TiO (Ginley and Bright, 2000) for novel applications in wide area of science and technology. Among the transparent conductive oxide nanomaterials, CdO is one among the important n-type semiconductor metal oxide with a direct band gap of 2.2 eV – 2.7 eV and an indirect band gap of 1.36 eV - 1.98 eV (Kuo and Huang, 2006). So far a number of CdO nanostructures have been synthesized with different interesting morphologies including nanoparticles (Askarinejad and Morsalli, 2008), nanowires (Peng *et al*., 2002), nanotubes (Bazargan *et al*., 2009), nanorods (Salunkhe *et al*., 2009), nanobelts (Pan *et al*., 2001) by different methods. CdO is non-toxic, low cost and chemically stable under exposure to both high temperature and capable of photo catalytic oxidation (Saeed Rezaei-Zarchi *et al*., 2010). According to literature transition and rare earth elements are added to CdO to enhance its carrier concentration and antibacterial efficiency. Recently, Z.A. ALahamed *et al*. (Dakhel and Ali-Mohamed, 2007) studied the influence of La doping on CdO thin films for opto-electronic applications. To the best of our knowledge CdO nanoparticles has not been studied so far using the above mentioned dopant and synthesise technique. Thus the present work focuses on the effect of La dopant on the physical, optical and antibacterial properties of CdO nanoparticle. The motivation behind the selection of La as dopant is that doping increases the CdO lattice parameters and the optical parameters decreases for 2.1 eV to 1.7 eV (Kittel, 1995). Simple precipitation method has been adopted for the present work because it reveals the smallest nanoparticle with good optical properties when compared to other synthesis procedures.

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Experimental

Material Synthesis

Undoped and La doped CdO nanoparticles were synthesized by precipitation method with cadmium acetate, lanthanum nitrate, and sodium hydroxide as starting materials. All these were used without further refinement. Double distilled water was used as solvent for sample preparation. Undoped and La doped CdO nanoparticles were efficiently synthesized. Initially, cadmium acetate as a precursor was dissolved in water. Sodium hydroxide which is dissolved separately were added to the above solution drop wise until pH value of about 8 is obtained under constant stirring. The precipitate was formed and it was allowed to settle overnight. Then, filtered and washed 3- 4 times with water. It was dried at 100°C and then grinded. The resulting powder was calcined at 400°C for 2h. During calcination, the as prepared powder losses the remaining water content and the unreacted compounds. For the synthesize dopants appropriate amount of cadmium acetate and lanthanum nitrate (3, 5, 10 and 15 at %) were subjected under the same experimental procedure.

Instrumentation

The crystalline structure of the samples was analyzed by X-ray diffraction (XRD) using a Bruker AXSD8 Advance instrument equipped with Ni filtered CuKa radiation (k = 1.54187 Å) in the range of 10°–80° in steps of 0.0025 at a scan speed of 2°/min. with scanning rate of 1°/min operated at 40 kV/30 mA. The morphology of the synthesized powder was examined by FE-SEM (JEOL-JSM-6301 FE-SEM) operated at an accelerating voltage, above 5 kV/20 mA and a magnification of $5x10^4$. Photoluminescence (PL) response of the powder samples was carried out by means PL spectrometer (Kimon, SPEC-14031 K, Japan) with a He-Cd laser source. A line spectrum of 450 nm has been used to excite the samples.

Antibacterial activity test was carried out following the modification of the method originally described by Bauer *et al.*, (1966). Muller Hinton agar was prepared and autoclaved at 15 lbs pressure for 20 minutes and cooled to 45ºC. The cooled media was poured on to sterile petri-plates and allowed for solidification. The plates with media were seeded with the respective microbial suspension using sterile swab. The various solvents extract prepared discs individually were placed on the each petri-plates and also placed control and standard (ciprofloxacin 10 µg for Bacteria) discs. The plates were incubated at 37ºC for 24 hrs. After incubation period, the diameter of the zone formed around the paper disc were measured and expressed in mm.

RESULTS AND DISCUSSION

Structural Analysis

Figure 1 shows the XRD patterns of undoped and La doped CdO nanoparticles. All the diffraction peaks are reflections of samples indexed to cubic phase of CdO with a lattice parameter of a=4.695Å. It is matched well with the standard JCPDS (05-0640). No diffraction peaks of the possible impurity peaks such as CdO_2, $Cd(OH)_2$ and $CdCO_3$ are found, which indicates the successful preparation of CdO. The observed diffraction peaks at 2θ = 33.6°, 39.1°, 55.3°, 66.1° and 69.3° are associated with (111), (200), (220), (311) and (222) lattice planes. The average crystalline size was calculated using Scherrer formula;

$$D = \frac{0.9\,\lambda}{\beta\ \cos\theta}$$

Where λ is the wavelength used, β is the peak width at half maximum and θ is the Bragg's diffraction angle. The average crystallite size D is calculated from the (111) lattice plane and found that particle size increases from 23 – 27 nm with respect to the increase in the diffraction peak. This is due to the crystal imperfection like vacancies and interstitials of La doping in CdO.

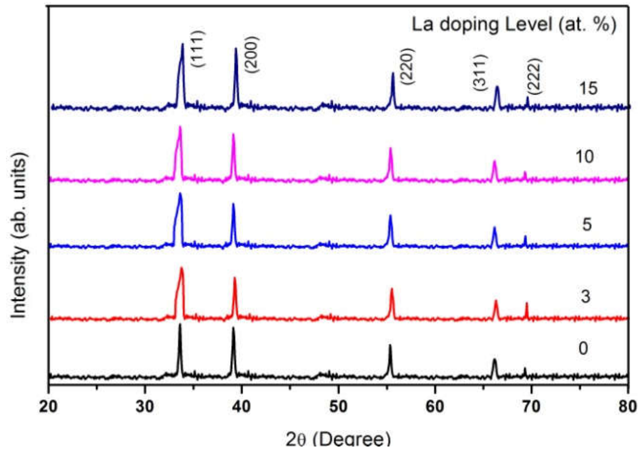

Fig. 1. XRD patterns of Undoped and La doped CdO nanoparticles

FESEM and EDAX

The FESEM image of undoped and La doped CdO nanoparticles are shown in the Figure 2. From the figure it is clear that the undoped CdO posses uniform structure. But when compared with that of La doped CdO they are seemed to be porous with some kind of agglomerated fibrous spheres which can be called as nanowires or nanorods. Based on the morphological studies the creation mechanism of nanospheres is explained as follows; Cd^{2+} ions are released from cadmium acetate and OH^- ions are released by sodium hydroxide in aqueous solution. These results are in the formation of cadmium hydroxyl ions (Anandhan and Thilak Kumar, 2015; Navaneethan *et al.*, 2012). Thus, this consists of irregular nanospheres in morphology. It is also noted that the average grain size is in the range of 23-27 nm. The EDAX image from the Figure 3 reveals that the presence of Cd, O and La atoms are present and no other characteristic peaks of impurities or other precursor compounds are observed.

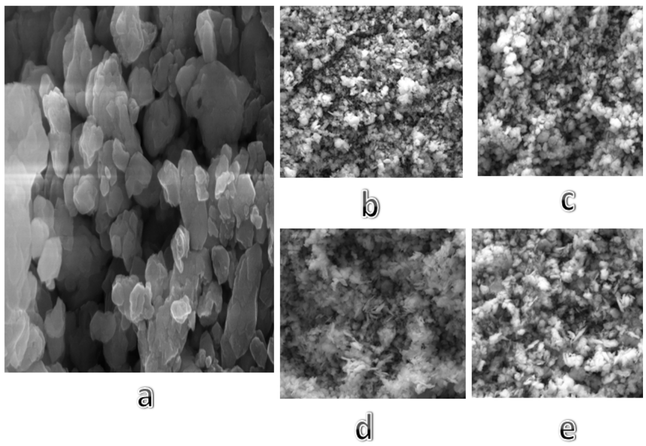

Figure 2. FESEM images of CdO: La nanopowders with doping level (a) Undoped CdO (b) 3 at % (c) 5 at % (d) 10 at % (e) 15 at %

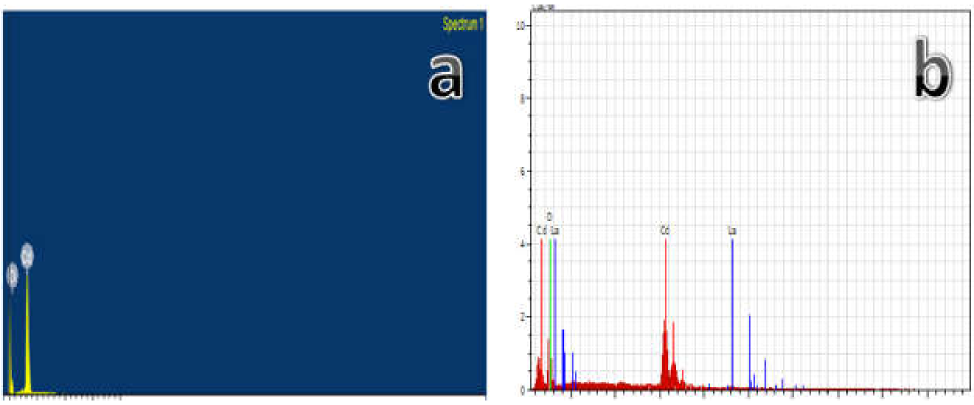

Figure 3. EDAX spectrum (a) Undoped CdO (b) La doped CdO

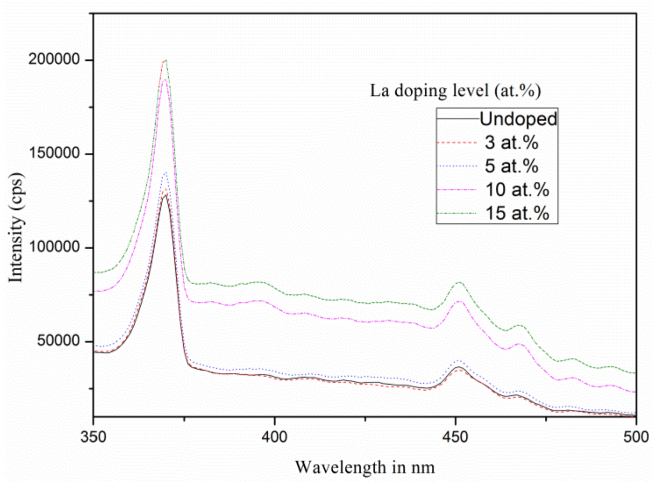

Fig. 4. Photoluminescence Spectrum of CdO and various concentration of La doped CdO nanoparticles

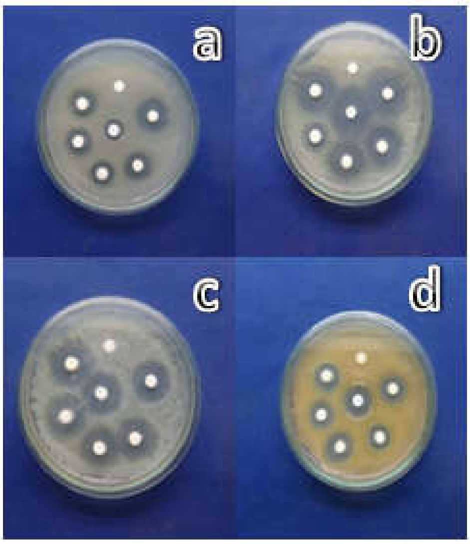

Figure 5. Antibacterial activity of CdO and La doped CdO microplates against (a) Bacillus subtilis (b) Escherichia coli (c) Klebsiella pneumonia (d) Staphylococcus aureus

Table 1. Antibacterial activity of CdO and La doped CdO against bacterial pathogenic organisms

S.No	Bacteria	Zone of Inhibition (mm in diameter)					
		S*	Undoped	La 3 at %	La 5 at %	La 10 at %	La 15 at %
1	Bacillus subtilis	14	16	16	17	18	20
2	Staphylococcus aureus	17	18	18	19	21	22
3	Escherichia coli	15	16	15	16	17	18
4	Klebsiella pneumoniae	21	21	20	23	23	25

Photoluminescence

Figure 4 shows the PL spectra of the undoped and La doped CdO nanoparticles measured in room temperature. The PL spectra show sharp and maximum emission peak around 370 nm. It can be seen from the figure that La^{2+} doped CdO nano particles show a dominant emission peak around 370 nm (violet emission). The intensity of the peak related to the Cd interstitials increases as the concentration of La increases which is a supporting evidence of the substitution of the dopant. This peak has been assigned to near band edge emission. It has been noted that if the concentration of the oxygen vacancy is reduced in the synthesized products then it results in the appearance of a sharp and strong intensity near band edge (NBE) (Aswani *et al*., 2014; Wahab and Ansari, 2007; Umar and Hahn, 2006; Ying *et al*., 2003). In this work the sample shows strong and sharp emission NBE which confirms the good optical property with fewer defects. It was reported that depending on the particle size and excitation wavelength, the different emission peaks could be seen in the range of 350-500 nm peaks (Ghosh *et al*., 2004; Dong and Zhu, 2003). The peak at 451 nm (blue emission) is a result which arise from the combination of the electron from the conduction band and holes from the valence band. A small intense peak at 468 nm is due to the singly ionised oxygen vacancy which plays a major role in antibacterial activity of the material.

Antibacterial Activity

The antibacterial effects of CdO and La doped CdO shows a level of inhibition effects against the tested pathogenic organisms in impregnated discs. Maximum zone of inhibitory action (ZOI) appeared in the entire test compared with undoped and La doped CdO. The antibacterial activity is carried against two different Gram positive (*Bacillus subtilis* & *Staphylococcus aureus*) and Gram negative (*Escherichia coli & Klebsiella pneumoniae*) bacterial strains. From the Figure 5 it is observed that there is no zone of inhibition around the control. The antibacterial efficiency increases with the increase in the La doping concentration may be of (i) the generation of Reactive Oxygen Species (ROS) (ii) Release of Cd^{+} ions and (iii) size of the nanoparticles. The generation of ROS can be written as (Ravichandran *et al*., 2015)

$CdO + h\nu \rightarrow h^{+} + e^{-}$

$h^{+} + H_2O \rightarrow OH^{\bullet} + H^{+}$

$O_2 + e^{-} \rightarrow O_2^{\bullet -}$

$O_2^{\bullet -} + H^{+} \rightarrow HO_2^{\bullet}$

$H^{+} + HO_2^{\bullet} + e^{-} \rightarrow H_2O_2$

$H_2O_2 + O_2^{\bullet} - \rightarrow OH^{\bullet} + O_2 + OH^{-}$

In the present study the zone of inhibition is found to be more for gram positive bacteria and gram negative for La doped CdO when compared with undoped CdO. The toxic hydrogen peroxide released damages the structure of the bacteria cell membrane and depresses the activity of some enzymes which cause it to die eventually (Karthik *et al*., 2014). The basic mechanism of antibacterial action of the material states that the production of reactive oxygen species on the surface of these nanoparticles in light cause oxidative stress in bacterial cell and leads it to die. The ROS contains the most reactive hydroxyl radicals (OH), less toxic super oxide anion radical (O_2^{-}). This damages the DNA, cell membrane etc., leading the cell to death. This is attributed to the electrostatic attraction between the negatively charged bacteria and the positively charged nanoparticles (Abdulrahman Syedahamed Haja Hameed *et al*., 2013). From the observed SEM images, we can say that the wire shaped nanoparticles possess highest antibacterial efficacy over the other nanostructures. The zone of inhibition values are stated in the Table 1. It is found that there is an increase in the inhibition value for La doped CdO when compared with undoped CdO.

Conclusion

Undoped and La doped CdO nanoparticles have been successfully synthesized by simple precipitation method. XRD pattern confirms the formation of CdO phase. There is an increase in the particle size as the concentration of La dopant increases. The FESEM image reveals undoped CdO posses uniform structure whereas La doped CdO posses some fibrous wire shaped structure. The EDAX shows that the sample contains only Cd, O and La atoms only. The photoluminescence studies show high intensity in the peaks of violet band emission at 370 nm and blue band emission at 468 nm with increase in the dopant concentration which are responsible for better antibacterial activity. The biological activities of the synthesized nanomaterials showed fast and strong activity against the gram positive and gram negative bacterial strains.

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