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Synthesis and Characterisation of Cdo-Ceo$_2$ and Zinc Doped Cdo-Ceo$_2$ Nan oparticles and its Photo catalytic Activity

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ABSTRACT

Nanotechnology is the art and science of manipulating matter at the nanoscale to create new and unique materials and products. Metal nanoparticles have been intensively studied within the past decade due to their potential application in electronic , optical and mechanical devices. This research work attempted synthesis , characterization and the photo catalytic application of a bimetallic nanoparticle. CdO-CeO$_2$ and Zn doped CdO-CeO$_2$ nano particles were prepared by Co-precipitation method. The synthesized nanoparticles were characterized by X-ray diffraction analysis (XRD), Scanning electron microscope (SEM), Energy dispersive x-ray analysis (EDX) and Fourier transform infrared spectroscopy (FTIR). X-ray diffraction study reveals that the synthesised nanoparticles have the particle size of 55 nm and 36 nm respectively .SEM analysis shows that the particles are of spherical shape. The Energy dispersive x-ray analysis (EDX) reveals the elemental composition of the prepared nanoparticles and the inclusion of Zn ions in the lattice. FTIR spectrum shows the characteristic Cd-O and Ce-O-O stretching modes of vibration. Photocatalytic degradation was investigated for congo red dye under UV-visible irradiation source for the Zn doped and undoped CdO –CeO$_2$ nanoparticles. It reveals that the zinc doped nanoparticle has enhanced photocatalytic activity than the undoped nanoparticle.

KEY WORDS : Nanoparticle , dopant ,, Co- precipitation method, XRD, FTIR, Photocatalytic activity.

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1.INTRODUCTION:

Over the past few years , the synthesis and functionalism of nanostructures have attracted great interest due to their significant potential application[1] . Nanotechnology is defined as the intentional design, characterization, production and applications of materials, structures, devices and systems by controlling their size and shape in the nanoscale range 1-100nm[2]. The term Nanotechnology was first coined by Tokyo Science University professor Norrio Taniguchi in 1974. He used the term 'nanotechnology' to represent extra high precision and ultra-fine dimensions, and also predicted improvements in integrated circuits, optoelectronic devices, mechanical devices and computer memory devices[3]. An important feature of nanotechnology is its ability to bridge the crucial dimensional gap between the atomic and molecular scale of fundamental sciences and the micro structural scale of engineering and manufacturing[4]. Coverage of nanotechnology with other science and technologies including biotechnology, chemistry, physics, and engineering may increase the magnitude of its transformative potential. Nanotechnology can be used in construction materials for floors, machines, new devices, and techniques in electronics, medicine, wastewater, water treatment, biology, biochemistry and agriculture, and food processing[5].

Pollution is an environmental problem of worldwide concern. Organic dyes in water are one of the important classes of pollutants. These dyes find application in many industries including textile, cosmetic, food colorants, printing and pharmaceutical industries[6]. Over $7x10^5$ tons and above 10,000 different types of dyes and pigments are produced worldwide yearly. The release of waste waters that contain high concentration of dye is a major trouble for the industry as well as the threat to the environment. Dyes are extensively used in textile industry and particularly those involved in finishing processes are among the major cause of water pollution[7]. Most of the dyes used in the textile industry are highly stable, soluble in water and are low biodegradable[8]. Water contaminated with dyes is a major threat to the environment. Even very low concentrations of dyes in the effluents is highly visible and undesirable. It reduces the light penetration resulting in the inhibition of photosynthesis and ultimate destruction of organisms living in water bodies[9].The heterogeneous photo catalysts are an important destructive technology that leads to higher mineralization of organic pollutants[10].Photo catalytic process has been found to be very active in the treatment of wastewater for the mineralization of broad range of organic pollutants.[11]

There is a great research interest for the synthesis of metal oxide nano particles due to their potential applications in electronic, optical and mechanical devices based on variable oxidation states [12]. Metal oxides play a very important role in many areas of chemistry, physics and materials science [13]. Metallic oxides are becoming prominent and important group of materials due to their versatile physiochemical, structural, and optical characteristics which include high temperature superconductivity, ferroelectricity, ferromagnetism, piezoelectricity, semi- conductivity, optical, opto-electronic, magnetic, electric, thermal, electrochemical, catalytic and sensor properties[14].

The brown cadmium oxide is generally formed by burning of Cd in air and is one of the promising candidates for optoelectronics. Cadmium oxide a II –VI n- type semiconductor has interesting properties like large band gap, low electrical resistivity and high transmission in the visible region etc which makes it useful for a wide range of applications such as solar cells, photo transistors, photo diodes, transparent electrodes and gas sensors. CdO has 2.5ev direct band gap and 1.98eV indirect band gap. The optical transmittance of CdO in the visible region of the spectrum has been reported to be low[15]. In medicine, one particularly important metal oxide NP is cadmium oxide (CdO), which is used as a starting material for the generation of QD, as well as for medical imaging and targeting of pharmaceutical agents to sites of disease (Chan et al., 2005)[16]. CdO nanoparticles have anticancer properties. They are used in various fields such as delivery of drugs to the tumor cells, pulling out the cancer of live cells, attacking to cancer cells, improving the sensitivity of cancer cells to imaging and observing them more accurately. Recently multifunctional CdO nanoparticles have been used for early diagnosis of pancreatic cancer[17].

Cerium oxide nanoparticles (CeO_2 NPs), also known as nanoceria, are one of the most economically valuable manufactured nanoparticles currently in production (Wang et al. 2008). They are used in catalysts (Zheng et al. 2005), solar panels, fuel cells (Murray et al. 1999; Corma et al. 2004), as diesel fuel additive (Park et al. 2008a,b), and for glass and ceramic applications (Eom and Choi 2009). Cerium is a lanthanide series rare earth element that can either exist as a free metal or cycle between the cerium (III) and cerium (IV) oxidation states (Heckert et al. 2008). Nanoceria also cycle between the Ce (III) and Ce (IV) valence states, and they contain oxygen vacancies that allow the nanoparticles to act as an regenerative catalyst (Heckert et al. 2008)[18]. CeO_2 is a well-known functional rare earth oxide and nano structured ceria has been extensively used in many areas including high storage capacitor devices, buffer layer for conductors, fuel cells, polishing materials, UV blocks and optical devices. In addition CeO_2 has been widely used in automotive catalyst, due to its unique characteristics of facile Ce (v) and Ce (11) switching.

2. MATERIALS AND METHODS:

2.1 Materials:

CdO-CeO_2 nanoparticle and Zn doped CdO-CeO_2 nanoparticle were prepared by Co-precipitation method. All the reagents used were analytical grade, obtained from Merck India Ltd, and used as received without further purification.

2.2. Synthesis of cdo-ceo$_2$ bi metal oxide nanoparticles

CdO-CeO_2 nanoparticle was prepared by adding an aqueous solution of 1 M NaOH drop wise to the aqueous solution of 0.1 M of both $Ce(NO_3)_3.6H_2O$ and $Cd(NO_3)_2.4H_2O$ with concurrent stirring. The P^H of the mixed solution was adjusted to 8. After 4 hours of continuous stirring, the precipitate was filtered and repeatedly washed with deionized water. The residue was dried in an oven at 110^0C overnight and then grounded in acetone, with mortar and pestle. The powder received was then calcined at 500^0C for 4 hours under static air in a muffle furnace.

Zn doped CdO-CeO_2 nanoparticle was prepared by adding an aqueous solution of $Zn(NO_3)_2$ in the above procedure.

2.3. Characterization of cdo- ceo$_2$ and zn doped cdo-ceo$_2$ nanoparticles.

The samples were characterized by powder X- ray diffraction (Bruker, Advance D8) with Cu Kα (λ=1.5406 Å) incident radiation. The size distribution and morphology of the samples were analyzed by scanning electron microscopy (SEM, Philips XL30) . Energy dispersive spectrometry (EDS) attached to SEM was employed to perform the elemental analysis of the nano structured materials. .FTIR spectrum was recorded at 400-4000cm^{-1}wavelengths using KBr pellets. Photocatalytic degradation was investigated with congo red under UV-irradiation source

3.RESULTS AND DISCUSSION:

3.1 XRD analysis

Structural parameters of the prepared nanoparticles are calculated from the XRD pattern. The crystallite size was calculated from broadening data using Debye scherrer's equation.

$$D=k\lambda/\beta\cos\theta$$

Where λ is the wavelength of the x-ray radiation used and is equal to $1.5406A^0$. k is the scherrer constant equal to 0.94,β is full width at half maximum (FWHM) intensity of the diffraction peak in (radian), θ is Bragg's diffraction angle of the diffraction peak and D is the crystallite size in nanometer(nm).

3.1.1 XRD analysis of cdo-ceo$_2$ bimetal oxide nanoparticles

The 2θ values ranges from 20 to 80^0 for the characteristic peaks of ternary oxides of cerium and lanthanum with transition metals is shown in fig. 1. The XRD pattern shows the characteristic peak of CdO and CeO_2.The synthesized particle is 55 nm as determined by scherrer equation.

3.1.2 XRD patterns of zn doped cdo-ceo$_2$ nanoparticles.

Fig. 2 shows diffraction Peaks at 2θ Values of 17.8702^0,30.4909^0, 33.0710^0, 37.2473^0. Based on the schrerrer equation the average crystallite size of the nanoparticles are observed as 36 nm.

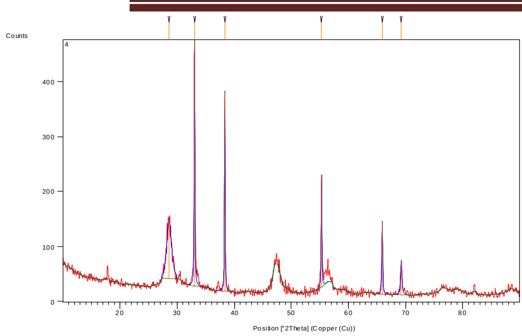

Fig. 1 : XRD parameters of cdo-ceo$_2$ cdo-cep$_2$ nanoparticles

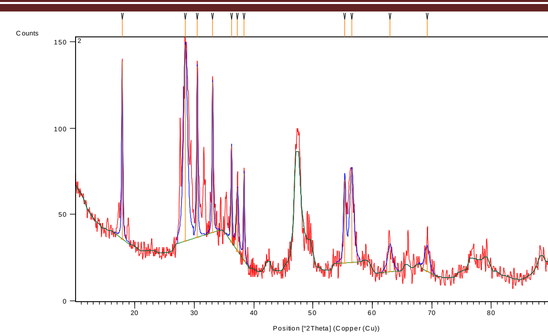

Fig. 2 : XRD patterns of Zn doped nanoparticles

3.2. SEM analysis

Scanning Electron Microscopy (SEM) was employed to analyze the morphology and the growth features of prepared nanoparticles

3.2.1.SEM analysis of cdo-ceo$_2$ and zn doped bimetal oxide nanoparticles

The morphological studies of the synthesized CdO-CeO$_2$ bimetal oxide nanoparticles have been carried out by scanning electron microscopy. Fig. 3 displays the SEM image of the product. It is observed that the product consist of agglomerated nanoparticles and is found to have spherical shape.

3.2.2.SEM analysis of zn doped cdo-ceo$_2$ nanoparticles

Fig. 4 displays the SEM image of Zn doped CdO –CeO2 nanoparticle.product. It is observed that the particles are of uniform spherical shape and is found to be agglomerated.

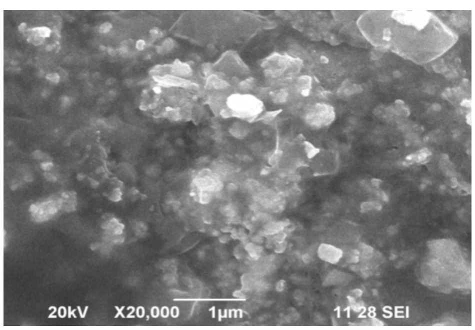

Fig. 3 : SEM image of cdo -ceo$_2$ nanoparticles

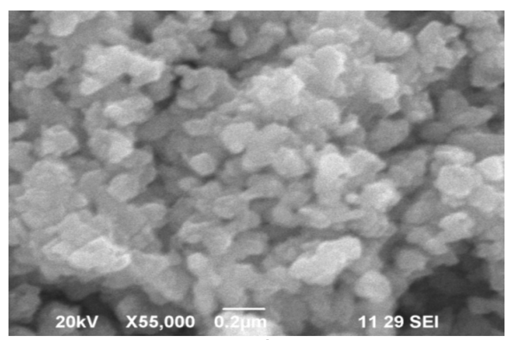

Fig. 4 : SEM image of Zn doped CdO -CeO$_2$ nanoparticles

3.3.EDX analysis

3.3.1. EDX spectrum of cdo-ceo$_2$ bimetal oxide nanoparticles

The elemental composition of CdO-CeO$_2$ bimetal oxide nanoparticles were carried out by EDX spectrum. Fig. 5 shows the EDX spectrum of CdO-CeO$_2$ bimetal oxide nanoparticles. The strong peaks observed in the spectrum related to Cd ,Ce and O. The elemental constitution of CdO-CeO$_2$ nanoparticles with three major peaks was found to have weight percentage at 31.14 of Cd

,29.21 of Ce, 39.65 of O. The prepared $CdO-CeO_2$ nanoparticles have atomic percentage at 9.35 of Cd,7.03 of Ce and 83.62 of O. This confirmed the formation of $CdO-CeO_2$ bimetal oxide nanoparticles.

3.3.2 EDX spectrum of zn doped cdo-ceo$_2$ nanoparticles

The elemental composition of Zn doped $CdO-CeO_2$ nanoparticles were carried out by EDX spectrum. Fig.6 shows the EDX spectrum of Zn doped $CdO-CeO_2$ nanoparticles. The strong peaks observed in the spectrum related to Zn, Cd and Ce. The elemental constitution of Zn doped $CdO-CeO_2$ nanoparticles with four major peaks was found to have weight percentage at 14.85 of Zn, 34.41 of Cd, 18.74 of Ce and 32 of O. The prepared Zn doped $CdO-CeO_2$ nanoparticles have atomic percentage at 8.52 of Zn, 11.48 of Cd, 5.01of Ce and 74.99 of O. This confirmed the doping of Zn ion in the $CdO-CeO_2$ nanoparticles

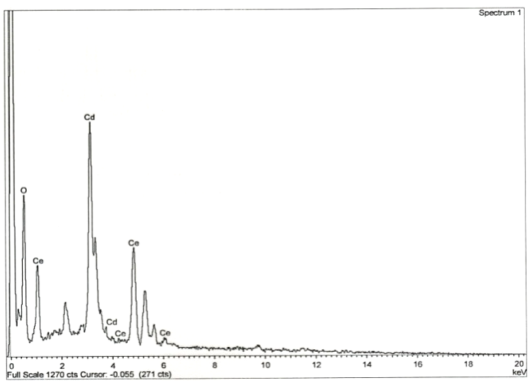

Fig. 5:EDX spectrum of cdo-ceo$_2$ bimetal oxide nanoparticle

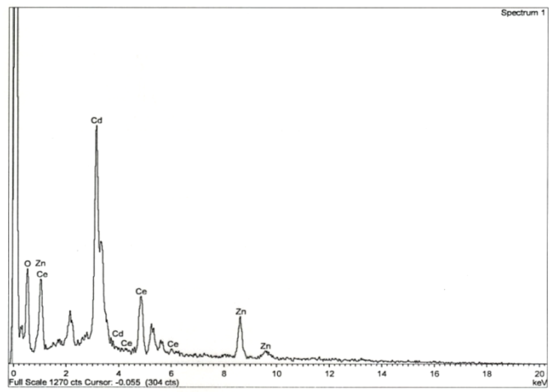

Fig. 6:EDX spectrum of Zn doped cdo-ceo$_2$ nanoparticles

3.4.FTIR analysis

FTIR spectrum of $CdO-CeO_2$ and Zn doped$CdO-CeO_2$ nanoparticles were shown in fig. 7 & 8. Figure illustrates the FTIR spectra of these nanoparticles in the range of 400-4000cm^{-1}.

The specified strong peaks at about 1690 cm^{-1}in fig. (7) belong to the stretching vibration bands of the carbonyl groups. The weak peak at 1182 cm^{-1}in fig. (7) is related to the C-O vibration band. The absorption band at 3385cm^{-1}in fig (7) and 3526cm^{-1}, 3587cm^{-1} in fig. (8) was attributed to the N-H symmetrical and asymmetrical stretching vibration band respectively. Peaks found in 1344cm^{-1}in fig.(8) corresponds to the N-O stretching.

In fig(7) the appearance of the weak absorption band at 696cm^{-1} indicates the formation of the

Cd-O phase in the structure. The peak observed at 791,897,864,836 cm^{-1} corresponds to the Ce-O-O stretching mode of vibration. In fig.(8) the appearance of the weak absorption band at 696cm^{-1}

indicates the formation of the Cd-O phase in the structure. The peak observed at 650cm^{-1} corresponds to the Ce-O-O stretching mode of vibration.

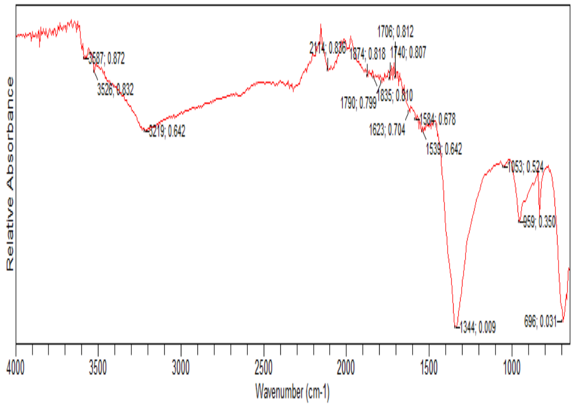

Fig.7 : FTIR spectrum of cdo-ceo$_2$ nanoparticles

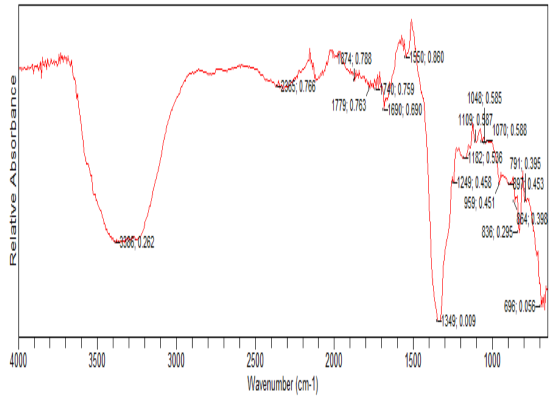

Fig.8: FTIR spectrum of Zn doped Cdo-ceo$_2$ nanoparticles

3.5 .Photo catalytic Activity

The photo catalytic activities of CdO-CeO_2 and Zn dopedCdO-CeO_2 nanoparticles particles were carried out using UV and visible light.In the UV region the doped CdO-CeO_2sample degraded the dye faster than the undoped CdO-CeO_2 nanoparticles. The reason is being increase in surface defects on account of doping leading to enhanced absorption in the visible region. Once the above samples are irradiated to visible light electron hole pair is generated. The electron so generated disrupts the conjugation in the dye and thus decomposition of dye and the hole so generated creates OH from water which again leads to degradation of dye.

The plot of absorption versus time at particular wavelength for the photo degradation of dye is represented in fig 5 (a) &5 (b), Figure shows that the degradation efficiency of Zn doped CdO-CeO_2 nanoparticles was higher than the undoped CdO-CeO_2nanoparticles for the organic dyes. Also the degradation is faster when the concentration of adsorbent is increased. The doped CdO-CeO_2 nanoparticles exhibit enhanced photo catalytic activity and can be efficiently used as photo catalyst in the process of removal of organic dyes and can be used for environmental cleaning.

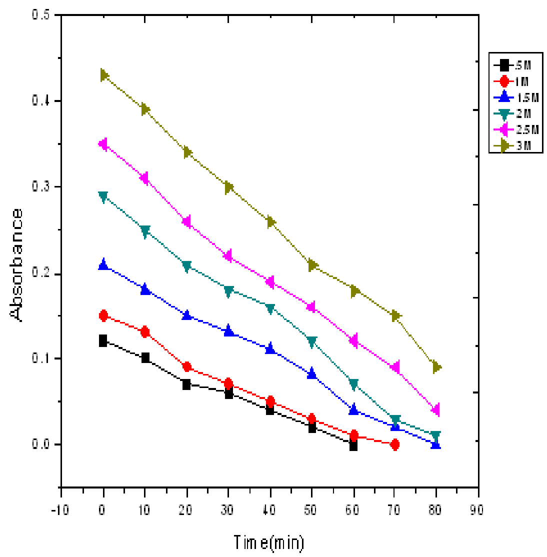

Fig. 9: photo catalytic degradation of congored with cdo-ceo$_2$nanoparticles

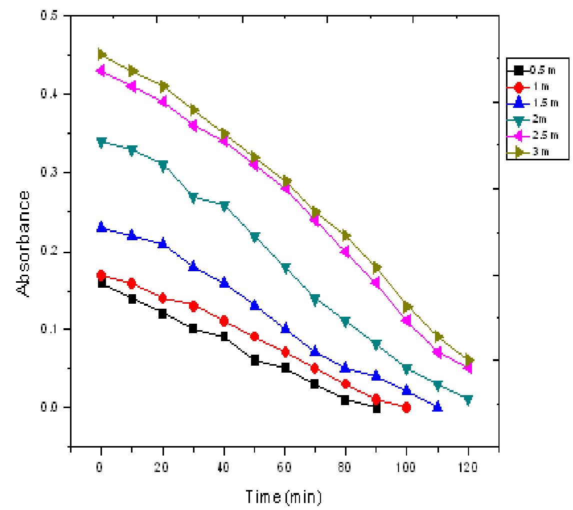

Fig. 10 : photo catalytic degradation of congored with Zn doped cdo-ceo$_2$ nanoparticles

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