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Bioinspired Synthesis And Electrochemical Characterization Of Cerium Doped Cadmiumoxide Nanoparticles Assisted By Citrus Sinensis Peel Extract

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Abstract: - The synthesis of semiconductor nanoparticles is an expanding research area due to the potential applications in the development of nanotechnologies. The CdO nanoparticles have been synthesized by adding a peel extract of Citrus sinensis into the aqueous solution of Cadmium nitrate. The aqueous citrus sinensis peel extract acts as a solvent with multiple roles as promoter, capping agent and reductant for the synthesis of undoped CdO and Ce ion doped CdO nanoparticles. Cadmium Oxide nanoparticles were characterized by using UV-Visible spectrophotometer, XRD and SEM. The size of the CdO nanoparticles and Ce ion doped CdO nanoparticles were estimated to be 43.09 nm and 46.72 nm using Debye-Scherrer equation. Photocatalytic degradation was also investigated with Rhodamine dye under UV-irradiation source. The CdO and Ce ion doepd CdO nanoparticles exhibited potential photocatalytic activity towards the degradation of Rhodamine dye. Green synthesis using Citrus sinensis found to be the best capping agent for synthesizing nanoparticles.

Keywords: Cadmium oxide nanoparticles, Green synthesis, Citrus sinensis, UV-Vis, XRD, SEM, Photo degradation.

INTRODUCTION

Nanoparticles have attracted great interest recently due to their unique physical and chemical properties, which are different from those of either the bulk materials or single atoms [1]. The field of nanotechnology is one of the most active researches in modern material science. Nanotechnology is emerging as a rapid growing field with its applications in science and technology for the purpose of manufacturing new materials at the nanoscale level. The nanoparticles possess unique physiochemical, optical and biological properties which can be manipulated suitably for desired applications. Green chemistry seeks to reduce pollution at source. Therefore the present investigation has been made to synthesize CdO nanoparticles by Citrus Sinensis.

CdO nanoparticles have found fabulous application such as photodiodes [2], phototransistors [3], photovoltaic cells, transparent electrodes, liquid crystal displays, IR detectors, solar cells [4,5] and anti-reflection coat. With this background of multi functionality CdO, it was thought worthwhile to use the nano-sized CdO as an inorganic counterpart in the composite preparation.

Citrus sinensis:

The orange is the fruit of the citrus species Citrus sinensis in the family Rutaceae. It is also called sweet orange, to distinguish it from the related Citrus aurantium, referred to as orange. The orange is a hybrid between pomelo (Citrus maxima) and mandarin (Citrus reticulata). It has genes that are ~25% pomelo and ~75% mandarin however, it is not a simple backcrossed BC1 hybrid, but hybridized over multiple generations. The orange tree is an evergreen, flowering tree, with an average height of 9 to 10 m (30 to 33 ft), although some very old specimens can reach 15 m (49 ft). Its oval leaves, alternately arranged, are 4 to 10 cm (1.6 to 3.9 in) long and have crenulate margins. Sweet oranges grow in a range of different sizes, and shapes varying from spherical to oblong. Inside and attached to the rind is a porous white tissue, the white, bitter mesocarp or albedo (pith). When unripe, the fruit is green. The grainy irregular rind of the ripe fruit can range from bright orange to yellow-orange, but frequently retains green patches or, under warm climate conditions, remains entirely green. Like all other citrus fruits, the sweet orange is non-climacteric.Orange is a popular fruit across the world for its numerous health and medicinal benefits. Oranges are good for overall development of the body because of the presence of vitamin, minerals, anti-oxidants, and other phyto-nutrients. An orange of 130 grams contains following nutrition. Vitamin C dominates in the nutrition profile of orange. It contain vitamin C (116.1%), Fibre (12.5%), Folate (9.8%), vitamin B1 (7.3%), Potassium (6.7%), vitamin A (5.8%), Calcium (5.2%) and Calories (3%). Oranges are abundant with Vitamin C. Vitamin C acts against free radicals and reduces the risk of colon cancer. Orange is having enough dietary fibre in the form of pectin, a great laxative, and prevents cancer causing cells to bind with colon. The presence of flavonoids group of anti-oxidants such as alpha and beta-carotene, beta-cryptoxanthin, zea-xanthin and lutein in orange help to protect against lung cancer, oral cancer, breast cancer and prostate cancer.

Fig.1 : Citrus Sinensis

METHODOLOGY

Collection of Plant: The peels of Citrus sinensis used in the present study were procured from the shops of Thoothukudi district, Tamilnadu.

Preparation of the peel extract:

Orange peels were prepared from fresh orange fruits. The peels were washed with water to remove the dust particles and then sun dried to remove the residual moisture. The extract used for the reduction of Cadmium ions (Cd2+) to CdO nanoparticles was prepared by placing 10g of dried fine cut peel in 250mL glass beaker along with 100mL of double distilled water. The mixture was then boiled for 60 minutes until the color of the aqueous solution changes from watery to light brown. The extract was cooled to room temperature and filtered using whatmann40 filter paper. The extract was stored in a refrigerator in order to be used for further experiments.

Synthesis of cadmium oxide nanoparticles using citrus sinensis peel extract:

50 mL of Citrus sinensis peel extract was taken and boiled to 800C using a stirrer heater. 5g of Cadmium nitrate was added to the solution as the temperature reached 800C. This mixture is then boiled until it is reduced to a deep brown colored paste. This paste was then collected in a silica crucible and heated in an air heated furnace at 4000C for half an hour. A light brown colored powder was obtained and this was carefully collected and packed for characterization purposes. The material was mashed in a mortar-pestle so as to get a finer nature for characterization.

Synthesis of Ce ion doped CdO nanoparticles using Citrus sinensis peel extract:

For the synthesis Ce ion doped CdO nanoparticle 50 mL of Citrus sinensis peel extract was taken and boiled to 800C using a stirrer-heater. 5g of Cadmium nitrate 1% Ammonium ceric sulphate (1g in 100mL) were added to this extract and the temperature reached 800C. The resulting solution was then boiled until it was reduced to a paste. This paste was then collected in a ceramic crucible and heated in an air heated furnace at 4000C for 30 minutes. A reddish brown coloured powder of CdO nanoparticles was obtained and this was carefully collected and preserved in the air-tight vials for further studies. The powder was mashed in a mortar-pestle so as to get a finer nature of the sample for further characterization studies. Similar procedure was adopted for the synthesis of Ce ion doped CdO nanoparticles of different concentrations of Ce such as 0.5%, 1.5% and 2% respectively.

Photocatalytic Measurement:

Nano sized CdO particle is a good photocatalyst to degrade organic contaminants, such as Rhodamine B dye. The photocatalytic degradation of Rhodamine B (RB) dye using CdO nanoparticles is investigated with the following process: six separate sets of experiments were performed to study the decomposition of RB dye in direct sunlight. In this experiment 0.1g of the synthesized undoped and doped Ce:CdO nanoparticles using Citrus sinensis were mixed with 100mL of 10-4 of rhodamine b dye solution. The suspension was constantly stirred for 60 min in the dark before irradiation to reach equilibrium absorption and desorption of the undoped and doped CdO nanoparticles in the organic dye solution. Then the suspension was placed in a closed chamber and irradiated with sunlight. All six sets of reactions were observed one by one in every time interval of 10 min for 1hr. Finally, the rate of dye decomposition was monitored by taking 4ml samples from each set and recording the UV-Vis spectra in the wavelength after centrifugation and filtration.

Cyclic voltammetry:
Cyclic voltammograms were recorded in the pH 1.0 for 1.0 % of doped and undoped CdO nanoparticles synthesized using aqueous peel extract of Citrus sinensis. The Glassy Carbon Electrode was (GCE) as working electrode Vs Ag/AgCl. CdO nanoparticles and Ce ion doped CdO nanoparticles showed one oxidation peak and one reduction peak in pH 1 conditions. The background current was recorded for all sweep rates studied in the potential range from -1.0 to 1.0 V and subtracted properly in calculating the peak currents.

Instrumentation: UV-Vis spectrophotometer (JASCO V-650) was used to obtain the absorption spectrum of the synthesized Cadmium oxide nanoparticles. The synthesized nanoparticles were investigated with a Philips CM 200 model using 200kV electron acceleration voltage and with a resolution of 2.4A0. XRD measurements were made by Panalytical X'Pert Powder X'Celerator Diffractometer measurement range: 10 to 80 degree in 2θ.

Ultraviolet-Visible Spectra Analysis: The UV-Vis spectrum of undoped CdO nanoparticles synthesized using Citrus sinensis peel extract was shown in Fig.2. An absorption band at 274 nm is observed which is effectively blue shifted compared to the wavelength of bulk CdO appeared at 350 nm [6]. The absorption wavelengths are seen to be slightly shifted towards lower wavelength. This blue shift is attributed to the smaller size of nanoparticles. This indicates the formation of smaller particles.

Fig.3. shows the UV-Vis absorption spectra of 1.0% of Ce ion doped CdO nanoparticles synthesized using citrus sinensis peel extract. Here the absorption band is observed at 231nm. The blue shift in this case is less compared to the undoped CdO nano particles.

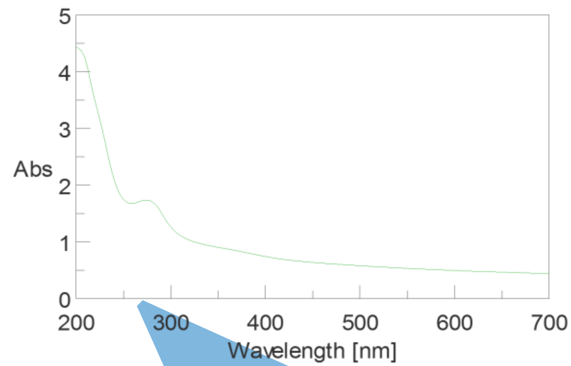

Fig.2 : UV-Vis absorption spectra of undoped CdO nanoparticles

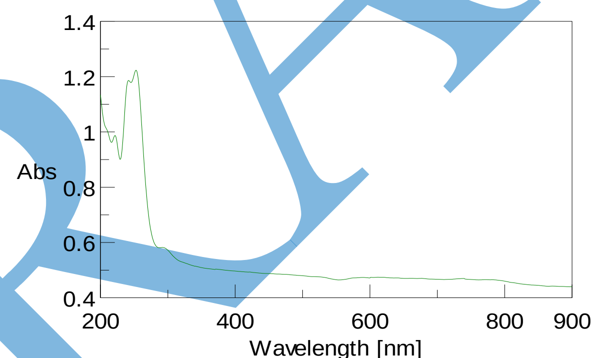

Fig.3: UV-Vis absorption spectra of 1.0% Ce ion doped CdO nanoparticles

XRD : Structural parameters of undoped and doped CdO nanoparticles synthesized using Citrus sinensis peel extract were calculated from the XRD pattern. Calcination at 4000C is essential for complete removal of water and to obtain higher crystallinity. The prominent peaks obtained for undoped CdO nanoparticles, Ce ion doped CdO nanoparticles corresponding to the diffraction planes {111}, {110} {002}, {211}, {211} and Ce:CdO:{100}, {002}, {101}, {102}, {110}, {103}, {200}, {112}, {201}; respectively. Diffraction peaks observed are well in correlation with JCPDS card No.75-0594 [7]. The prepared doped and undoped materials were of face centered cubic (fcc) structure. Presence of several peaks indicates random orientation of the crystallites, confirming the face centered cubic (fcc) structure of the CdO nanoparticles. The average crystallite size (D) was calculated using the well-known Scherer's formula.

$$\mathbf{D = k\lambda / \beta\cos\theta}$$

where D is the average crystalline diameter in nanometer (nm), k is the Scherer constant equal to 0.94, λ is the wavelength of the X-ray radiation used and is equal to 1.5406Å, β is the full width at half maxima (FWHM) intensity of the diffraction peak (in radian) and θ is the Bragg diffraction angle of the concerned diffraction peak.

XRD spectra of undoped CdO nanoparticle synthesized using aqueous peel extract of Citrus sinensis:

The X-ray diffraction pattern of undoped CdO nanoparticles synthesized using *Citrus sinensis* peel extract was shown in Fig.4. The spectrum of CdO nanoparticles exhibits sharp peaks at 2θ equal to 24.86^0, 18.14^0, 27.62^0, 35.78^0, and 37.54^0. These peaks are identified to originate from {111}, {110}, {002}, {211}, and {211} planes of the hexagonal CdO phase respectively. The average crystallite size of synthesized nanoparticles was found to be 49.05nm.

XRD spectra of Ce ion doped CdO nanoparticles synthesized using aqueous peel extract of Citrus sinensis:

Fig 5. shows the XRD pattern of Ce ion doped CdO nanoparticles synthesized using *Citrus sinensis* peel extract. The spectrum of Ce ion doped CdO exhibits sharp peaks at 2θ equal to 29.21^0, 32.63^0, 34.44^0, 36.21^0, 47.57^0, 56.58^0, 62.84^0, 67.95^0 and 89.65^0. These peaks are identified to originate from pattern {100}, {002}, {101}, {102}, {110}, {103}, {200}, {112}, {201}. The increase in FWHM suggests that Ce is incorporated into the CdO matrix. The average crystallite size (D) of synthesized nanoparticles was found to be 50.78 nm

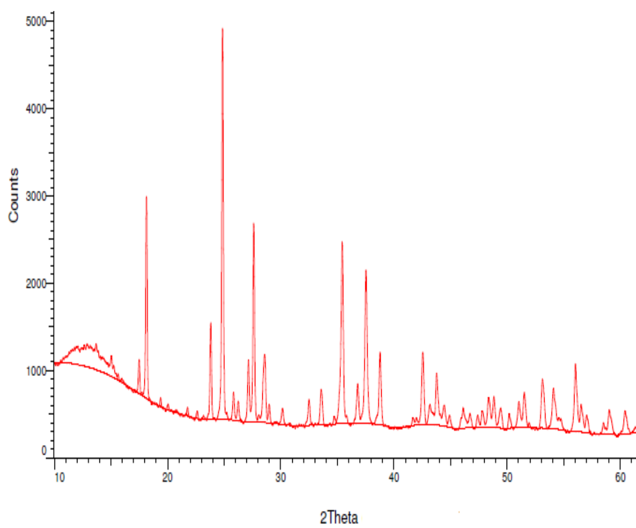

Fig.4 : XRD spectrum of undoped CdO Nanoparticles synthesized using aqueous peel extract of Citrus sinensis

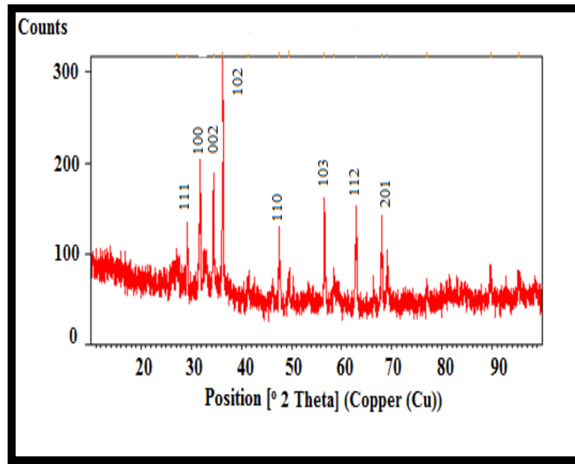

Fig.5: XRD spectrum of Ce ion doped CdO Nanoparticles synthesized using aqueous peel extract of Citrus sinensis.

SEM

Scanning Electron Microscopy was employed to analyze the morphology and the growth features of the as prepared nanoparticles.

Fig.6 represents the SEM image of CdO nanoparticles synthesized using Citrus sinensis peel extract. This picture substantiates the approximate hexagonal cubic shape to the CdO nanoparticles with a crystalline nature, and most of the particles exhibit some agglomeration [8]. The aggregation of particles should have been originated from the large specific surface area and high surface energy of CdO nanoparticles [9]. The aggregation occurred may be probably due to the drying process [10,11]. Fig.7 shows the SEM image of Ce ion doped CdO nanoparticles synthesized using citrus sinensis peel extract and it exhibited crystalline nature.

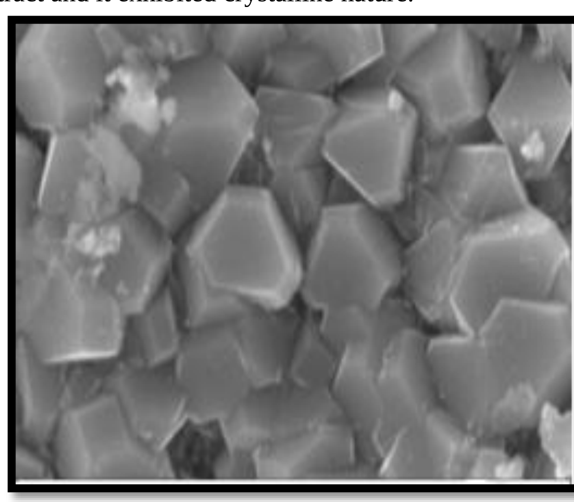

Fig.6: SEM image of CdO nanoparticles synthesized using Citrus sinensis peel extract

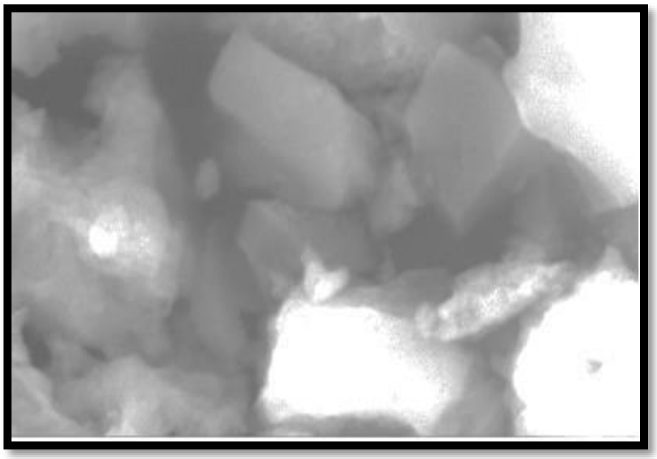

Fig.7: SEM image of Ce ion doped CdO nanoparticles synthesized using Citrus sinensis peel extract

Photocatalytic activity

The UV visible absorbance values of pure Rhodamine B dye solution show absorption wavelength at 544nm. The characteristic absorbance value at 544nm was used to track the photocatalytic degradation process. The absorption peaks at 280 nm and 350 nm can be attributed to the heterocyclic rings and benzene components, respectively. The spectra reveal that there was no formation of new intermediates or products. The absorption peaks decreased in intensity with increasing irradiation time, vanishing almost completely within 60min. The rapid disappearance of the 544nm absorption band suggests that the chromophore structure responsible for the characteristic color of the dye is breaking down. In addition, opening of benzene or heterocyclic rings underwent a speedy decolourization which is due to the bond-breaking between aromatic rings.

Absorbance values of pure dye with and without UV irradiation exposure clearly noticed that no significant changes of the concentration of Rhodamine dye after 3 hrs irradiation, which indicated that pure Rhodamine dye solution cannot be easily degraded by UV light as shown in (Fig.8). The degradation efficiency of pure Rhodamine dye within 3 hrs irradiation time was about 51.83%. The result showed that the photocatalytic activity of pure Rhodamine B dye was very less when compared with the CdO nanoparticles and Ce ion doped CdO nanoparticles synthesized using Citrus sinensis peel extract.

Fig.9, and Fig.10 showed that the change in the absorbance spectra and the fluorescence quenching efficiency of Rhodamine B dye in the presence of the undoped CdO nanoparticles and Ce ion doped CdO nanoparticles synthesized using Citrus sinensis peel extract as photocatalyst. The Rhodamine B dye color was greatly disappeared after UV irradiation for 60 min for undoped CdO nanoparticles. The decrease in absorption spectra of undoped CdO nanoparticles at maximum wavelength of Rhodamine dye is indicated by the degradation of Rhodamine B dye in applied conditions. After irradiation with UV light, the absorption intensity decreased due to the decolouration of the dye. The dye has almost disappeared after UV irradiation for 70 min and almost completed after 1 hour. The absorption intensity of Rhodamine B dye in the presence of undoped CdO nanoparticles and Ce ion doped CdO nanoparticles decreases with increasing irradiation time when it is exposed in sun light. Fig.9. shows the bleaching of Rhodamine-B dye on photodegrdation in the presence of undoped CdO nanoparticles as photocatalyst. The degradation efficiency was higher in the presence of Ce ion doped CdO nanoparticles than that for undoped CdO nanoparticles. The photocatalytic bleaching was faster in case of Ce ion doped CdO nanoparticles and almost completed after 60 min.

The decolorization efficiency % has been calculated as:

Efficiency % = $[C_o - C] / C_o \times 100$

where Co is the initial concentration of the dye and C is the concentration of the dye at the selected irradiation time. The degradation efficiency of metal ion doped CdO nanoparticles was increased with increasing irradiation time due to the function of UV light. It was observed that the maximum degradation efficiency of Rhodamine dye within 60 min irradiation time was about 94% for CdO nanoparticles and 93.6 % for Ce ion doped CdO nano particles. Therefore, it is observed that the Ce ion doped CdO nanoparticles possessed higher photocatalytic activity than the undoped CdO nanoparticles. The results showed that Ce ion deposited on the surface of CdO nanoparticles is more efficient for color removal of Rhodamine dye.

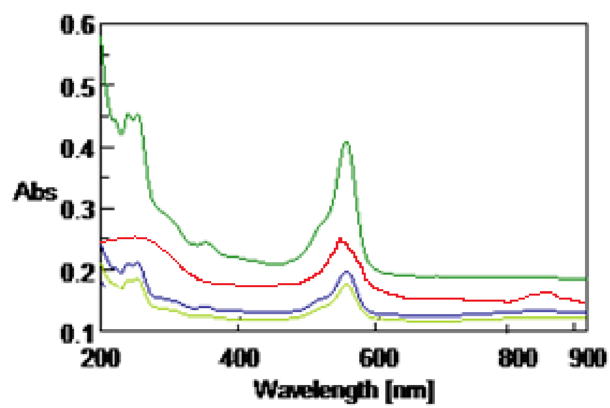

Fig.8:UV-Vis absorption spectra of pure Rhodamine-B dye under UV irradiation

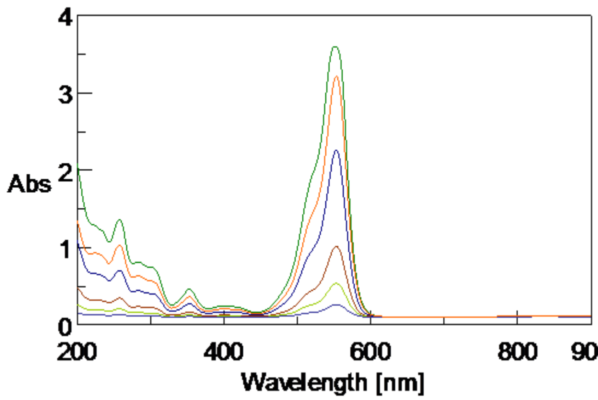

Fig.9: UV-Vis absorption spectra of Rhodamine B dye in the presence of undoped CdO nanoparticles under different duration of UV irradiation

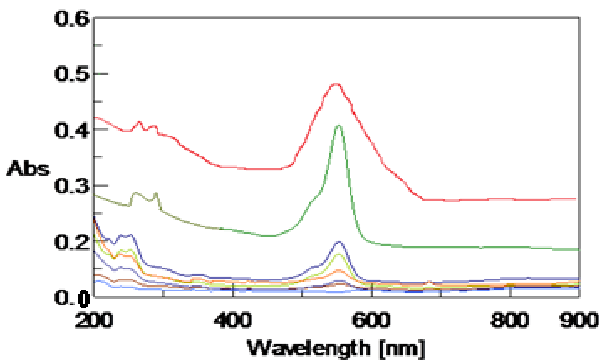

Fig.10: UV-Visible absorption spectra of Rhodamine B dye in the presence of Ce ion doped CdO nanoparticles under different duration of UV irradiation

Cyclic Voltammetric behavior of undoped CdO nanoparticles and Ce ion doped CdO nanoparticles using Citrus sinensis peel extract:

The cyclic voltammetric behavior of 1.0 % of CdO nanoparticles in 0.1M H2SO4 (pH 1.0) was studied at GCE as shown in Fig.11. In this cyclic voltammogram, two sharp anodic peaks and two cathodic peaks were observed in the potential range from –1.2V to 1.0V. The first anodic peak was observed at -0.8289V, the second anodic peak was observed at -0.1722V. The first reduction peak and second reduction peak were seen around at the potential of about -0.6519 V and -0.8696 V respectively.

The cyclic voltammetric behavior of 1.0 % of Ce ion doped CdO nanoparticles in 0.1M H2SO4 (pH 1.0) was studied at GCE as shown in Fig.12. In this cyclic voltammogram, one anodic peak and one small cathodic peak were observed in the potential range from –1. 2V to 0.6 V. The anodic and cathodic peaks were seen around at the potential of about 0.0300V and -0.7860V respectively [12].

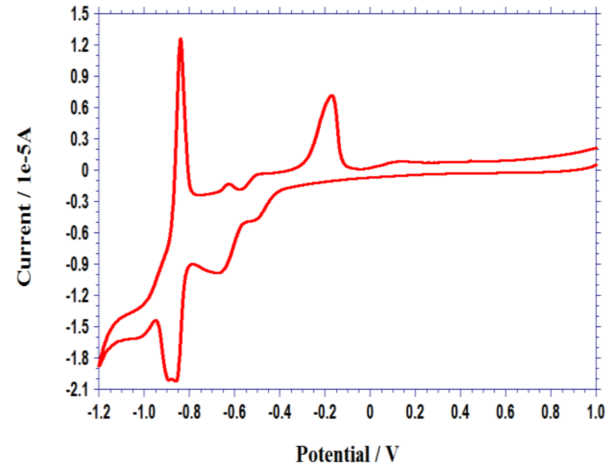

Fig.11.Cyclic Voltammogram of CdO nanoparticles synthesized using Citrus sinensis peel extract

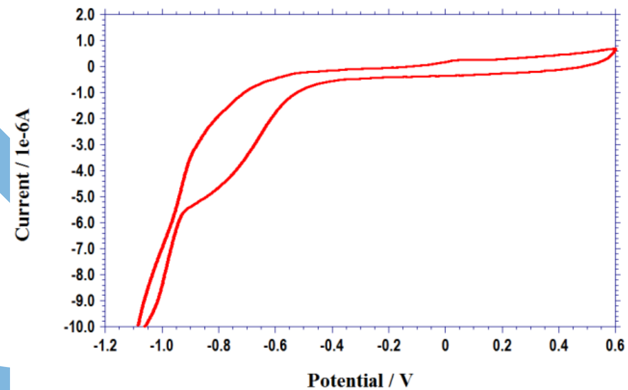

Fig.12.Cyclic Voltammogram of Ce ion doped CdO nanoparticles synthesized using Citrus sinensis peel extract

CONCLUSION

Cadmium oxide and Ce ion doped Cadmium oxide nanoparticles are synthesized by green method (simple and cost effective) method using peel extract of Citrus sinensis. The blue shifted UV-Vis absorption peak at 350 nm confirmed the nano-size of the synthesized CdO nanoparticles. The absorbance increases in the metal ion doped CdO nanoaparticles. From XRD data the crystallite size was found to be 43.09 nm for undoped CdO nanoparticles and 46.72 nm for Ce ion doped CdO nanoparticles. Diffraction peaks observed are well in correlation with JCPDS card No.75-0594. The surface morphology of the CdO and Ce ion doped CdO nano particles is characterized by SEM analysis and suggested different morphological structures. From cyclic voltammetric studies, good redox behavior was observed for undoped and doped CdO nanoparticles.

Photocatalytic degradation was also investigated with Rhodamine dye under UV-irradiation source. CdO nanoparticles showed significant photocatalytic degradative ability with and without dye. The degradation efficiency of Ce ion doped CdO nanoparticles was higher than the undoped CdO nanoparticles. Hence it can be used as a catalyst for the removal of dyes from dye contaminated water resources. The Ce:CdO and undoped CdO nanoparticles exhibited enhanced photocatalytic activity and can be efficiently used as photocatalysts in the process of removal of organic dyes and used for environmental cleaning and water purification.

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