



Electrochemical determination of harmful catechol and rapid decolorization of textile dyes using ceria and tin doped ZnO nanoparticles

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ABSTRACT

Electrochemical sensing of toxic pollutants as well as the degradation of toxic dyes using cost effective nanoparticles-based photocatalyst are one of the most effective ways to reduce environmental contaminants. Herein, ZnO and different percentage (1, 3, 5 & 10%) of Ce and Sn doped ZnO nanoparticles were synthesized by a facile chemical method. The synthesized nanoparticles were used as modified electrode towards electrochemical detection of catechol (CA). It was found that the limit of detection and the sensitivity of the Ce/ZnO (5%) to be 0.21 μM and 0.494 $\mu\text{M} \mu\text{A}^{-1}$, respectively. The doped ZnO exhibited lower band gap compared to pure ZnO, which facilitates to rapid photocatalytic degradation (~93%) of textile dyes (Crystal Violet & Rhodamine B) and catechol under visible light radiation. The environmental pollutants such as catechol, crystal violet and rhodamine B dye were effectively determined and degraded very successfully using couple of techniques such as cyclic voltammetric and photodegradation.

1. Introduction

Nowadays, the living world is facing very serious issues due to environmental pollutions caused through the release of industrial byproducts directly into the ecosystem. Mainly, the industrial wastages from pharmaceutical drugs, pesticides, leathers, textile, cosmetics, and dye making industries are the major source of contamination to water and land. The organic dyes effluents from textile industries are mostly carcinogenic in nature and affect the water ecosystem as well as the living species even in a very minute concentration.

Phenolic compounds and its derivatives are mainly used for large scale production of intermediate compounds in the industrial process. In particular, catechol is the isomer of the dihydroxybenzene which is used for production of pesticides, herbicides, pharmaceutical drugs, preservatives, dye, stabilizer, antioxidants, cosmetics, and secondary coloring matters. The pollution monitoring environmental agencies of United States of America declared the catechol compounds are highly toxic [1–3] and intake of catechol affect human health particularly liver function, fatigue, and headache. So, determination and degradation of

catechol is much essential to monitor the environmental pollution and also to eliminate pollutants from the surroundings. Researchers focusing on waste water treatment always tried to reduce the pollutant component present in the land and water. There are several methods developed for determination of toxic catechol such as surface-enhanced Raman spectroscopy (SERS) [4], spectrophotometry [5], capillary electrophoresis [6], chemiluminescence [7], calorimetric sensor [8], gas chromatography-mass spectrometry (GC-MS) [9], high performance liquid chromatography (HPLC) [10] and electrochemical sensor [11] etc. Among them electrochemical sensor is one of the best methods to determine the catechol molecules because of its fast response, low cost, high sensitivity, selectivity, and very low-level concentration detection even in nano molar range.

In other hand, researchers focusing on environmental issues are also trying to solve the dye related contamination by using of efficient catalysts to degrade the colored species present in water that obstacle the passing of sunlight to the water bodies. Although several methods have been used to minimize the toxic pollutant from the environment such as adsorption, electrolysis, biological treatment, and membrane filtration.

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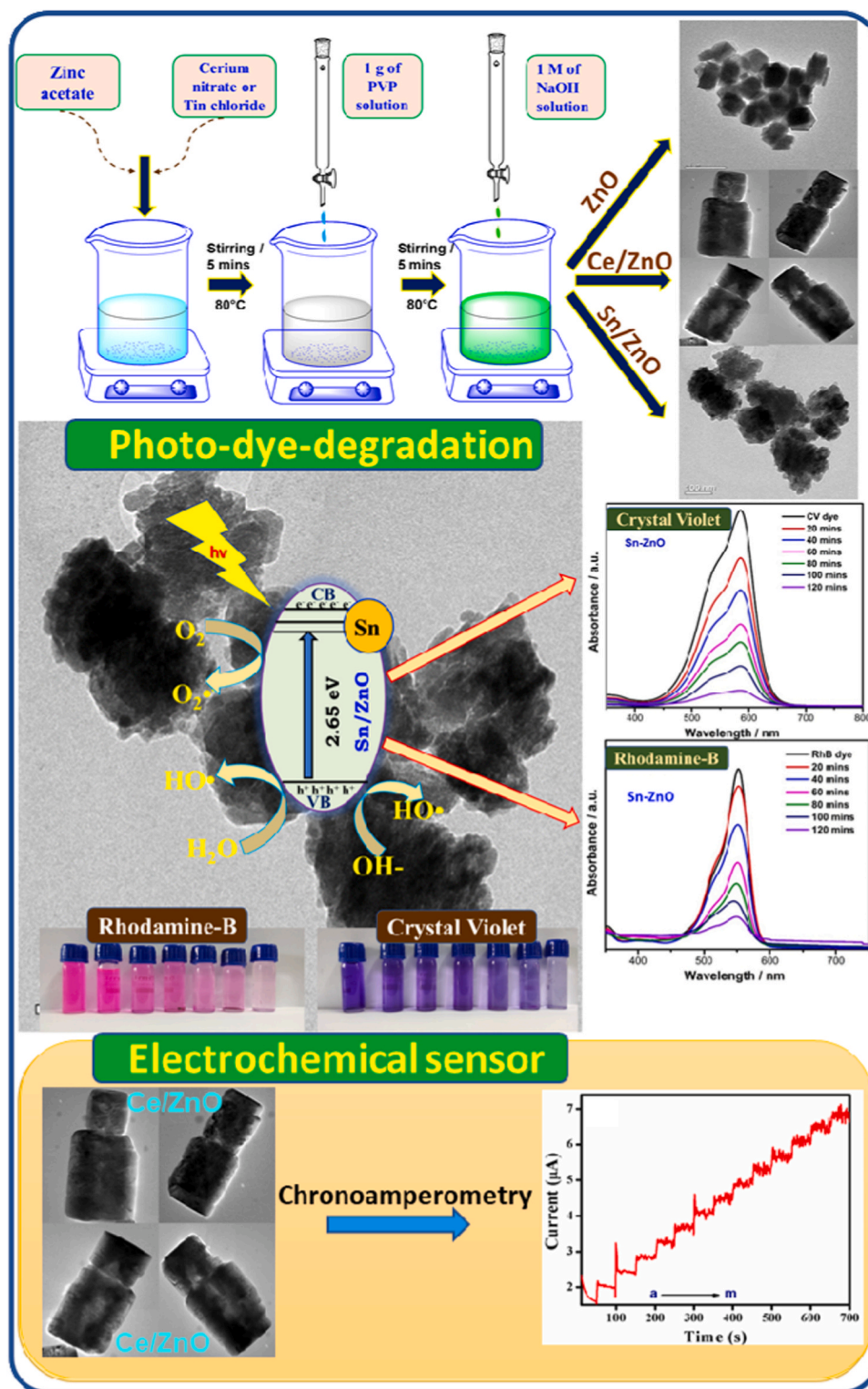
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Scheme 1. Preparation of nanoparticles, photocatalytic degradation mechanism and electrochemical determination of catechol.

Those methods have encountered several drawbacks which are cost intensive regeneration process, concentrated sludge production, economically unfeasible, and poor removal of toxic dyes, so more efficient technique is needed for waste water treatment. Photocatalytic degradation process is one of the best methods for waste water treatment and the basic requirements for a suitable photocatalyst should be cost-effective, eco-friendly, and more efficient as well as readily react with toxic dyes [12]. Photo-dye-degradation activity is significantly

influenced by various factors such as dye adsorption on catalyst surface, absorption spectral overlap between dyes and photocatalysts, electrostatic interaction, and the properties of dye degradation intermediates [13]. Up to date, there are several materials used for catalysis such as ZnO [14], TiO_2 [15], CeO_2 [16], SnO_2 [17], Cu_2O [18], and NiO [19], etc. Among those metal oxides, ZnO is used for several applications like photocatalyst [20], biosensors [21], light-emitting diodes [22], solar cells [23], and photodetectors [24], etc. ZnO is a semiconductor

material with the direct bandgap of 3.37 eV and commercially available cost-effective material, apart from that it is non-toxic, bio-compatible, physically stable, and widely used for photocatalysis. Typically, when light is irradiated and absorbed on ZnO surface, the electron excited from the occupied orbital of the valence band to the unoccupied orbital of conduction band and the holes remain in the same valence band. The photogenerated electron and hole pairs react with surface oxygen and water molecules to create the superoxide anion ($O_2^{\bullet-}$) and the hydroxyl radicals ($OH^{\bullet}$). Finally, both the reactive radical species react with pollutant molecules to get the degraded products. Even though ZnO is widely used materials, but it also has some disadvantages due to the high bandgap, it gets reacts in the UV region and allows the fast recombination of e^-/h^+ which results the reduction of the catalytic efficiency. To tune energy band gap of ZnO material, a suitable dopant metal can be incorporated which will gain ability to absorb light in visible light region. The band gap and surface modification will suppress the fast recombination of e^-/h^+ and subsequently tunes to achieve better photocatalytic properties of the catalyst. There are several metals such as Fe, Co, Ni, Cu, Mo, Ce, Sn, and Li were used as dopants to create surface defects in ZnO. In this work, Ce and Sn metals are used as dopant in ZnO. These dopant metals are occupied by the substitution or the interstitial position of ZnO lattice which acts as host material. Cerium is one of the rare earth metals and is widely used for several applications [25,26] due to its variable oxidation states, and redox properties, cerium exhibits excellent catalytic activity. Likewise Sn is also n-type semiconductor materials which is non-toxic, stable, low cost, and widely studied due to its interesting properties [27,28].

In our previous report, Ce, Eu co-doped ZnO nanorods were prepared and their optical as well as structural properties were investigated [29]. Selective metal ions doped CeO_2 used for photocatalytic degradation under visible light and super capacitor applications [26]. In recent years, Siddarth et al. has been proposed the binary metal oxide nanocomposite CuO-ZnO used for multifunctional applications: Catalytic degradation of organic dyes and electrochemical sensing of glucose molecules [30]. Similarly, Muhammad et al. has been reported the noble metal nanoparticles functionalized with ZnO used for photocatalytic degradation of rhodamine dye and electrochemical sensing of H_2O_2 [31]. Moreover, Hadis et al. has been suggested the SnO_2 -ZnO materials used for photocatalysis and electrocatalyst [32]. Manjari et al. has been applied to the Ag-Cu decorated ZnO for electrochemical sensing of nitrite ions [33]. Rashed et al. has been indicated the rGO/ZnO/Nafion based materials for sensitive and selective determination of nitrite ions [34].

In this work, different amount of Sn and Ce doped ZnO was synthesized by a simple chemical method and its utility towards photocatalysis and electrochemical sensing application was explored. The modifying bandgap by incorporation of dopants plays a key role in enhanced photocatalytic degradation of textile dyes (crystal violet & rhodamine B) and catechol under visible light. Along with the photocatalytic activity, it was also demonstrated the electrochemical sensing of potentially toxic catechol which is one of the key components of industrial effluent. The beauty of the present study is to demonstrate photo-degradation as well as sensing of environmental hazards by simply tuning the electronic structure of ZnO using doping the different metal ions with different amount. The dopant materials which occupy in the ZnO lattice position which creates defects with interesting morphologies. The doped materials modified the surface morphology, and it creates active sites on the surface of the materials which enhances the electrochemical sensing as well as photocatalytic efficacy of the synthesized nanoparticles.

2. Experimental section

2.1. Materials

Zinc acetate dihydrate (98.5%), cerium nitrate (99.5%), tin chloride (99.9%) and polyvinylpyrrolidone (PVP) were purchased from Sigma-

Aldrich. Sodium hydroxide pellets (97%) were purchased from Rankem RFCL limited. All the reagents used without further purification. Deionized water was used as solvent in the whole experimental procedure. Analytical grade ethanol and acetone were used for washing purpose.

2.2. Synthesis of Ce and Sn doped and ZnO nanoparticles

Ceria (Ce) and tin (Sn) doped nanoparticles preparation method is demonstrated in Scheme 1. The doped nanoparticles were synthesized using the previous report [29]. The doped ZnO nanoparticles were synthesized from the stock solutions of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.5 M) prepared in 50 mL deionized water under stirring. For the preparation of Ce doped ZnO, various concentration (1, 3, 5 and 10 wt%) of Ce ($(NO_3)_3 \cdot 5H_2O$) was added to the above zinc acetate solution. Then, 1 g of PVP was added to the metal solution mixture to prevent the agglomeration of the particles during formation. Then, 2 M of NaOH was added drop by drop into the reaction mixture under continuous stirring in order to get the pH 11. The resultant mixture was stirred for 2 h at 80 °C. In case of, Sn doped ZnO the same procedure was followed where the tin chloride with different concentrations (1, 3, 5 and 10 wt%) were used instead of cerium nitrate. After the completion of the reaction, the resulting white solid products were washed with ethanol and acetone. Then the obtained product was filtered and dried at 120 °C in hot air oven for 8 h.

2.3. Electrochemical study

2.3.1. Preparation of catechol stock solution

The accurately weighed catechol (0.1 mM) was dissolved in 100 mL double distilled water to make the stock solution which was sonicated for 30 min and was diluted according to the required concentrations for the measurements.

2.3.2. Electrode modification process

Initially, bare glassy carbon electrode (GCE) was polished by using 0.05 μm alumina powder with a drop of distilled water on the smooth surface of cloth pad. Furthermore, the bare GCE was gently rubbed on the smooth surface and it was washed with double distilled water and ethanol. Then, 1 mg of prepared nanoparticles was taken in 2 mL of ethanol and sonicated for 30 min. Then the polished GCE surface was modified by a drop casting method and allows to dry in room temperature for few minutes. Then, allowed the solution to evaporate in room temperature for 3 h. As simple drop of a nanoparticle solution casted onto the electrode surface, so it was called drop casting method. This process is very simple for surface modification on the glassy carbon electrode and also helps in obtaining a uniform distribution of the drop casted nanoparticles across the area of the electrode. Finally, the modified GCE electrode was used as working electrode for all voltammetry measurements.

2.3.3. Electrochemical analysis

All the electrochemical experiments were performed by electrochemical workstation in the three-electrode system, saturated calomel (SCE) reference electrode at 25 °C, glassy carbon electrode (0.0707 cm^2) working electrode, and Pt wire as counter electrode. Firstly, the modified electrode was optimized by cyclic voltammetry in presence of different phosphate buffer solution (PBS) of pH ranging from 3 to 10. By varying the pH of the solution, it was observed at particular pH the modified electrode exhibits higher current with lower potential. Moreover, varying the different scan rate in cyclic voltammetry, material stability, number of electron transfer, kinetics of the electrode and electrode process (adsorption or diffusion) were studied. Chronoamperometry (CA) was also carried out to study the sensing of catechol in 0.1 M phosphate buffer solution (PBS) at pH 7. The measurement was observed by adding catechol solution of 1×10^{-4} M into PBS

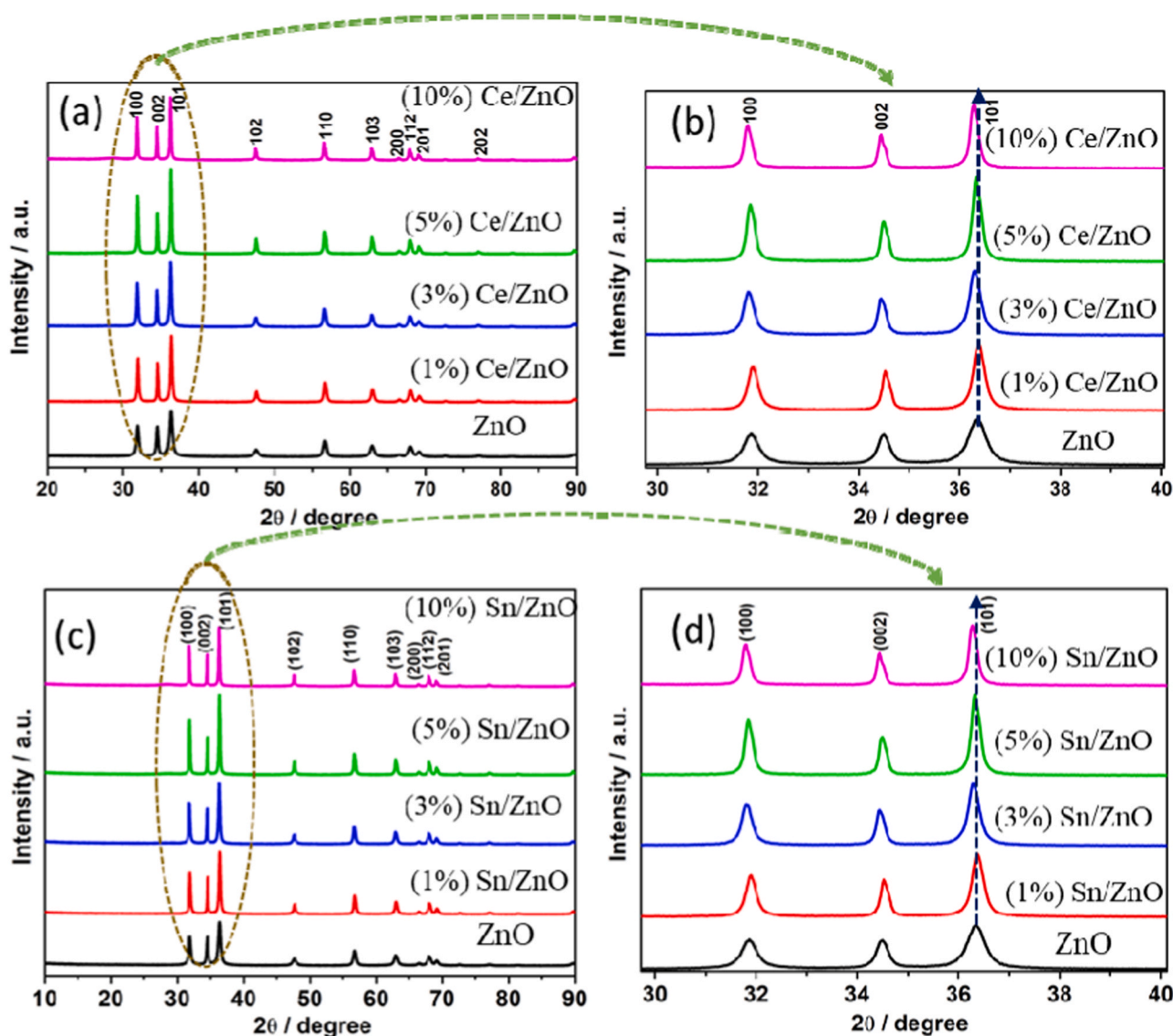


Fig. 1. XRD pattern of (a) Ce/ZnO (1, 3, 5, 10%), (b) Maximized view of Ce/ZnO, (c) Sn/ZnO (1, 3, 5, 10%), (d) Maximized view of Sn/ZnO.

solution and 1 min stirring and 30 s settle down time was maintained for every consecutive catechol addition.

2.4. Photocatalytic activity test

Crystal violet (CV) and Rhodamine B (RhB) were used as the model organic dye pollutants and synthesized nanomaterials act as catalyst for photodegradation process. Typically, (20 mg) catalyst was added into the 50 mL of aqueous dye solution (10 mg L^{-1}) then, the dye solution was kept in dark room at particular time to attain the adsorption and desorption equilibrium of dyes on the surface of catalyst. Then, UV-Vis spectrum was measured for the dark room solution. Next, the dye solution was irradiated on visible light using direct sun light (to prevent UV light, UV filter was used) for time interval. After certain time interval, a 5 mL of solution was taken for centrifuge and then the solution was filtered using a $0.2 \mu\text{m}$ syringe filter. Using the UV-Vis spectrophotometer, filtered dye solution was studied and determined efficiency of degradation using the Eq. (1),

$$\text{Degradation efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

Where C_0 and C are initial and final concentration of dye molecules.

After the dye degradation process completed and the solution was centrifuged. The obtained catalyst was collected and washed with water for several times and dried at 70°C . Then the regenerated catalyst was used to evaluate the stability and reused for photocatalytic degradation the dye solution.

Likewise, the organic pollutant of the 50 mL of catechol solution (40 ppm) degraded by using of prepared photocatalyst (25 mg) in similar experimental condition.

The first order kinetic reaction value was used to determine the correct degradation rate of crystal violet and Rhodamine B using the following equation;

$$-\ln(C/C_0) = kt \quad (2)$$

Where, k = rate of reaction constant and t is time. The photocatalytic dye degradation activity was performed during the well sun shining between 11:00 AM to 2:00 PM in clear sky. The average solar light intensity was measured about $1.08 \times 10^5 \text{ lux}$ ($85.32 \text{ mW}\cdot\text{cm}^{-2}$). Likewise, the effects of some other important operational parameters such as pH of dye solution and catalyst dosage study were performed. In the pH variation test, pH of dye solution was adjusted by adding required amount of 0.1 M hydrochloric acid solution and 0.1 M of sodium hydroxide solution. The modified electrode preparation mechanism is

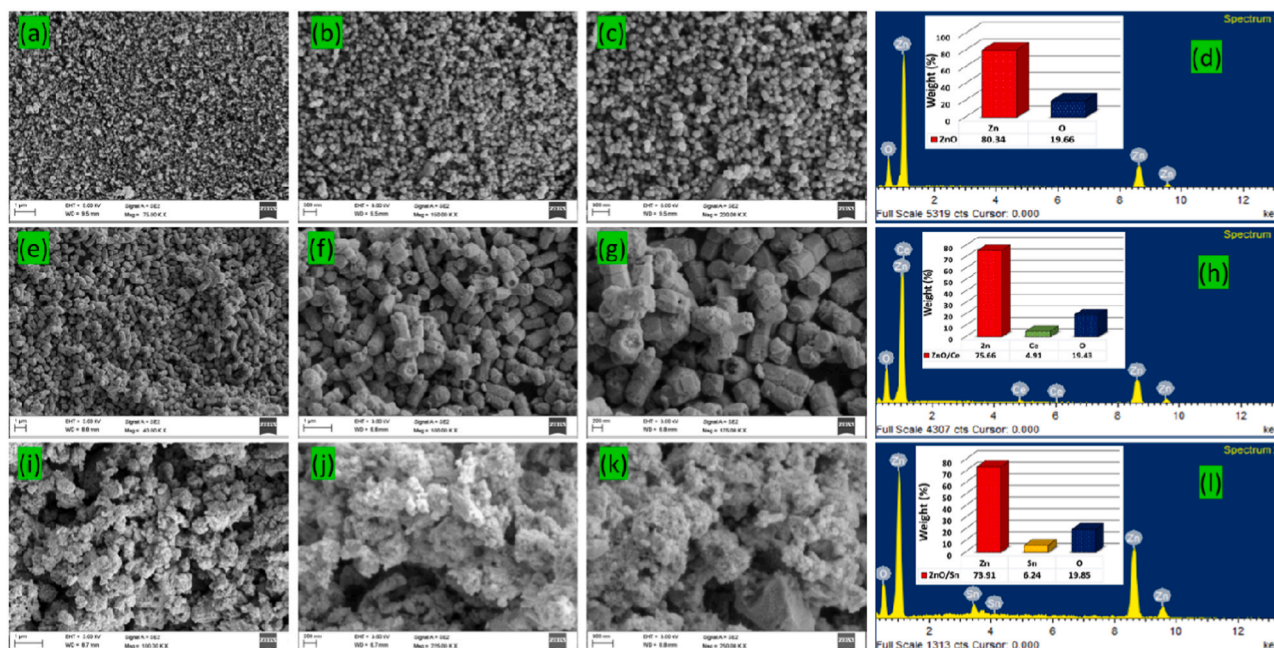


Fig. 2. FE-SEM images of (a–c) ZnO, (e–g) Ce/ZnO (5%), (i–k) Sn/ZnO (5%) and their corresponding EDS spectra (d, h, l) respectively. The weight percentage of the corresponding samples represented by a bar diagram.

simply demonstrated in Scheme 1.

2.5. Characterization

Crystal structure of the synthesized powder samples were characterized by X-ray diffraction (XRD) using a powder diffractometer (PAN Analytical X' pert PRO Model X-ray diffractometer) with monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The XRD was measured with range of $20\text{--}80^\circ$ at a scan rate of $5^\circ/\text{min}$. Surface and cross-sectional image was measured by FESEM (JEOL JSM-6700F) operated at 10 and 30 kV. Morphology and size of the samples were evaluated using transmission electron microscopy (TEM, JEM 2100F) performed with an acceleration voltage of 200 kV. The sample was well dispersed in absolute ethanol and then it was drop casted on a gold grid under a sodium light irradiation. Functional groups presence on the samples was studied using Fourier-transform infrared (FTIR) analysis with a Bruker optic GmbH TENSOR-27 spectrometer from Thermos electron at room temperature. To study optical properties of the samples, UV-Vis diffuse reflectance spectra were recorded in the wavelength range of $200\text{--}800 \text{ nm}$ using a UV/Vis-NIR double beam spectrophotometer (VARIAN, Cary 5000). Electron paramagnetic resonance (EPR) measurements spectra were performed using a Bruker EMX plus system with a microwave frequency of 9.8645 GHz and a microwave power of 10 mW at room temperature. Thermal analysis was carried out using thermogravimetric/differential thermal analyser (TG/DTA, SDT Q 600 V20) within the temperature range from room temperature to 800°C under air atmosphere.

3. Results and discussion

3.1. XRD analysis

Fig. 1(a) shows the XRD pattern of pristine ZnO and different weight % of Ce doped ZnO. The diffraction peak observed at 2θ values at 31.7° , 34.3° , 36.3° , 47.5° , 56.6° , 62.8° , 66.4° , 67.8° , 69.1° and 77.0° corresponding to hkl planes of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), (2 0 1) and (2 0 2), respectively. The observed XRD pattern is well matched with JCPDS card no (89–1397) which confirmed

the formation of hexagonal crystal structure. When increasing the dopant concentration of Ce, the slight peak shifting observed in the lower region which might be due to change in lattice parameters [29]. The ionic radii of zinc is $0.74 \text{ \AA}$ and the ionic radii of cerium is $1.03 \text{ \AA}$, when the higher ionic radii Ce replaced the smaller ionic radii Zn, the lattice position facilitates peak shifting towards lower region [35,36]. However, no other extra peaks observed in the XRD pattern, which indicates the good crystallinity and purity of the material. The dopant metal of Ce and Sn substituted on the ZnO lattice, so defects may arise in the semiconductor material which can enhance the catalytic property of the prepared material. For clear understanding the maximized view of Ce/ZnO is shown in Fig. 1(b). Different weight % of Sn doped ZnO and the maximized view of the prominent planes are shown in Fig. 1(c) & (d), respectively. The diffraction peaks of different concentration of Sn doped ZnO showed at 2θ value of 31.7° , 34.4° , 36.2° , 47.5° , 56.6° , 62.8° , 66.3° , 67.9° , and 69.0° and their corresponding hkl planes are (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), and (2 0 1) respectively. The XRD pattern confirms the hexagonal crystal system of Sn/ZnO at different concentration and the observed peaks are good agreement with the (JCPDS card no. 89–1397) [36]. When increasing the Sn concentration, the position is slightly shifted towards lower angle side as seen in the Fig. 1(d). Likewise, the Ce dopant, the Sn ions also occupies the substitution position in the ZnO lattice. The average crystallite size was calculated by the Debye-Scherrer formula shown in Eq. (3).

$$d = [(k\lambda)/(\beta\cos\theta)] \quad (3)$$

Where 'd' is size of particles, 'k' is constant (0.9), ' λ ' is X-ray wavelength, ' β ' is full width and half maximum of the diffraction peak and ' θ ' is the peak position. The calculated size of the ZnO, Ce/ZnO (5%), and Sn/ZnO (5%) is 21.3, 28.7 and 26.6 nm, respectively.

3.2. Morphological analysis

FESEM analysis is used to explore the morphology of prepared nanopowders. Fig. 2(a–c) shows the FESEM images of pristine ZnO at the different magnifications. The obtained morphology found to be agglomerated with spherical particles. The 5% Ce doped ZnO showed

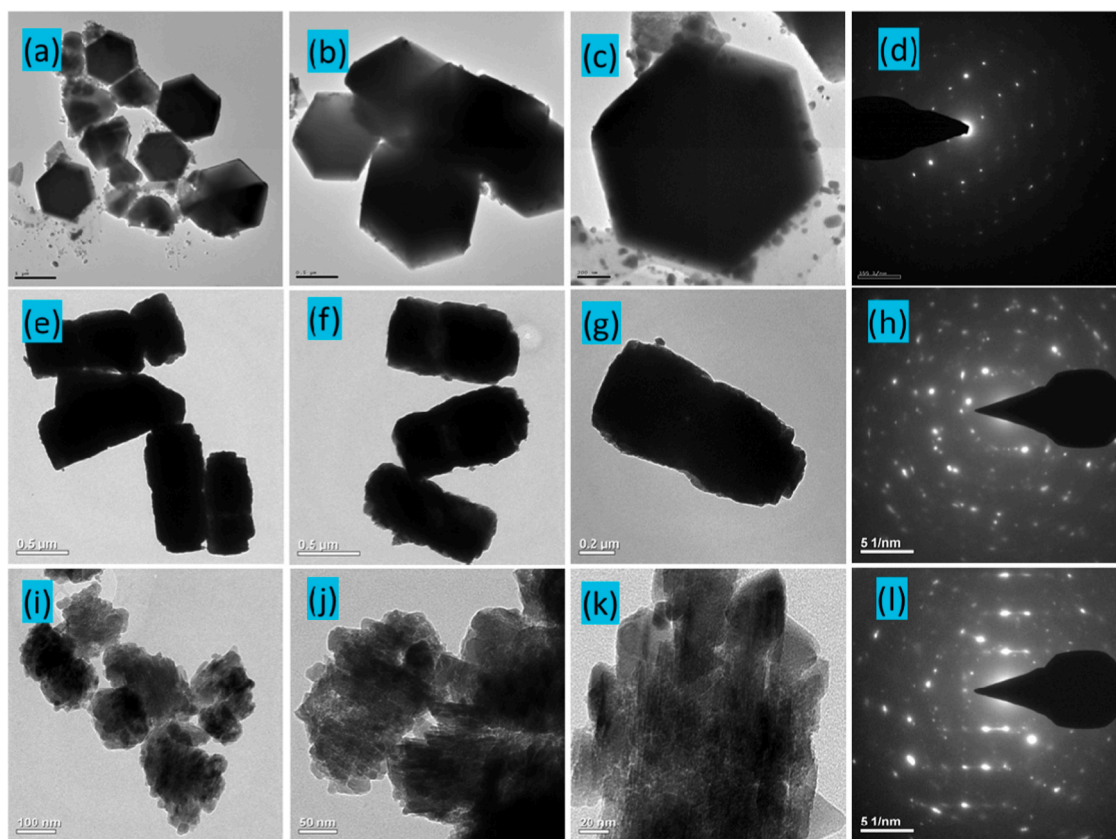


Fig. 3. HRTEM images of (a–c) ZnO, (e–g) Ce/ZnO (5%), (i–k) Sn/ZnO (5%) and their corresponding SAED spectra (d, h, l) respectively.

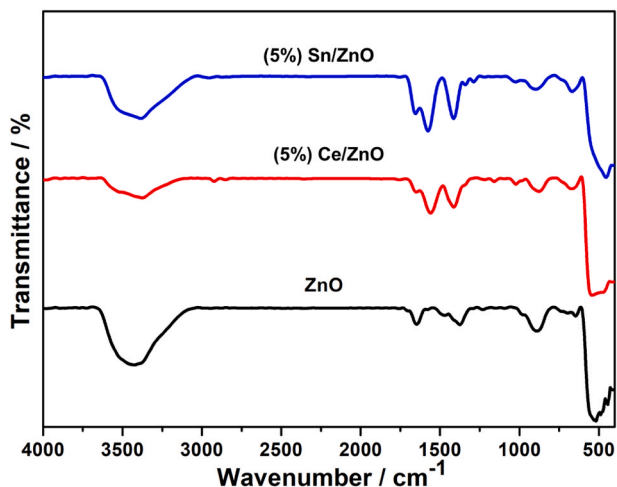


Fig. 4. FTIR spectra of ZnO, Ce/ZnO (5%), Sn/ZnO (5%).

hexagonal structure with “nut shape” morphology as displayed in Fig. 2 (e–g). Changing the doping ion causes the morphological change that affect on the mechanisms of the nucleation and shape of the nanoparticles. This instability caused by Ce atoms encouraged the growth of rod network- nut shape and reduce the energy of the system. Moreover, morphology of doped samples depends on the value of ionic fraction of the bond between the dopant and zinc ion [37]. The similar morphology was obtained in previously reported work using same chemical method, it clearly depict the chemical method is highly reproducible and more suitable for industrial-scale production [29]. In case of 5% Sn doped ZnO, different magnification of aggregated flake like morphology obtained as seen in Fig. 2(i–k). The EDS spectrum of ZnO, Ce/ZnO (5%),

and Sn/ZnO (5%) were shown in Fig. 2(d, h, l), it confirms the presence of Zn, O, Ce, & Sn in the corresponding samples and no other impurity was found. The weight percentage of the element is presented in a bar diagram (insert).

Fig. 3(a–c) shows the HRTEM images of ZnO with different magnifications. Fig. 3(a) shows the well-defined hexagonal shape of the nanoparticles and it shows as agglomeration with the tiny spherical particles. Different magnifications of Ce/ZnO (5%) showed as nut shape with hexagonal structure seen in Fig. 3(e–g). Fig. 3(g) shows the clearest view of stacking arrangement of nut shaped hexagonal morphology with the porous nature which leads to the high surface area and became suitable material for enhanced catalytic activity. The HRTEM images of different magnifications of Sn/ZnO (5%) shown in Fig. 3(i–k) and the obtained morphology found to be agglomerated irregular nanoflakes. The SAED pattern of ZnO, Ce/ZnO (5%), Sn/ZnO (5%) are shown in Fig. 3(d, h, l), respectively and the SAED pattern confirms the crystallinity of the materials.

3.3. FTIR analysis

Fig. 4 shows the FTIR spectra of ZnO, Ce/ZnO (5%), Sn/ZnO (5%). The FTIR spectrum of ZnO exemplifies the significant absorption in the region of 524 cm^{-1} , 890 cm^{-1} , 1379 cm^{-1} , 1657 cm^{-1} and 3441 cm^{-1} . The band at 524 cm^{-1} corresponds to stretching vibration of Zn–O. The peak observed at 890 cm^{-1} corresponds to bending vibration of CH_2 . The band at 1379 cm^{-1} attributed to the C–N stretching. The characteristic FTIR peak appearing at 1650 cm^{-1} is due to the C=O stretching vibration appears from coated PVP. For Ce doped ZnO, the peak appeared between 570 cm^{-1} to 400 cm^{-1} is attributed to the Zn–O and Ce–O bond vibration. Similarly, for Sn/ZnO, the peak range between 550 cm^{-1} to 400 cm^{-1} corresponds to Zn–O and Sn–O bond vibration. The peak at around 3400 cm^{-1} corresponds to stretching vibration of the O–H bond due to absorption of moisture [38].

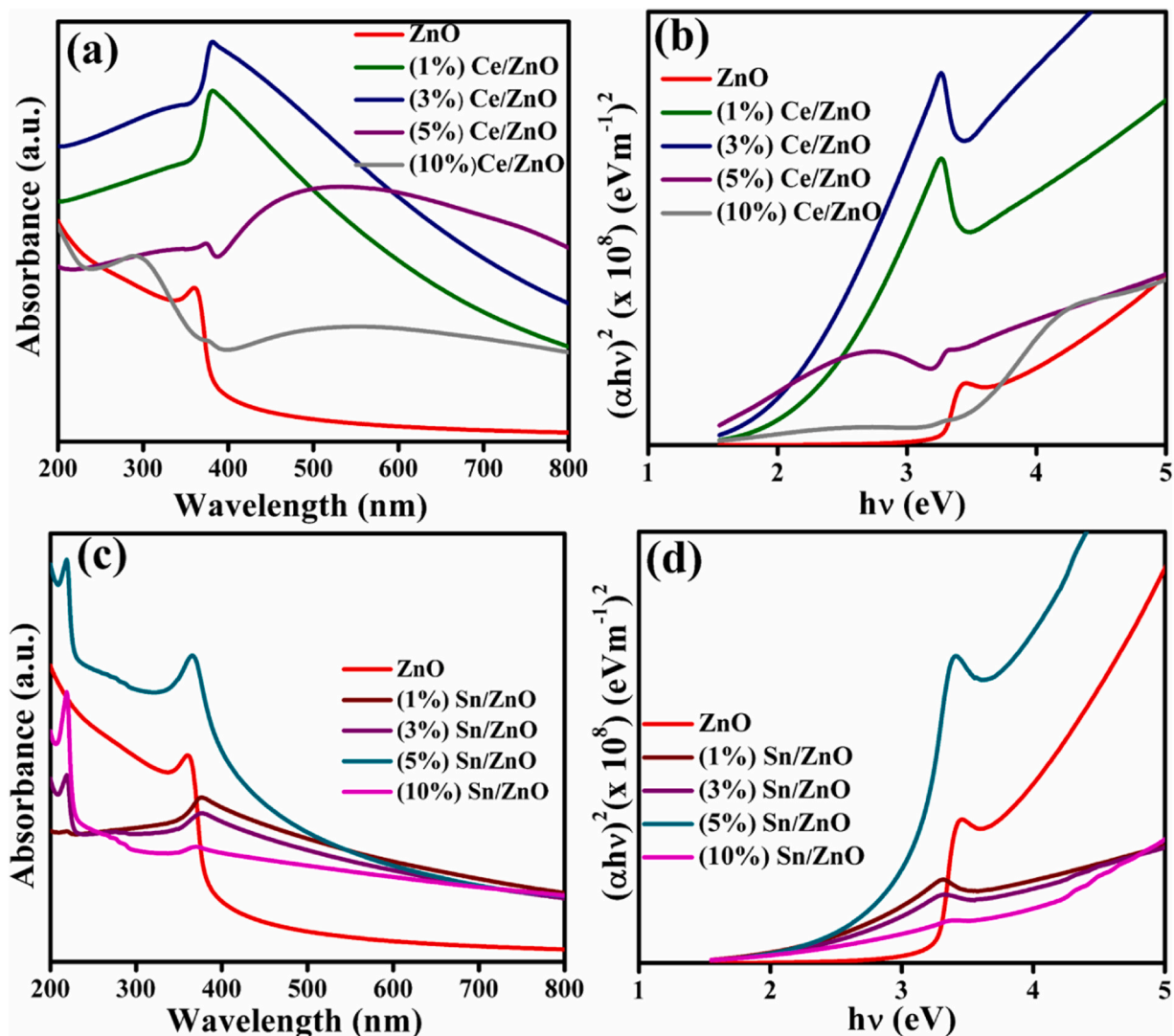


Fig. 5. DRS UV-Vis spectra of (a) ZnO, Ce/ZnO (1, 3, 5, 10%), (c) Sn/ZnO (1, 3, 5, 10%) and their corresponding tauc plot of (b, d) respectively.

3.4. Optical studies

The UV-Vis absorption spectra of different wt% (1, 3, 5, 10%) of Ce and Sn doped ZnO shown in Fig. 5(a & c). The absorption edge of ZnO is significantly shifted towards higher wavelength region for Ce and Sn doped samples. The substitution of Ce and Sn in the ZnO lattice produce additional electronic state which leads to red shift in absorption spectra [36,39]. The band gap can be calculated by following Eq. (4).

$$\alpha h\nu = A(h\nu - E_g)^n \quad (4)$$

Where 'α' is absorption coefficient, 'hν' is electromagnetic wave energy, 'n' is index number and 'A' is a constant.

Fig. 5(b) shows the Tauc plot of different concentration of Ce doped ZnO, the result showed as the decreasing band gap when increasing the dopant concentration. This may be facilitating the visible activity which reduced the electron hole recombination, as a result it enhances the effective degradation of organic pollutants in visible region. The 5% Ce doped ZnO nanoparticle showed a broad absorption peak which appeared in the range of between 400–800 nm and result confirms the doped sample can be active in visible region. The absorption spectra of different concentrations (1, 3, 5, 10%) of Sn doped ZnO were shown similar results as displayed in Fig. 5(c). The Tauc plot of the Sn/ZnO (1, 3, 5, 10%) were shown in Fig. 5(d). When increasing the Ce & Sn dopant

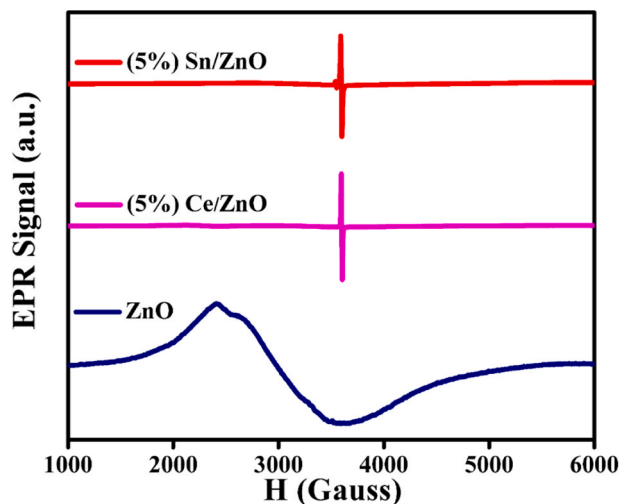


Fig. 6. EPR spectra of ZnO, Ce/ZnO (5%), Sn/ZnO (5%).

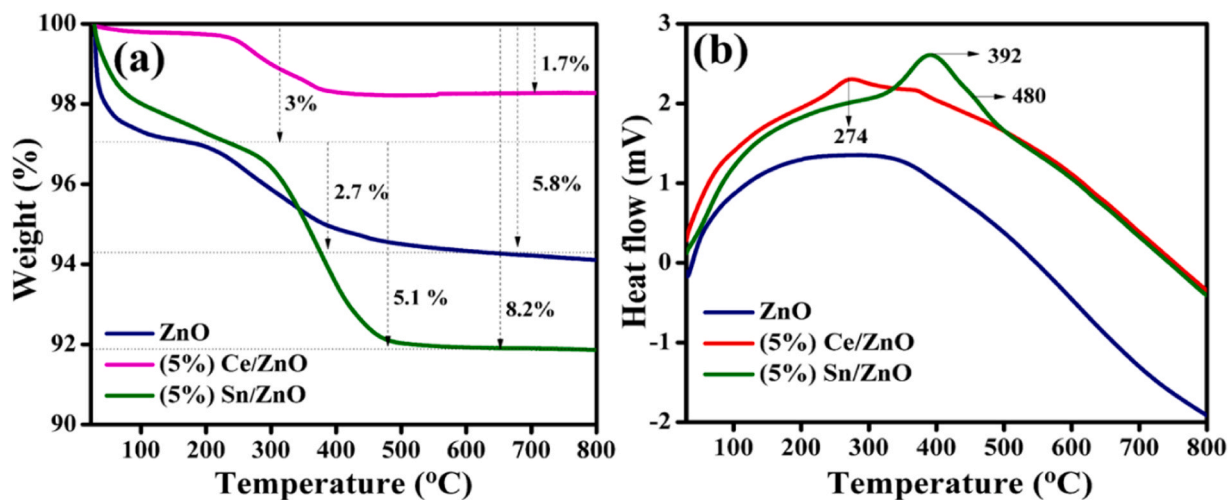


Fig. 7. (a) TGA curves and (b) DTA Curves of ZnO, Ce/ZnO (5%), Sn/ZnO (5%).

concentration, the bandgap value was reduced. The calculated band gap values for ZnO, Ce/ZnO (5%), & Sn/ZnO (5%) were 3.21 eV, 2.81 eV, & 2.65 eV respectively. The absorption result of the both samples showed a significant red shifting when Ce and Sn was incorporated as dopants.

3.5. EPR analysis

The room temperature EPR analysis was used to detect the unpaired electrons of the pure ZnO, Ce/ZnO (5%) and Sn/ZnO (5%) samples, which shown in Fig. 6. The pure ZnO shows a broad signal, corresponds to absence of active unpaired electron in the surface [40]. A sharp EPR signal obtained at g value of 1.9594, it is due to photogenerated electron

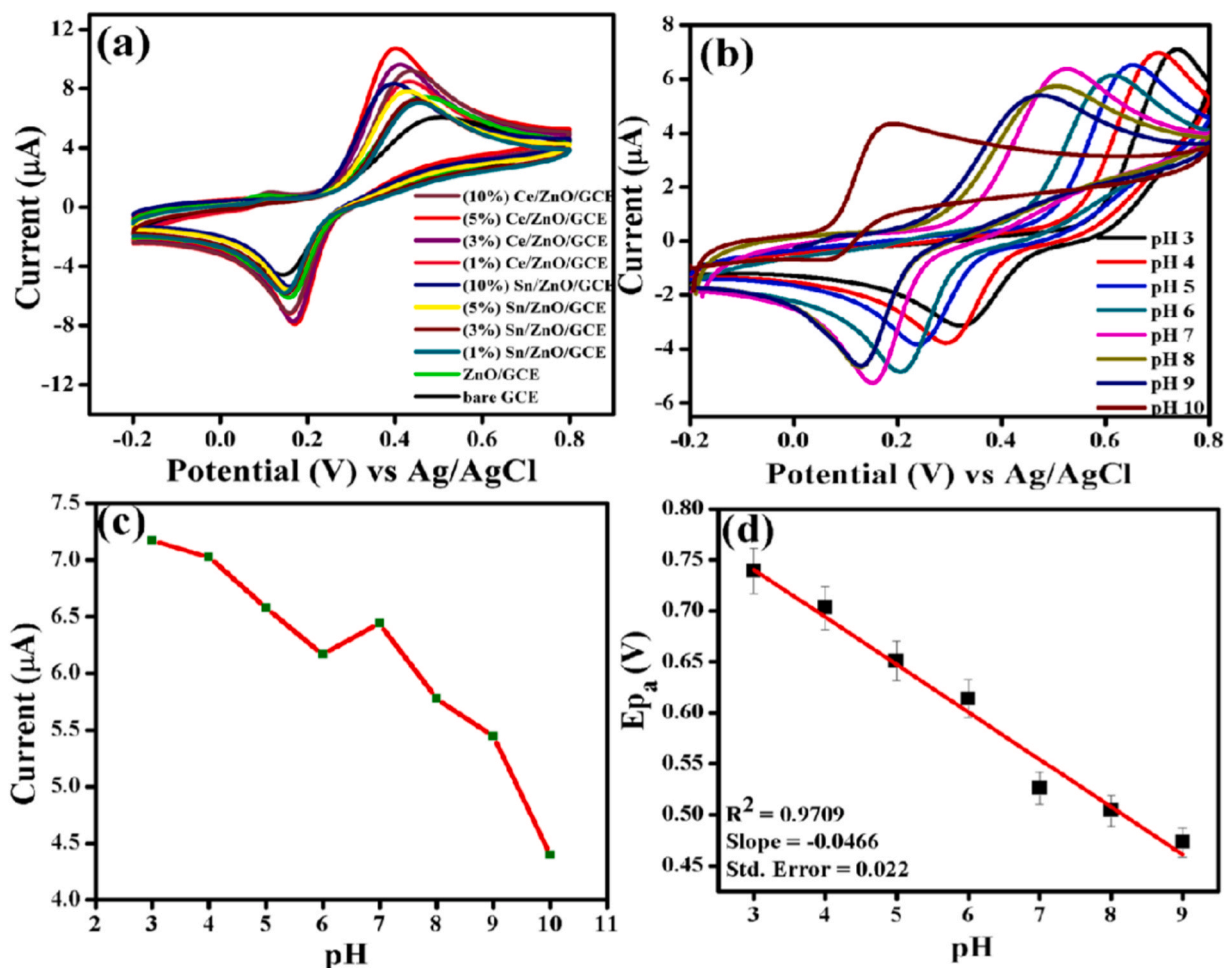


Fig. 8. Cyclic voltammetry curves of (a) different modified electrode (b) different pH of Ce/ZnO (5%), (c) Plot of pH vs current, (d) Plot of pH vs Ep_a.

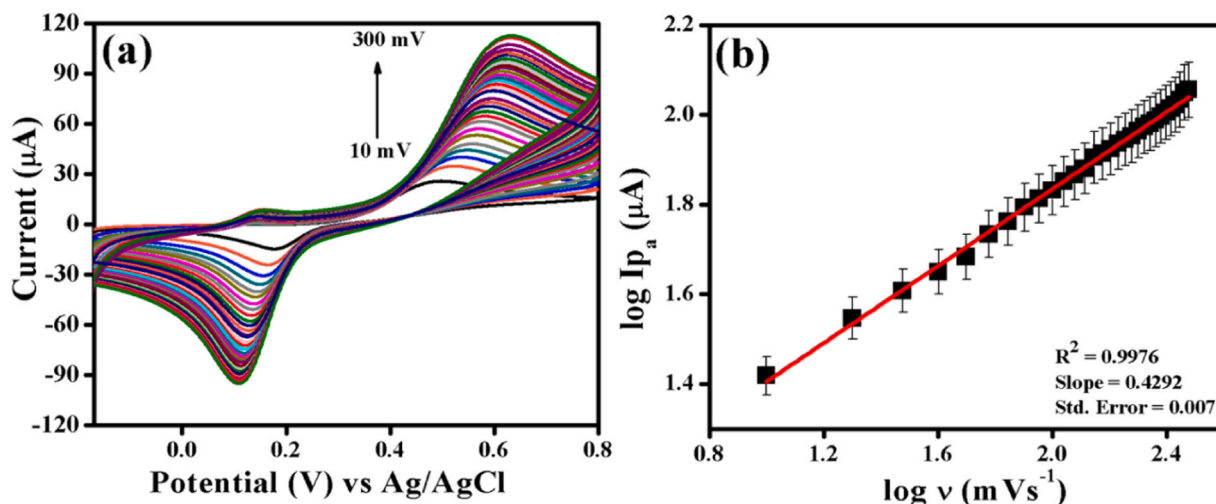


Fig. 9. Cyclic voltammetry curves of (a) different scan rate of Ce/ZnO (5%)/GCE in presence of catechol, (b) double logarithmic plot of current vs potential.

stability of the Zn^{2+} and the Ce^{4+} located at crystallization defect [41]. EPR result revealed that electron is trapped Ce^{3+} centered at 3604.6G, while the holes are trapped as oxygen centered as radical covalent linkage to surface of ZnO material. In the case of Sn/ZnO (5%), two signals, a small hump and a sharp signal with resonance at g value of 0.7958 is because of photogenerated electron stability in Zn^{2+} and the Sn^{4+} located at crystallization defect. EPR result reveal that electron is trapped Sn^{2+} centered at 3590.3G due to the holes are trapped as oxygen centered as radical covalent linkage to surface of ZnO.

3.6. TGA & DTA analysis

The combined TGA & DTA curves of ZnO, Ce/ZnO (5%), and Sn/ZnO (5%) were recorded for confirmation of stability of the samples, the obtained results are displayed in Fig. 7(a, b) respectively. The analysis carried out at temperature range from 30 °C to 800 °C with an increment of 10 °C/min in air atmosphere. The ZnO was attained two weight losses, the first is from room temperature to 100 °C with a weight loss of 3% due to evaporation of moisture trapped in the surface of ZnO. Further, the second weight loss attained about 2.7% at the temperature range of 250–350 °C due to decomposition of residual PVP molecules on the surface of ZnO. In the other hand, the Sn/ZnO (5%) material was attained three weight losses, the first one from room temperature to 100 °C with weight loss of about 3% due to evaporation of absorbed moisture from the surface of Sn/ZnO (5%). However, the second weight loss of 8.2% occurred between the temperature ranges of 270–470 °C due to decomposition of residual organic molecule and might be due to minute sublimation of Sn. Nevertheless, Ce/ZnO (5%) nanoparticles attained one weight loss (1.7%) in the temperature range of 210–390 °C due to decomposition of PVP. On the other hand, there was no weight loss was observed due to loss of absorbed moisture content on the surface of cerium doped ZnO as shown in Fig. 7(a). The major weight loss obtained between room temperature to 100 °C for pure and Sn doped ZnO and less weight loss for Ce doped ZnO is good agreement with result obtained from FTIR. The DTA curves (Fig. 7b) showed a broad exothermic for all the samples regarding to the weight loss for the corresponding samples between the room temperature to 500 °C.

3.7. Electrochemical sensing of catechol

Fig. 8(a) shows the cyclic voltammetric curve of different modified electrodes such as bare GCE, ZnO/GCE, Ce doped ZnO/GCE, and Sn doped ZnO/GCE. The electrochemical sensing of catechol was performed at the scan rate of 50 mVs^{-1} using 0.1 M phosphate buffer solution (pH 7) in presence of 1×10^{-4} M catechol. Fig. 8(a) bare GCE

exhibits the both oxidation and reduction peak of catechol and the oxidation peak potential and current response observed at 0.50 V and 6.18 μA respectively. The modified ZnO/GCE electrode shows the peak potential at 0.46 V and current response at 7.51 μA . For Ce doped (1%, 3%, 5% and 10%) ZnO, the peak potential obtained at 0.43, 0.41, 0.40, 0.43 V and current response obtained at 8.51, 9.65, 10.78, 9.26 μA respectively. Similarly, the Sn doped (1%, 3%, 5% and 10%) showed peak potential at 0.45, 0.44, 0.42, 0.39 V and current response of 7.07, 7.28, 7.85 and 8.36 μA respectively. When comparing all the bare and modified electrode, the 5% Ce doped ZnO showed lower potential with high current response so, it exhibits better electrocatalytic sensing behavior compared to other electrodes. From the CV result, an optimum concentration of 5% was chosen. Such enhanced electrochemical sensing behavior might be due to (i) the dopant of Cerium which alters the conductivity of materials due to its redox behavior, (ii) the number of active sites gets increased due to its porous nature. To further evaluate electrochemical properties, electrochemical impedance spectroscopy (EIS) analysis was investigated for the 5% Ce/ZnO and the obtained result was compared with commercial ZnO. The Nyquist plot shows good conducting behavior when compared with commercial ZnO and other prepared samples which was shown in Fig. S1.

3.7.1. Effect of pH

Fig. 8(b) shows the CV curve of Ce/ZnO (5%)/GCE modified electrode which was recorded at 1×10^{-4} M concentration of CA in (0.1 M) PBS with different pH values from 3 to 10. The influence of pH effect on current is clearly shown in Fig. 8(c), it showed that pH 7 with high current response because catechol has a pK_a value of 9.4 in pH 7 medium and therefore it exhibits high electroactive redox behavior [42]. This is due to high dissolution of H^+ ions at neutral condition compared to acidic and alkaline medium which facilitates the structural changes in catechol. During the experimental process, the catechol is converted into 1,2-benzoquinone by oxidation and the 1,2-benzoquinone is reverted to catechol by reduction process. The obtained pH vs anodic peak current is illustrated in Fig. 8(c). Similarly, the plot of potential vs pH is shown in Fig. 8(d). The pH 7 shows high current response towards oxidation of CA for the Ce/ZnO (5%)/GCE modified electrode. The expression for the linear regression equation is given as:

$$E_p(\text{V}) = -0.0466 \text{ pH} - 0.8804 \quad (R^2 = 0.970) \cdot (\text{Ce/ZnO}(5\%)/\text{GCE})$$

By using m/n ratio equation, the number of electron and proton involved in the reaction can be calculated by following Eq. 5.

$$E_p = E - [(2.303 \text{ mRT})/nF] \quad (5)$$

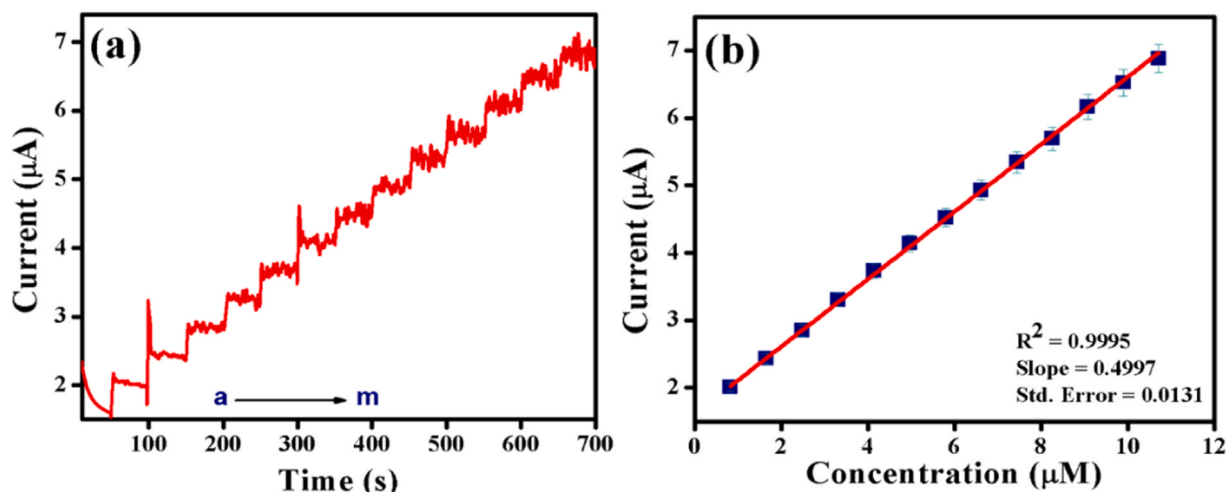


Fig. 10. (a) Chronoamperometry curves of Ce/ZnO(5%)/GCE at constant operating potential of 0.4 V with addition of different concentration 0.83×10^{-6} to 10.80×10^{-6} M in the PBS solution. (b) Calibration curve of current vs concentration.

The m/n ratio is found to be 1.02, that clearly indicates the equal number of electrons and protons are involved in the electrochemical process of CA. Therefore, pH 7 shows the better electrocatalytic activity than the other pH for Ce/ZnO (5%)/GCE material.

3.7.2. Effect of scan rate

By studying the effect of the scan rate, the kinetics of the electrode was examined. Fig. 9(a) represents the cyclic voltammetric response of Ce/ZnO(5%)/GCE electrode which carried out in presence of 1×10^{-4} M CA at pH 7 (0.1 M PBS buffer solution) with different scan rates ($10\text{--}300 \text{ mVs}^{-1}$). The direct proportionality between scan rate and peaks current was studied, the peak potential and the peak current increases with increasing the scan rate. When increasing the scan rate, the oxidation peak current moved positively and the reduction peak current moved negatively. This occurs due to diffusion processes, slow electron transfer and ohmic resistance at the electrode/electrolyte interface [42]. Fig. 9(b) illustrates the double logarithmic plot of $\log v$ versus $\log I_{pa}$, by using the slope value, the nature of electrode process is confirmed and it was found to be diffusion-controlled process. The linear relationship was obtained from the plot with the following linear regression equation, $\log(I_{pa}) = 0.429 \log v - 0.976$, ($R^2 = 0.9976$). Fig. S2 shows the linear relationship plot between E_{pa} and $\ln(v)$ and their linear regression equations are $E_{pa} = 0.039 \ln(v) + 0.4036$ ($R^2 = 0.9970$) (Ce/ZnO/GCE). From Laviron Eq. (6) gives the relationship between the potential (E_{pa}) and scan rate (v) [41].

$$E_{pa} = \frac{E^\circ - \frac{RT}{(1-\alpha)nF} \ln \left(\frac{RTk^0}{nF} \right)}{(1-\alpha)nF} + \frac{RT}{(1-\alpha)nF} \ln v \quad (6)$$

Where, α = electron transfer coefficient, k^0 = standard rate constant, F = Faraday constant, R = Gas constant, and n = number of electron transfer. The values such as $\alpha = 0.931$ $k^0 = 0.3212$ were calculated for the modified electrode. From Eq. (7) gives the number of electrons involved in the overall reaction.

$$I_p = \frac{nFQv}{4RT} \quad (7)$$

Where, Q = charge, and v = scan rate. Therefore, the total number of electron transfer for the redox process of CA is found to be 2 which is in consistent with the previous literature [43].

3.7.3. Chronoamperometry

Fig. 10(a) chronoamperometry curve of Ce/ZnO(5%)/GCE modified

Table 1

Comparison of the analytical performance of different electrochemical sensor for catechol.

S. no.	Modified Electrode	Limit of detection (μM)	Linear range (μM)	Method	Ref.
a	[Cu(Sal- β -Ala)(3,5-DMPz)2]/SWCNTs/GCE	3.5	5–215	DPV	[44]
b	PGCE	3.99	10–300	CV	[45]
c	ZrO ₂ NPs/Au	7.68	–	CA	[46]
d	NiO/CNT/GCE	2.5	10–400	DPV	[47]
e	EGr-TPyP/GC	0.303	1–100	SWV	[48]
f	PEDOT/GO/GCE	1.6	2–400	DPV	[11]
g	Pt/C60/PGE	2.97	50–1500	DPV	[49]
h	TpBD-COF Modified CPE	0.46	1–2000	DPV	[50]
i	Ce/ZnO(5%)/GCE	0.21	0.8–10.71	CA	This work

a) Copper(II) complex [Cu(Sal- β -Ala)(3,5-DMPz)2] (salicylaldehyde- β -alanine), (3,5-dimethylpyrazole) / single-walled carbon nanotubes, b) Polarized glassy carbon electrode, c) Zirconium oxide nanoparticles/Gold electrode, d) Nickel oxide/carbon nanotube/glassy carbon electrode, e) Extrapolation of graphene-tetra(4-pyridyl) porphyrin/glassy carbon electrode, f) Poly(3,4-ethylenedioxythiophene)/Graphene oxide/Glassy carbon electrode, g) Platinum/Fullerene/Pyrolytic graphite electrode, h) Tetra phenyl butadiene-covalent organic frame work modified carbon paste electrode, i) Zinc oxide/cerium(5%)/glassy carbon electrode.

electrode at the applied potential of 0.4 V in presence of different concentration of CA at pH 7. In chronoamperometry analysis, when increasing the concentration of CA (a - m; 0.83, 1.66, 2.49, 3.32, 4.14, 4.97, 5.79, 6.62, 7.44, 8.26, 9.08, 9.90, 10.71×10^{-6} M), the corresponding oxidation peak current also gradually increased. Fig. 10(b) illuminates the plot of CA with different concentration vs current and their linear range was found to be 0.83×10^{-6} to 10.80×10^{-6} M. The linear regression equation is given as.

$$I_{pa} (\mu\text{A}) = 0.4997 [\text{CA}] (\mu\text{M}) - 1.609 (R^2 = 0.9991)$$

From the above linear regression equation, the Ce/ZnO(5%)/GCE modified electrode exhibits good sensitivity. The determined sensitivity value from the slope is $0.4942 \mu\text{M} \mu\text{A}^{-1}$. Limit of detection (LOD) was estimated from Eq. (8) the calculated value is $0.21 \mu\text{M}$.

$$\text{LOD} = 3 \text{ S/q} \quad (8)$$

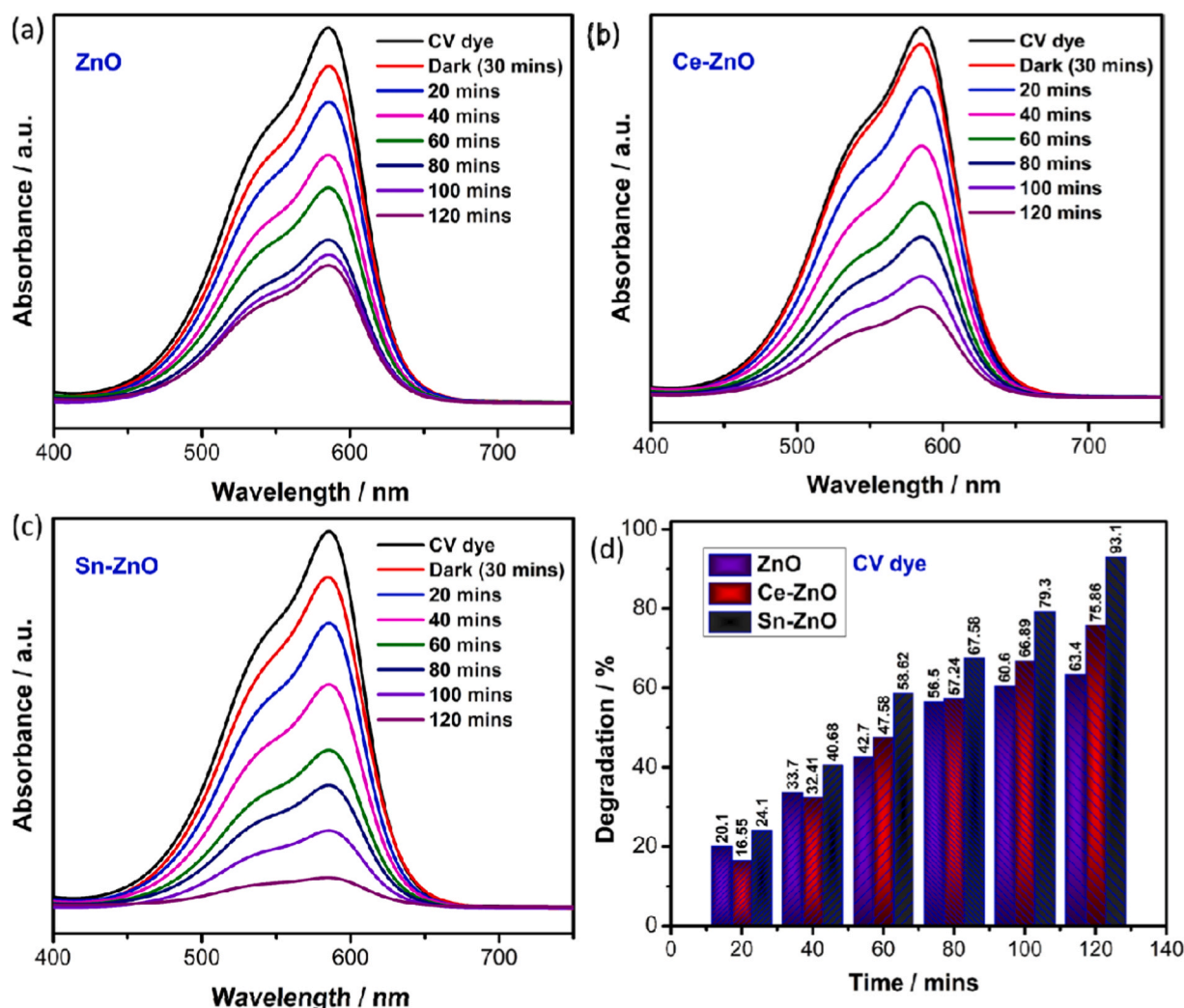


Fig. 11. (a–c) Reaction profiles of Photocatalytic degradation of CV dye for the pure ZnO, Ce/ZnO (5%) and Sn/ZnO (5%) nanoparticle, respectively. (d) Degradation efficiency of CV dye.

Where, q = slope value from the regression equation, and S = standard deviation. The above results showed that the modified electrode showed as good electrochemical sensing towards CA molecule. The comparison Table 1 shows appreciable limit of detection and linear range compared to previous reports [11,44–50].

3.7.4. Reproducibility and stability

The reproducibility of Ce/ZnO (5%) /GCE modified electrode was studied by CV, the four different bare GCE was modified and it was examined by the presence of 10×10^{-6} M CA (Fig. S3a). The measurements were repeated for several times and the relative standard deviation was studied. From the CV results, only the 3% deviation of the current response was observed. Moreover, the stability of the modified electrode was investigated by CV in every 3 days for 2 weeks [51]. The modified electrodes were stored at 4 °C, and 10% of deviation in oxidation current response was observed after 2 weeks (Fig. S3(b)). The obtained result revealed that the fabricated Ce/ZnO (5%)/GCE modified electrode exhibited good stability.

3.7.5. Interference studies

The influences of some possible interference were examined by the standard solution of catechol at 10×10^{-6} M concentration. The modified electrode was used to measure the possible interference, and the obtained result showed obviously no interference detected even at

concentration of 1000 fold of Na^+ , K^+ , Mg^{2+} , NO_3^- , Cl^- , and SO_4^{2-} . The catechol may interfere with several organic compounds like hydroquinone (HQ), resorcinol (RC), 4-Nitrophenol (4-NP), 2,4- Dinitrophenol (2,4- NP), and 4-Chlorophenol (4-ClP). The two-fold excess concentration of interfering materials were added to catechol and the results shows other materials did not interfere with Ce/ZnO (5%)/GCE electrode materials as shown in Fig. S4. From the result, the modified electrode showed good selectivity for the electrochemical sensing of catechol. Moreover, the detection mechanism of catechol for ZnO/Ce (5%)/GCE modified electrode is demonstrated in Fig. S5.

3.8. Photocatalytic degradation studies of crystal violet (CV) and rhodamine B (RhB) dye solution

The photocatalytic degradation efficiency of as prepared catalysts of ZnO, Ce/ZnO (5%) and Sn/ZnO (5%) nanoparticles were resolved by the deprivation of crystal violet (CV) and rhodamine B (RhB) dye under irradiation of sun light. Fig. 11(a–c) represents the UV-Vis spectra for the CV solution with the occurrence of catalysts (ZnO, Ce/ZnO (5%) and Sn/ZnO (5%)) were irradiated by sun light for 120 min.

When irradiating the CV dye solution, the concentration of the dye was noticeably reduced and it was confirmed by the significant color variation. For pure ZnO, the catalyst influences the organic molecule to achieve the efficiency of about 63.4% within 120 min. The photocatalyst

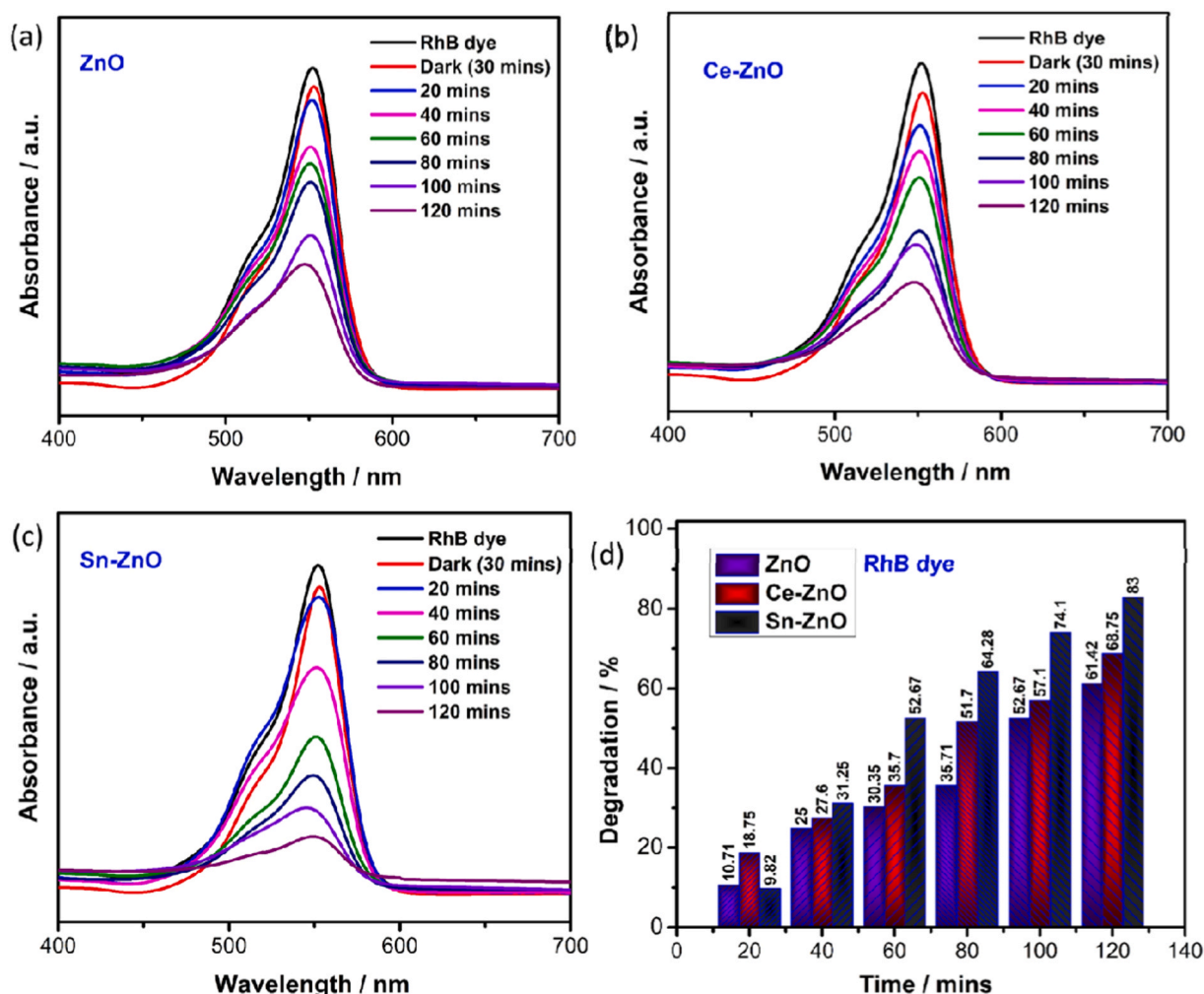


Fig. 12. (a–c) Photocatalytic degradation of RhB dye for ZnO, Ce/ZnO (5%) and Sn/ZnO (5%) nanoparticle respectively. (d) Degradation efficiency of RhB dye.

experiment was further extended to doped samples. The degradation reaction using Ce (5%) & Sn (5%) doped ZnO nanocatalysts were performed by the same process. The rate of electron-hole pair recombination was delayed by doping the metal ions into the ZnO hexagonal structure results increased the degradation efficiency. Compared to ZnO catalyst, Ce and Sn doped ZnO catalysts possessed high efficiency of degradation of 75.8% and 93.1%, respectively. Fig. 11(d) shows bar diagram of photo dye degradation efficiency of crystal violet dye.

Similarly, the photocatalytic degradation reaction was performed for the ZnO, Ce/ZnO (5%) and Sn/ZnO (5%) nanoparticles against another model pollutant dye of RhB, the obtained degradation result is shown in Fig. 12(a–c). For the undoped ZnO, the efficiency reached about 61.2% within 120 min. Under the identical experimental condition, the Ce/ZnO (5%) and Sn/ZnO (5%) catalysts were achieved about 68.7% and 83%, respectively. Fig. 12(d) shows a bar diagram of degradation efficiency of RhB dye. The significant improvement of the degradation efficiency is due to the doping effect of Ce^{4+} and Sn^{4+} ions at the Zn^{2+} lattice sites, it reduces recombination of excited charge carriers (electron-hole pair).

Fig. 13(a & c) depicts the changes in initial and final concentration of dye in the presence and absence of photocatalyst against the light irradiation with respect to time (t) for the CV and RhB, respectively. The Sn/ZnO (5%) catalyst shows highest degradation ability due the fact that sub energy-level act as traps for recombination. Based on the sub energy level of the conduction band helps to produce the large number of reactive oxygen species (ROS). Addition investigation of pseudo-first

order kinetics studies shown in Fig. 13(b & d), the degradation rates were 0.020 min^{-1} , 0.027 min^{-1} , and 0.046 min^{-1} for ZnO, Ce/ZnO (5%) and Sn/ZnO (5%) respectively against crystal violet dye. Similarly, the degradation rate was calculated using the at 0.017 min^{-1} , 0.019 min^{-1} and 0.034 min^{-1} pseudo-first order kinetics studies for ZnO, Ce/ZnO (5%) and Sn/ZnO (5%) respectively against RhB dye. From the dye degradation studies, rate constant value and R^2 values are listed in the Table 2.

The pH of the solution plays as an important role for efficiency of photo degradation. Particularly, it alters the surface charge of the catalyst due to the interaction of catalyst and dye molecules. Hence, the pH effect was determined to best performed catalyst Sn/ZnO (5%) in the range of pH from 3 to 10 for the both dyes. Fig. 14(a) illustrates the highest CV dye degradation was occurs at pH 8. Similarly, the Fig. 14(b) shows the maximum degradation efficiency for RhB dye at pH 9. The above pH study is clearly demonstrated that the basic medium of the dye solution was more suitable to achieve high degradation efficiency due to higher adsorption of dye molecules on the surface of the catalyst [52].

Since highest degradation efficiency obtained for the 5% Sn doped ZnO, it was only chosen for the scavenger study for further understanding the degradation activity. In general, the photo active catalyst generates the reactive oxygen species (h^+ , $\text{OH}^\bullet$, and $\text{O}_2^\bullet$) and it is essential to identify which reactive species influences a great role during photo degradation. It also more supportive to determine the mechanism of the photo degradation of the Sn doped ZnO. Hence, the h^+ , $\text{OH}^\bullet$, and $\text{O}_2^\bullet$ are eliminated by accumulation of related scavengers such as EDTA

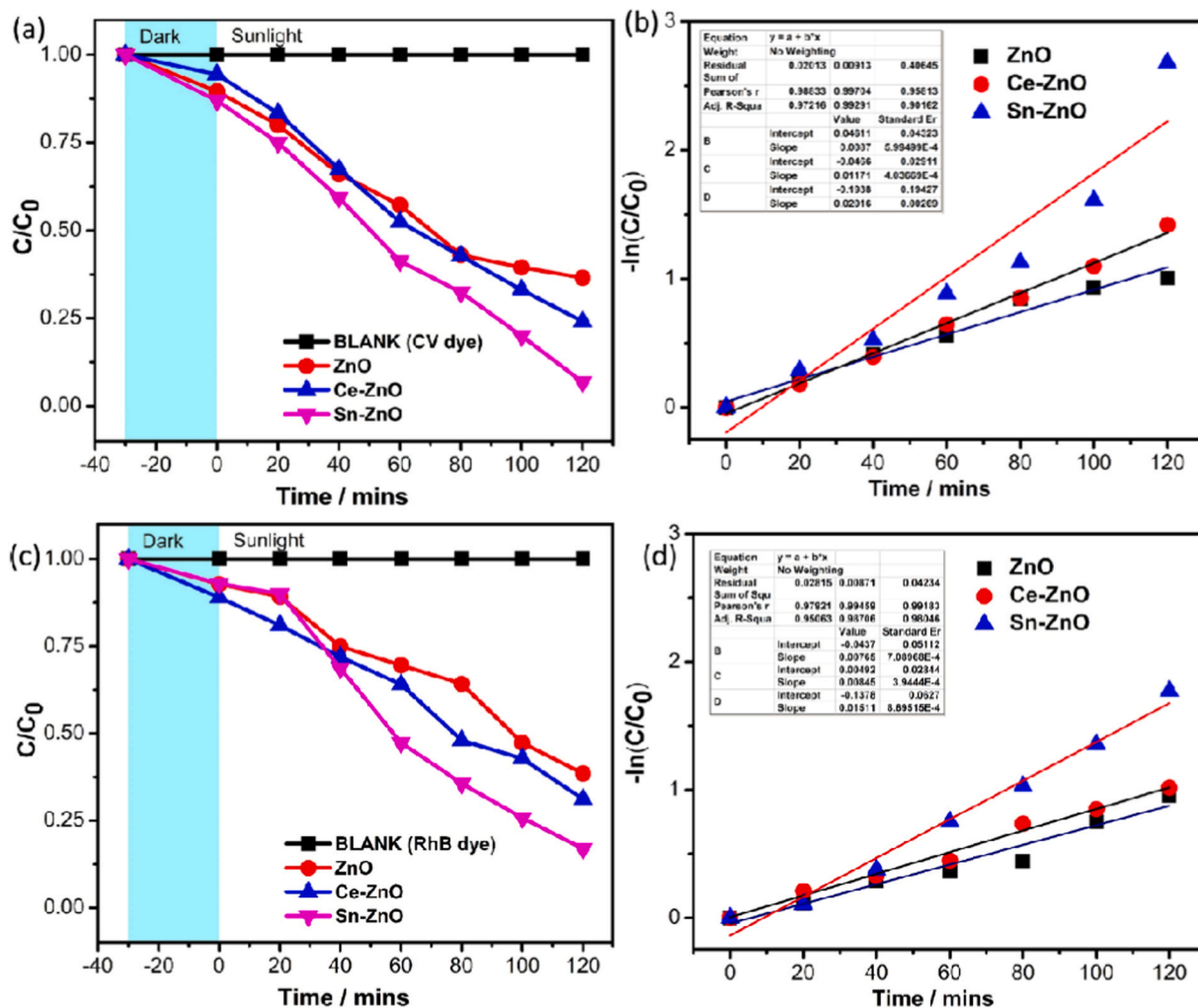


Fig. 13. (a) C/C_0 versus time interval plot of CV dye (b) $-\ln(C/C_0)$ versus time interval plot of crystal violet dye (c) C/C_0 versus time interval plot of RhB dye (d) $-\ln(C/C_0)$ versus time interval plot of RhB dye.

Table 2

Photocatalytic activity result of ZnO, Ce/ZnO (5%) and Sn/ZnO (5%) nanoparticles.

S. no.	Catalyst	Degradation efficiency (%) (120 min)	k^0 (min^{-1})	R^2
Crystal violet dye (10 ppm)				
1	Pure ZnO	63.4	0.020	0.9721
2	Ce/ZnO (5%)	75.8	0.027	0.9929
3	Sn/ZnO (5%)	93.1	0.046	0.9016
Rhodamine B dye				
4	Pure ZnO	61.4	0.017	0.9506
5	Ce/ZnO (5%)	68.7	0.019	0.9870
6	Sn/ZnO (5%)	83.0	0.034	0.9804

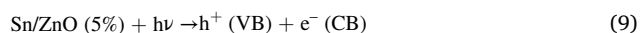
(h^+ scavenger), methanol ($\cdot\text{OH}$ scavenger), and 1,4-Benzoquinone (p-BQ) ($\text{O}_2^{\cdot-}$ scavenger) into reaction solution, respectively.

From the Fig. 15(a) illustrates the efficiency with and without scavengers. As can be seen from scavenger studies, the p-BQ only shows the notable variations in efficiency of both dyes. Hence, the superoxide radicals play important role the overall efficiency. Another important study is stability and reusability of photocatalyst (Sn/ZnO (5%)). For

reusability test, the catalyst is again used for further analysis followed by washing with water and ethanol, and dried in air. The results reveal the stability of the catalyst and there is no significant loss in degradation efficiency even after five cycles of the photocatalytic process shown in Fig. 15(b). After 5 cycles, the efficiency of catalyst is decreased due to the loss of sample while washing process.

The mechanism of CV and RhB dye degradation for the Sn/ZnO (5%) catalyst is described as follows,

(i) Formation of electron hole pair



(ii) Formation of hydroxyl radicals



(iii) Formation of superoxide radicals



(iv) Photo-degradation of CV and RhB dye

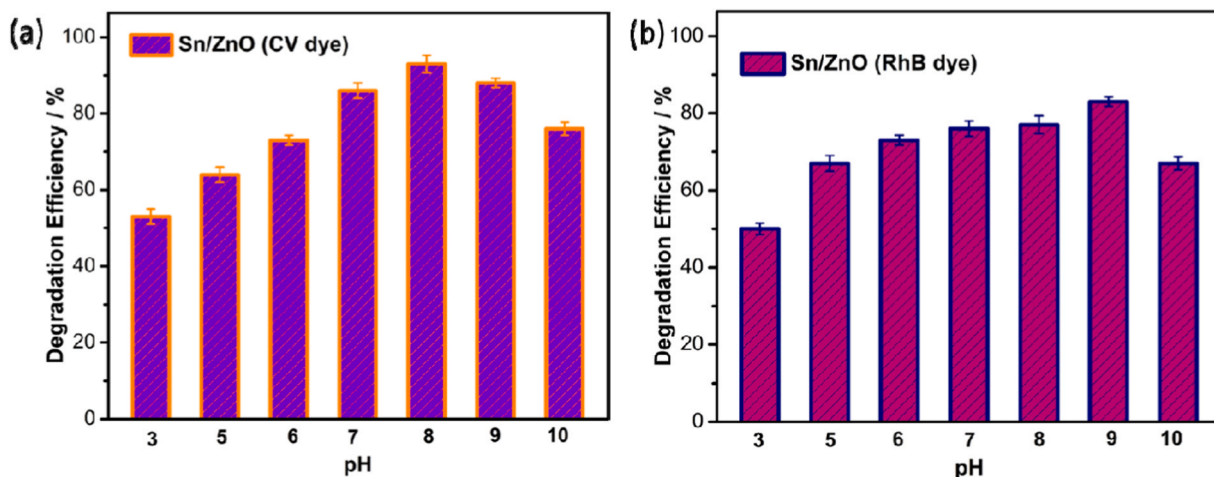


Fig. 14. (a) Photocatalytic dye degradation efficiency as a function of pH (CV 10 mg L⁻¹ at 0.4 g L⁻¹ catalyst load); for CV and (b) RhB dye.

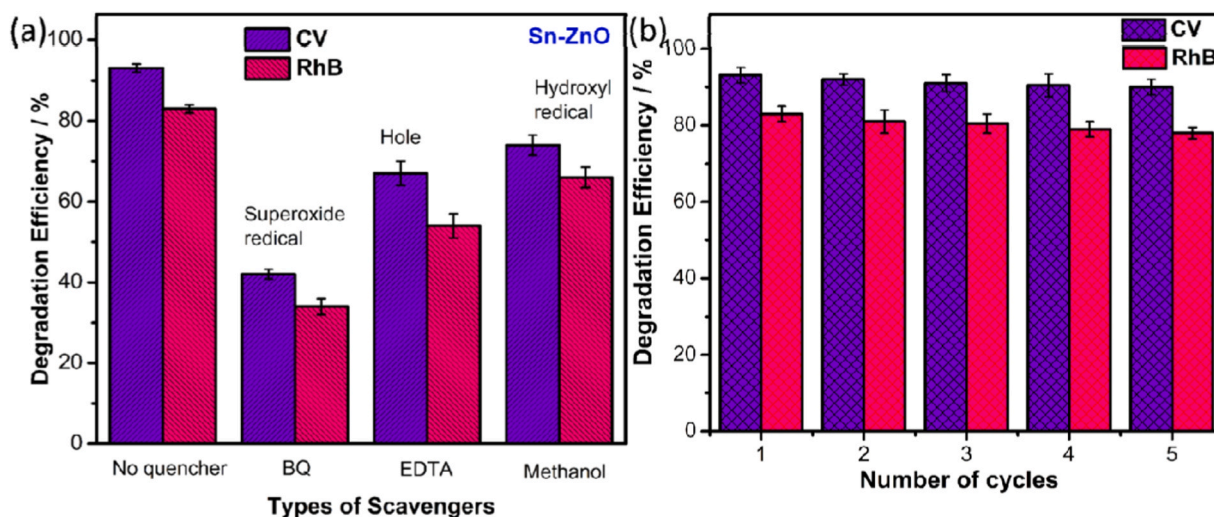
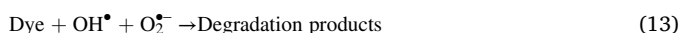


Fig. 15. (a) photocatalytic dye degradation efficiency of CV and (b) RhB at presence of different scavengers with concentrations of 10 mg L⁻¹ at 0.4 g L⁻¹.

Table 3

Comparison of current and reported studies of various ZnO based nanoparticles.

S. no.	Catalysts	Dye	Dye Conc.	Dose/volume	Source	Time (min)	Efficiency (%)	Ref.
1	ZnO/GO	CV	5 ppm	80 mg/100 mL	Visible	240	99	[54]
2	CdS/CMS	CV	20 ppm	100 mg/50 mL	Visible	120	81.03	[55]
3	F-TiO ₂ (B)/Fullerene	CV	30 ppm	10 mg/100 mL	Visible	120	77.23	[56]
4	TiO ₂ /Fullerene	RhB	10 ppm	20 mg/20 mL	Visible	150	95	[57]
5	ZnO/g-C ₃ N ₄	RhB	10 ppm	50 mg/50 mL	Visible	100	96	[58]
6	GR-ZnO/CoPc	RhB	10 ppm	10 mg/100 mL	Visible	140	100	[59]
7	ZnO Nanostructure	RhB	10 ppm	100 mg/-	Visible	120	97	[60]
8	Co ₃ O ₄ @ZrO ₂	RhB	10 ppm	100 mg/100 mL	Visible	180	32	[61]
9	Au-ZnO	RhB	10 ppm	30 mg/100 mL	UV	180	85	[62]
10	Ag/ZnO	RhB	100 ppm	50 mg/50 mL	UV	120	90	[63]
11	TiO ₂ /ZnO	RhB	1 × 10 ⁻⁵ Mol/L	50 mg/25 mL	Visible	180	89	[64]
12	Ag/AgBr/ZnO	RhB	5 ppm	100 mg/100 mL	Visible	180	95	[65]
13	Sn/ZnO	CV, RhB	10 ppm	20 mg/50 mL	Visible	120	93.1 & 83	Present study



In the present study, Sn doped ZnO photocatalyst shows superior photocatalytic degradation than pure ZnO. The efficiency enhancement of Sn/ZnO (5%) catalyst may be attributed due to two important aspects, (i) reduction in band gap energy and (ii) trapping charge conditions.

Mainly, the Sn doped ZnO nanoparticle band gap energy was decreased to 2.65 eV compared to pure ZnO (3.21 eV). In this aspect, the Sn/ZnO (5%) catalyst shows higher photocatalytic activity due to absorption of incident light in visible region. Furthermore, the presence of Sn is act as a scavenger and traps the e⁻ from the conduction band of ZnO and this trapping process is shifting the fermi level towards conduction band. Subsequently, the equilibrium establishes with the conduction band of

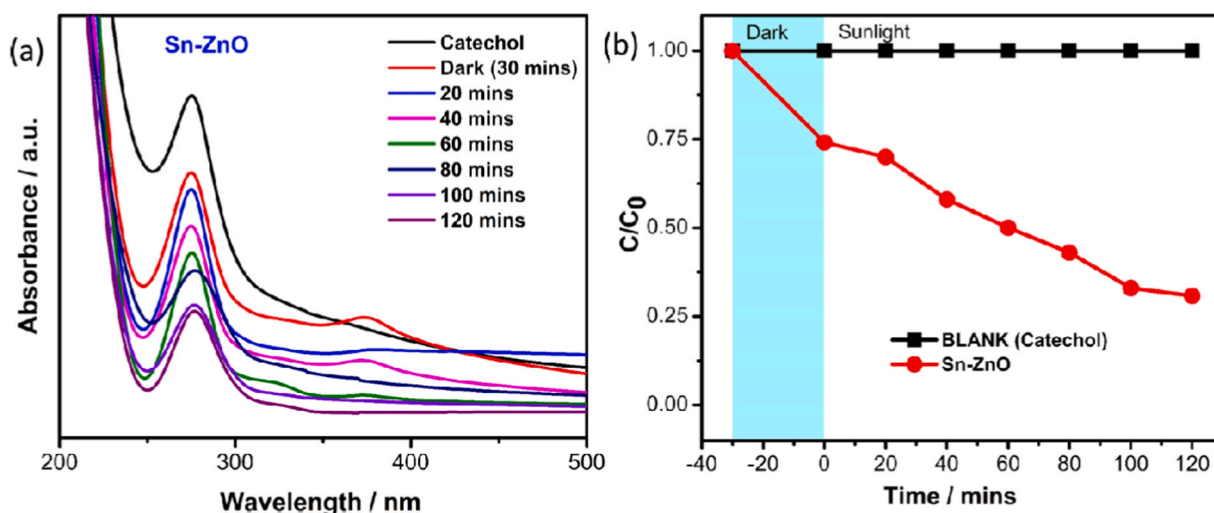


Fig. 16. (a) Photocatalytic degradation of catechol solution for Sn/ZnO (5%) nanoparticle (b) C/C_0 versus time interval plot of catechol solution.

catalyst. Therefore, the Sn played a significant role to stop the recombination process of electron and hole and successively enrich the photocatalytic dye degradation efficiency [53]. The photocatalytic dye degradation activity of Sn/ZnO (5%) was compared with other catalysts reported for degradation of CV and RhB dye, the Table 3 shows comparison of the degradation efficiency. The Sn/ZnO (5%) can be considered as more effective catalyst for mineralization of CV and RhB dye under the natural sun light with short time interval.

3.9. Photocatalytic degradation studies of catechol solution

The photocatalytic degradation efficiency of the best photocatalysts of Sn/ZnO (5%) nanoparticles was studied by organic pollutant of catechol solution dye under irradiation of sun light. For Sn/ZnO (5%) the catalyst influences the organic molecule to achieve the better efficiency of about 69.1% within 120 mins. Fig. 16(a) and (b) shows the UV absorption spectra of catechol solution and efficiency diagram respectively.

4. Conclusion

The different concentration of Ce and Sn doped ZnO materials were synthesized by a facile chemical method. The chemical method is adoptable for synthesis of the nanoparticles in industrial-scale with small size. Modified electrode fabricated using Ce and Sn doped ZnO nanoparticles for determination of catechol by voltammetric techniques. The doped Ce/ZnO(5%) exhibited better electrochemical sensing activity compared to other modified electrodes. The calculated limit of detection and the sensitivity of the Ce/ZnO (5%) were found to be $0.21 \mu\text{M}$ and $0.494 \mu\text{M} \mu\text{A}^{-1}$, respectively. Apart from that, the photocatalytic activity of the synthesized nanoparticles was investigated for degradation of catechol which reveals the good catalytic efficacy. Moreover, the Ce and Sn doped ZnO were used as efficient catalyst for degradation of textile dye pollutants such as CV and RhB under visible light irradiation in direct sunlight. Due to lower band gap of Sn/ZnO (5%), it exhibited better photocatalytic efficiency (93.1%) when compared with undoped ZnO. The obtained results demonstrated that the 5% of Ce and Sn doped ZnO showed as good catalytic activity for determination of catechol via electrochemical route and decomposition of textile dyes (CV and RhB) by photocatalytic method, respectively.

CRediT authorship contribution statement

Annamalai Padmanaban: Conceptualization, Methodology, Data

curation, Writing - original draft. Govindhasamy Murugadoss: Conceptualization, Methodology, Data curation, Writing - original draft, Project administration, Writing - review & editing, Funding acquisition. Nachimuthu Venkatesh: Formal analysis. Subhenjit Hazra: Resources, Writing - review & editing. Manavalan Rajesh Kumar: Formal analysis, Writing - review & editing. Ramasamy Tamilselvi: Formal analysis. Pachagounder Sakthivel: Data curation, Funding acquisition, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2021.105976.

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