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Fabrication and Interpretation of Zinc-Cerium Composite: Structural and Thermal Studies

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The zinc oxide and zinc-cerium (ZC) oxide composites have been synthesized by varying zinc (Zn) and cerium (Ce) ratios to obtain different $Zn_{1-x}Ce_xO_2$ compounds using the hydrothermal method. The composition of the samples was varied with $x = 0.0$, 0.05, 0.1, 0.3 and 0.5 to obtain compounds named as ZC-1, ZC-2, ZC-3, ZC-4 and ZC-5, respectively. To understand the effect of cerium on zinc oxide, all samples were characterized by FT-IR, SEM-EDX and TGA-DSC. The effective doping of cerium with zinc is confirmed by FT-IR and EDX. All samples were obtained with different particle sizes. Initially, ZC-1 had rod-shaped particles and by doping cerium the particles slowly turned to quasi-spherical shape with reduced size from 150 nm to 60 nm. From thermal studies, the cerium doped zinc oxide showed higher stability than the undoped zinc oxide. The detailed analysis of the properties indicates that these composites can be potential candidates for the biological applications and also they can be promising for catalysis and dye degradation.

Keywords: Composite, Functional group, Hydrothermal, SEM-EDX, Zinc-Cerium oxide.

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1. INTRODUCTION

In recent years, many experiments are conducting by the scientists and researchers to synthesize the desired nanomaterials for the applications of the medical field like antimicrobial, antifungal, anticancer and engineering fields for good thermal stable materials, semiconducting materials etc. But many people fail to develop the required material as it is needed for. There are some major drawbacks in materials synthesis methods, some are morphological defects and some have poor properties. To overcome these all we tried and successfully synthesized a new nanomaterial. Nowadays we have all kinds of facilities like money, types of equipment, healthy lifestyle and so on, but people still are lagging behind to fulfill their basic needs and facing problems in water purification, usage of the excess of sunlight radiation, genetic issues, lack of necessary and particular antibiotics for major diseases like cancer, AIDS, COVID-19, etc.

People also synthesized many composites in microstructures and studied their catalytic activity, and some others failed to give their best in applications that is maybe due to low density, poor thermal stability, high specific surface area [1]. Some of the researchers synthesized the individual elements like V_2O_5, TiO_2, ZnO and many more, but these materials did not show effective behavior in catalytic activity and drug delivery [2-4].

There are some day-to-day problems such as ozonation (wastewater treatment), increased effluent toxicity and disinfection of by-products. For these problems, some of the scientists are trying new and relevant alternative techniques like the advanced oxidation process, heterogeneous photocatalysis and inactivation of bacteria [5]. Even though there are much research has done on polymeric nanocomposites in the form semi-crystalline with good mechanical and conducting properties, they have shown good applications in the field of optoelectronics but amorphous polymers failed because there are trapping sites and carrier mobility is very low [6].

Owing to these studies, we have decided to fabricate a composite of two potential nanomaterials which can give better results than previous. As we have already studied and reported about ZnO and CeO_2 individually [7], these really have remarkable results so herein, we synthesized the mixture of these two materials to enhance all properties and applications. We have synthesized the mixture of zinc-cerium oxide (Zn-CeO_2) specially prepared with the aim of good biological applications and photocatalysts hence; we focused on their synthesis method and chosen the hydrothermal method. So far, all materials were studied for their optical behavior and electrical properties, but here we report the thermally stable material and dimensionally different materials with nano range for five different concentrations and studied their complete functional groups which can help to predict the material for their catalytic activity and apply for dye degradation as well. With the study of morphology and thermal behavior, we can apply it further for electrical applications also. Further, we the authors suggesting and applying these for the antimicrobial studies too.

2. EXPERIMENTAL DETAILS

2.1 Particulars of Materials

To synthesize the mixture of zinc-cerium oxide, all the chemicals and compounds were purchased from HIMEDIA Laboratories Pvt. Ltd (Mumbai, India) such as cerium (III) nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$; 434.29 g/mole) of AR grade with 99 % purity, zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$; 189.36 g/mole) of AR grade with 99 % purity and sodium hydroxide (NaOH; 40.0 g/mole) of AR grade with 98 % purity. To synthesize all solutions we used double distilled water from USIC, KUD, Dharwad (Karnataka, India) after the preparation of precipitation for the washing and annihilation process, we used ethanol (CH_3CH_2OH; 46.06 g/mole) of AR grade with 99.9 % purity which was purchased from CHF chemical Co. Ltd (China city, China).

2.2 Preparation of Mixture of Zinc-Cerium Oxide

The hydrothermal method has been used to synthesize the $Zn_{1-x}Ce_xO_2$ composites of different stoichiometric compositions by varying x, and subsequently five samples have been produced with $x = 0.0$, 0.05, 0.1, 0.3 and 0.5. For the zinc-cerium oxide-1 (ZC-1), $Zn(NO_3)_2.6H_2O$ (2.9 g, 0.1 M) was dissolved in 10 ml of distilled water and 0.1 M of NaOH solution was prepared in water. The above solutions were mixed under stirring for 15 min and then transferred to a Teflon lined autoclave. The autoclave was then placed inside an oven for 3 h at 200 °C. After natural cooling, the resulting precipitate was washed with deionized water and collected by centrifugation. Further, the obtained compound was washed with ethanol and annealed in open-air conditions at 60 °C to get zinc oxide. For ZC-2, $x = 0.05$, so that $Ce(NO_3)_3.6H_2O$ solution is prepared using (0.1085 g, 0.05 M) 5 ml distilled water and $Zn(NO_3)_2.6H_2O$ solution is prepared using (2.82 g, 0.95 M) 10 ml distilled water. There are no changes with NaOH solutions, and the whole process remains the same to obtain ZC-2. Similarly, different compounds are obtained for ZC-3 ($x = 0.1$), for ZC-4 ($x = 0.3$), and for ZC-5 ($x = 0.5$). All compounds are obtained in powder form. Further, these are applied for different characterizations.

2.3 Instrumentation

Fourier Transform – Infrared Spectroscopy (FT-IR) was used for functional group analysis of synthesized nanoparticles. These spectra were recorded using KBr powder. FT-IR spectrophotometer (model: Nicolet 6700).

Scanning Electron Microscope (SEM) with Energy Dispersive X-ray Spectroscopy (EDX) was used for sample morphology and elemental composition studies. SEM-EDX (model: JSM-IT500 LA In Touch Scope).

Thermo-gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were used to study decomposition and transformation of the synthesized nanoparticles. It is recorded from room temperature to 700 °C TGA (model: SDT Q600) and DSC (model: Q20 V24.10).

All the instruments for characterization were used at USIC, KUD, Karnataka, India.

3. RESULTS AND DISCUSSION

3.1 Functional Group Analysis

FT-IR spectra were recorded in the frequency range of 400-4000 cm^{-1}. Infrared spectroscopy was performed to study the possible interaction of the functional groups and vibration structures of synthesized Zn-CeO_2 nanoparticles. The spectrum is formed by the absorption of electromagnetic radiation at frequencies that correlate with the vibrations of specific organic and inorganic bonds present in the synthesized nanomaterials. Several peaks were observed and shown in Fig. 1.

In this, we can observe that for all ZC-1, ZC-2, ZC-3, ZC-4, and ZC-5 almost all bonds are similar to each other. The major difference is in their intensities and the broadness of higher wavenumber. Around 3450 cm^{-1} the peak is going to decrease from ZC-1 to ZC-5, and for lower wavenumbers the peak approaches 445-470 cm^{-1} which indicates that initially the only ZnO was present, and by mixing CeO_2 the peak shifts to higher wavenumbers. The remaining all peaks of compounds are observed at the same frequencies. The observed various peaks and groups of frequencies are listed below in Table 1 with their corresponding functional groups.

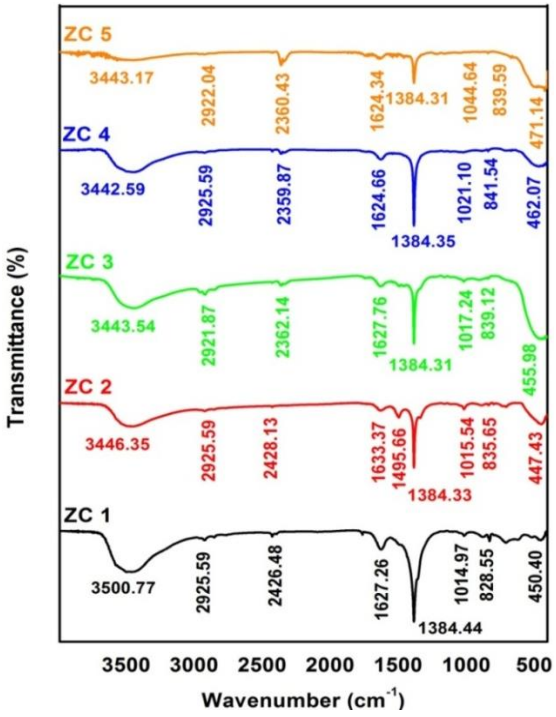

Fig. 1 – FT-IR spectra of all samples (ZC-1 to ZC-5)

3.2 Size, Morphology and Elemental Analysis

Fig. 2 shows the SEM images of ZC-1, ZC-2, ZC-3, ZC-4, and ZC-5, respectively. The first sample, ZC-1, is the pure form of zinc oxide, it is obtained in the form of flakes or rods and has the size around 100-150 nm. For the next sample, we dope the cerium so that we get zinc-cerium oxide, and the image indicates that cerium is developed at the tips of the zinc oxide materials and the sizes of the particles are now 90-120 nm. Similarly, the zinc oxide is doped with more cerium to get a good mixture of zinc-cerium oxide, then the material started to take rod/flakes to quasi-spherical shape with a reduced size of around 75 nm. For the sample ZC-4, we increased the cerium content and both zinc and cerium were well mixed that is observed in the ZC-4 image. Further, in the ZC-5 image we observed the size of the particles around 60 nm and also noticed that as we go on increase the cerium, the material will be reduced by its size but all particles started to agglomerate. We got a better size and shaped materials than the other researchers [11-14]. We can conclude that the cerium strongly affects the growth and shape of zinc oxide. This reveals that we can monitor the shape and size of the particles for the biological and catalytic applications.

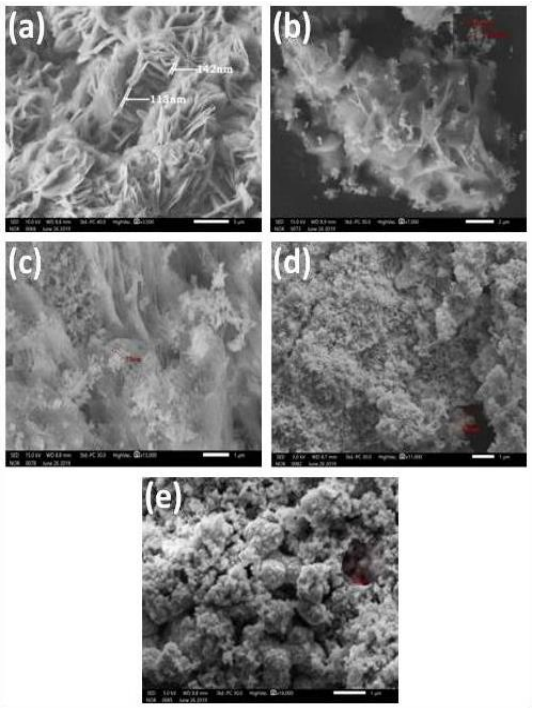

Fig. 2 – SEM images of all samples: (a) ZC-1, (b) ZC-2, (c) ZC-3, (d) ZC-4, (e) ZC-5

The EDX is used for quantitative analysis of the materials. The percentage of all the elements, which are present in the synthesized nanoparticles, is examined using EDX analysis. Using this spectrum we can also investigate accurately the atomic and mass of each element. The EDX spectrum of ZC-1 (Fig. 3a) indicates that there is 53.02 % of zinc (Zn) and 39.36 % of oxygen (O) in the sample and the nitrogen (N) percentage is about 7.62 % due to the design of detectors [14, 15]. By this analysis, we can say that the sample ZC-1 is the pure form of zinc oxide. In Fig. 3b (ZC-2), we can observe that there is a major part of Zn with 48.42 % and the considerable amount of cerium (Ce) 22.64 %. As usual, 14.22 % of O and 14.31 % of carbon (C) are present. This indicates that the sample is a mixture of zinc-cerium oxide. ZC-3 spectra (Fig. 3c) show 20.14 % of Zn and 30.18 % of Ce with 24.83 % of O and 23.78 % of C. This indicates that there is overlapping of C on samples that maybe because of overheating at the annihilation process [16, 17]. The spectrum of ZC-4 (Fig. 3d) confirms the presence of Zn, Ce, O with weight % of 1.12 %, 35.54 % and 35.69 %, respectively, in this sample and also there is a C content of 35.69 %. Further, Fig. 3e (ZC-5) shows 1.76 % of Zn, 72.40 % of Ce and 14.39 % of O and 9.625 % of C. In all these spectra, we can see that there is good agreement of different molar percentage of zinc and cerium, and EDX data also show the homogeneous distribution of all substituents.

3.3 Thermal Studies

Fig. 4 shows the TGA/DSC curves of the samples ZC-1, ZC-2, ZC-3, ZC-4, and ZC-5, respectively. This analysis is used to check and study the decomposition of the materials with respect to temperature. The thermal stability of materials can also depend on the methods of synthesis. The decomposition is not only by the core materials, it may also occur by the elements like hydrogen, nitrogen and oxygen present in the sample. The TGA of ZC-1 shows the first weight loss of ~ 2 % around 30-80 °C which is due to the evaporation of water molecule present in the sample [18].

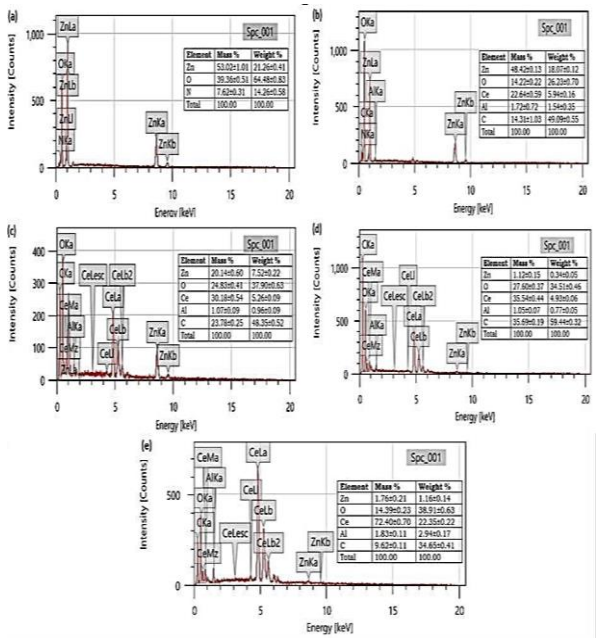

Fig. 3 – EDX spectra of (a) ZC-1, (b) ZC-2, (c) ZC-3, (d) ZC-4, (e) ZC-5

Next weight loss is 10 % at 100-320 °C which attributes to hydroxyl groups a further 6 % weight loss up to 700 °C [18]. Totally, there is ~ 18 % loss of the sample from room temperature to 700 °C. For the second sample ZC-2, there is a small weight loss at initial temperature, which is around 3 % up to 150 °C. After that, there is a gradual loss of 9 % up to 420 °C. Totally, there is 14 % weight loss up to 700 °C. For the sample ZC-3, there is a continuous decrease in weight loss totally of 11 %. Similarly, we can observe a total 7 % weight loss in ZC-4. Finally, there is 5.5 % weight loss for the sample ZC-5. As we go on increasing the molar ratio of the cerium with zinc, we get thermal stability in the samples. This directly indicates that initially zinc majored samples had weight loss around 18 % that is maybe due to change in the transformation of crystals, and the size of the particles was also large. Zinc oxide may increase the generation of high energy due to cavitation [15, 18]. This may lead to an increase in the randomness of the Brownian motion of the zinc oxide which does not allow regular crystal formation [15, 18]. This transformation may be controlled by cerium that has better thermal stability than the zinc oxide, so we observe less weight loss in ZC-2, ZC-3, ZC-4, and ZC-5 compared to ZC-1. The average size of the particles may also be the reason for this, which will conduct thermal radiation more efficiently and gives significant effect throughout the temperature range. Therefore, we can say that the application of zinc oxide in biological, electrical, semiconductor and dye degradation fields can be enhanced by mixing/doping the cerium to that.

Corresponding to TGA, the DSC curves of all samples illustrate the physical absorption of water on the zinc-cerium oxide of the samples by showing exothermic peaks. Based on this, we can analyze that in the graph of sample ZC-1 an exothermic peak is observed at 480 °C and a small peak at 300 °C, which are attributed to the crystallization of zinc oxide. In fact, no remarkable weight loss is observed by DSC curves [18]. In the ZC-2 graph, we observe two exothermic peaks around 450 °C and 280 °C, which reveal the presence of zinc oxide and cerium, respectively. As we go on increasing the molar ratio of cerium, the ZC-3, ZC-4 and ZC-5 show almost negligible peaks and a gradual line, which again indicates the sample crystallization of amorphous materials. In fact, the ZC-1 and ZC-2 have maximum amount of Zn; it is suggested that the crystallization temperature is Zn-dependent.

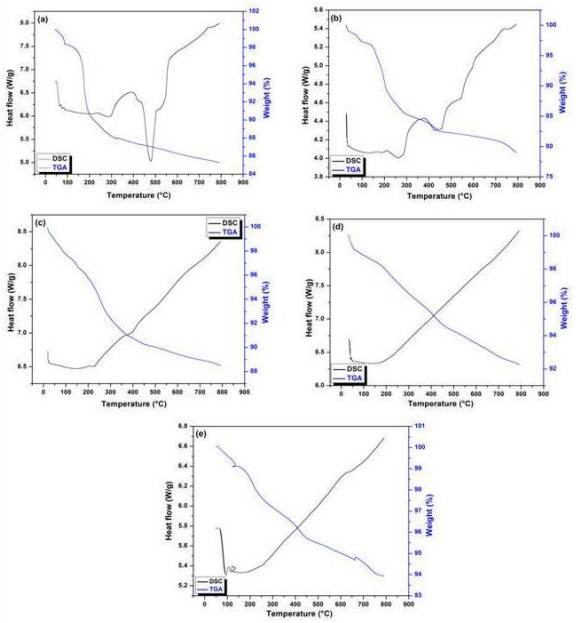

Fig. 4 – TGA-DSC spectra of (a) ZC-1, (b) ZC-2, (c) ZC-3, (d) ZC-4, and (e) ZC-5

Table 1 – Interpretation of FT-IR peaks of the samples ZC-1, ZC-2, ZC-3, ZC-4, and ZC-5

Group of frequencies/wave number (cm^{-1})	Functional groups/assignments	References
3500.77 3446.35 3443.54 3442.59 3443.17	Due to alcohol and hydroxyl groups, OH stretching	[7, 8]
2925.59 2925.59 2921.87 2925.59 2922.04	These are saturated aliphatic group frequencies. Methyl C-H asymmetric stretching	[7, 8]
2426.48 2428.13 2362.14 2359.87 2360.43	C-C stretching	[7, 8]
1627.26 1633.37 1495.60 1627.76 1624.66 1624.34	These are examples of nitrogen multiple and cumulated double bond compound group of frequencies. Open chain imino C=N vibrations	[8]
~ 1384	This is may be for nitrogen-oxygen compounds or C-O vibrations	[8]
1014.97 1015.54 1017.24 1021.10 1044.64	C-H aromatic and C-H in plane bending	[8, 9]
828.55 835.65 839.12 841.54 839.59	These peaks reveal C-O-O stretching. Nitrate ion – inorganic ions stretching/vibration	[8, 9]
450.40 447.43 455.98 462.07 471.14	These represent the Zn-O and Ce-O	[4, 10-12]

4. CONCLUSIONS

In this work, the cerium doped zinc oxide materials have been synthesized using a simple hydrothermal method in ambient temperature. The obtained powder form of all samples was subjected to functional group, morphological and thermal studies. The resulting zinc-cerium oxide exhibited good agreement with chemical compositions. All samples were obtained in the range from 150 nm to 60 nm. The thermal stability and weight percentage loss of zinc oxide was 15 % and reduced to 5 % by doping cerium. Therefore, we strongly recommend this method and all synthesized potential nanosamples for applications in the field of photocatalysis, dye degradation and especially for antimicrobial activity.

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Виготовлення та інтерпретація композиту цинку-церію: структурні та теплові дослідження

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Композити оксиду цинку та оксиду цинку-церію (ZC) були синтезовані варіюючи співвідношення цинку (Zn) та церію (Ce) для отримання різних сполук $Zn_{1-x}Ce_xO_2$ за допомогою гідротермального методу. Склад зразків змінювався з x = 0,0; 0,05; 0,1; 0,3 та 0,5 для отримання сполук, названих відповідно ZC-1, ZC-2, ZC-3, ZC-4 і ZC-5. Для розуміння впливу церію на оксид цинку всі зразки характеризувалися FT-IR, SEM-EDX та TGA-DSC. Ефективне додавання церію до цинку підтверджено FT-IR та EDX. Всі зразки були отримані з різними розмірами частинок. Спочатку зразок ZC-1 мав частинки у формі стрижнів, а з додаванням церію частинки повільно набували квазісферичну форму зі зменшеними розмірами від 150 нм до 60 нм. У результаті термічних досліджень, оксид цинку, легований церієм, виявив кращу стабільність, ніж нелегований оксид цинку. Детальний аналіз властивостей показує, що ці композити можуть бути потенційними кандидатами для біологічних застосувань, а також вони можуть бути перспективними для каталізу та деградації барвника.

Ключові слова: Композит, Функціональна група, Гідротермальний, SEM-EDX, Оксид цинку-церію.