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FABRICATION OF MULTIFUNCTIONAL $Zn^{2+}_{x}Fe^{2+}_{1-x}Ce^{3+}_{y}Fe^{3+}_{2-y}O_4$ FERRITE@GRAPHENE OXIDE@TITANIA AND STUDIES OF CYCLIC VOLTAMMETER, ANTIBACTERIAL, ANTIFUNGAL, AND ANTIOXIDANT ACTIVITY

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ABSTRACT

Zinc-Cerium-Ferrite $Zn^{2+}_{x}Fe^{2+}_{1-x}Ce^{3+}_{y}Fe^{3+}_{2-y}O_4$@Graphene oxide@Titania nano-composite prepared at different ratios exhibit many better properties and improve their structural properties. The Nano-particles of ferrite $Zn^{2+}_{x}Fe^{2+}_{1-x}Ce^{3+}_{y}Fe^{3+}_{2-y}O_4$ Spinal ($0\leq x$ & $y \geq 2$) (x=0,0.2,0.4,0.6,0.8,1 and y=1,0.8,0.6,0.4,0.2,0) powder were synthesized by substitution of A- and B- sites in a sol-gel method the multi-metallic complex precursor route using citrate. The obtained powders calcinated at 800 ºC for 4 hours. The Modified Hummer process was used to create the Graphene oxide layer by solvothermal hydrolysis and powders obtained on calcinations at 600 º c for 2 hours. Again, the second coating of Titania was prepared by the solvothermal method of the obtained powders calcinated at 600 ºC for 2 hours. The result shows Zinc-Cerium-Ferrite@Grapheneoxide@Titania on various ratios to obtain microstructure, crystallite sizes obtained in the range of 25-52 nm, and good cyclic voltammeter stability 250 cycles, antibacterial, Antifungal, and Antioxidant activity.

Keywords: Sol-Gel Method, Graphene Oxide, Titania Nanoparticles, Antibacterial Activity, Antifungal Activity, Antioxidant Activity, Cyclic Voltammeter Studies.

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INTRODUCTION

Nanotechnology material with appealing antibacterial, antifungal, and antioxidant properties can create novel therapeutic goods and potent therapies. Zinc is a less toxic, inexpensive metal, and cerium is an excellent anti-bacterial agent with low toxicity. Various metal oxide-based Nano-materials have been integrated into antibacterial applications and achieved excellent performance. Zinc-cerium-Ferrite@graphene oxide@Titania-based nanomaterials have received good attention in environmental performance [1-2]. The selection of the sol-gel method, synthesis on $Zn^{2+}_{x}Fe^{2+}_{1-x}Ce^{3+}_{y}Fe^{3+}_{2-y}O_4$ Spinal ($0\leq x$ & $y \geq 2$) (x=0,0.2,0.4,0.6,0.8,1 and y=1,0.8,0.6,0.4,0.2,0) doping at various ratio synthesized and calcinated at 800 º c.[3] Graphene oxide is used in Nanomaterial's research because of its excellent thermal and electrical properties.[4] In this paper, the Graphene oxide (GO) preparation method used by the modified Hummer method because of its promising good water solubility and low toxicity is documented in the literature survey.[5-6] The graphene oxide coating makes use of its multifunctional features.[7-8] TiO_2 is called "Titania." TiO_2 is a nontoxic compound with various applications, including antibacterial activity. This paper uses the second coating of Titanium dioxide (TiO_2) because it's sound absorbent and environmentally friendly.[9]

EXPERIMENTAL

Material and Methods

Zinc chloride dihydrate ($ZnCl_2.2H_2O$), Iron chloride anhydrous ($FeCl_3$), Citric acid anhydrous ($C_6H_8O_7$), Millipore water, Potassium permanganate, Hydrogen peroxide 30% solution, titanium isopropoxide [TTIP] from Merck. Cerium chloride pent hydrate ($CeCl_3.10H_2O$), ferrous chloride tetrahydrate ($FeCl_2.4H_2O$) from Loba, and Ammonia 25% aqueous solution from Aura. Fine graphite powder from Loba, Sulphuric acid, Methanol from S.D. Finar.

Synthesis of Zinc Cerium Ferrite Nanoparticle by Sol-Gel Method (Magnetic Core)

$Zn^{2+}_{x}Fe^{2+}_{1-x}Ce^{3+}_{y}Fe^{3+}_{2-y}O_4$ Spinal ($0\leq x$ & $y \geq 2$) (x=0,0.2,0.4,0.6,0.8,1 and y=1,0.8,0.6,0.4,0.2,0) the Sol-gel process was used to make powder for the use of metal chlorides. The citric acid and metal chlorides were

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dissolved into Millipore water. The homogeneous distribution of the metal ion's continuous stirring and citric acid as a chelating agent. The pH value 7 at keep up by drop-wise ammonia solution was added. To form the sol-gel, to heat, increase the temperature to 80 ºC on a hot plate to continuously stir on condensate to form a xerogel. The increased temperature of 100 ºC is required to produce ferrite powders. The obtained powder was calcinated for 4 hr at 800 ºC to improve the crystallinity. These samples are denoted symbols (ZC1 to ZC6).

Synthesis of Graphene Oxide Coated Zinc Cerium Ferrite Nanoparticle by Solvothermal Method [$Zn^{2+}_xFe^{2+}_{1-x}Ce^{3+}_yFe^{3+}_{2-y}O_4$@GO] (Core/Shell)

The Modified Hummer technique uses synthetic graphene oxide. Take 20 g of Graphite powder to add with concentrated sulphuric acid (H_2SO_4) (500 ml) to mix in a breaker at 0 ºC to set the ice bath with continuous stirring to add 60 g of $KMnO_4$ to maintain the heat of the mixture below 15 ºC. The continuously stirred and a raised temperature of 35 ºC solution changed to a Brown color; the solution was added to dilute with 1.5 liters of Millipore water to maintain below 90 ºC temperature. After stirring at 100 ºC for 30 min, 20 percent of H_2O_2 was added. The solution eliminated any remaining metal ions and was washed with Millipore Water, Acetone, and 10 percent Hydrochloric acid added to the solution. Graphene oxide products filter and dry in a 90ºC oven for 24 hr. For further purification, take 1 g of a graphene oxide powder, add 250 ml Millipore water to the solution, and set up with ultrasonication for 30 ºC and 2 hr. To obtain graphene oxide powder, filter it and dry it in an oven for 24 hr at 90 ºC temperature. The synthesized Zinc Cerium ferrite@graphene oxide coating is prepared by taking a beaker to add 1g of graphene oxide and 1g of Zinc Cerium ferrite powder to add 250 ml of Millipore water to set ultrasonicated for 100 min at 30 ºC temperature, after continuous stirred for 5 hr at 90 ºC temperature, to increase the temperature up to 100 ºC at the removal of the solvent, to obtained graphene oxide powder. The powder sample calcinated at 600 ºC for 2 hr to obtain coated the Zinc Cerium ferrite@ graphene oxide powder is denoted as a symbol (ZG1 to ZG6).

Synthesis of Titanium Dioxide Coated Magnetic Nanoparticle@GO by Solvothermal Method [$Zn^{2+}_xFe^{2+}_{1-x}Ce^{3+}_yFe^{3+}_{2-y}O_4$@GO@$TiO_2$] (Core/Shell/Shell)

Furthermore, to synthesize a colloidal TiO_2 solution, 2mltitanium isopropoxide (TTIP) and 250 ml methanol were mixed with 1g Zinc-cerium@graphene oxide powder by using a setup ultrasonicated for 30ºC for 100 min; after continuous stirring, the set temperature in 60ºC for 5 hr. The increased temperature at 80ºC to remove solvent to obtain powder and set up the temperature on calcinated at 600 ºC for 2 hr to obtain coated Zinc Cerium ferrite@grapheneoxide@Titanic powder is denoted as a symbol (ZGT1 to ZGT6).[10]

Characterization Techniques

Structural analysis using a Philips X-ray diffract meter with Cu as the anode material. Microstructure studies were conducted using HITACHI-S3400 Variable Pressure SEM by spreading the sample over a thoroughly cleaned microscopic slide after applying vacuum grease. The Energy Dispersive X-ray analysis (EDAX) uses a super dryer-II model. The UV-VIS spectroscopy Optical Absorption Spectra range 200-1200 nm, for spectrophotometer JASCO UV Vis NIR. The antibacterial activity of ferrite Nano powders was tested against Escherichia coli and Staphylococcus aureus using mueller-hinton Agar plates. Antifungal activity to prepare use yeast in MHA with glucose-supplemented agar plates. For Antioxidant activity, DPPH at different concentrations dissolved in methanol solution was added to the tubes with water and incubated at 25 ºC for 20 minutes. Using a Shimadzu UV 1800 spectrophotometer, the absorbance value was measured at 510 nm. Equipment was using cyclic voltammeter model CHI650C instrument. Using an Alpha Bruker FT-IR with a resolution of 2 cm^{-1}, infrared spectra were captured.

RESULTS AND DISCUSSION

X-ray Diffraction Analysis

The room temperature powder XRD patterns of ZC1-ZC6, ZG1-ZG6, and ZGT1-ZGT6 were illustrated in Fig.-1 (a-c). In Zn-Ce-Fe oxide (ZC1-ZC6) samples, all diffraction planes agreed with the α-Fe_2O_3 hematite

phase (rhombohedral) with JCPDS card No. 72-0469. Graphene oxide was added with ZC1-ZC6 (Fig.-1(b)) oxide samples, indicating a solid peak at 26.47º corresponds to the (002) plane in ZG1-ZG6 samples with a hexagonal phase. For ZGT1-ZGT6 (Fig.-1(c)), the presence of peaks at 2θ = 25.3º, 37.8º, 48.1º, 53.9º and 55.06º correspond to (101), (004), (200), (105) and (211) planes of Anatase TiO_2 [JCPDS Card no 21-1272] along with the peaks of Zn-Ce-Fe oxides (ZC1-ZC6) and Graphene oxide (ZG1-ZG6) confirmed the formation of the composite. Using the Scherer formula, crystal sizes were determined from the full width at half maximum (FWHM) and 2 Theta highest intensity peak value using the Scherer formula; Crystallite size is mentioned in Table-1. The crystallite size was increased by adding Titania to graphene oxide-coated ferrite samples. The samples' crystallite sizes are shown in Fig.-1 (d).[11-13]

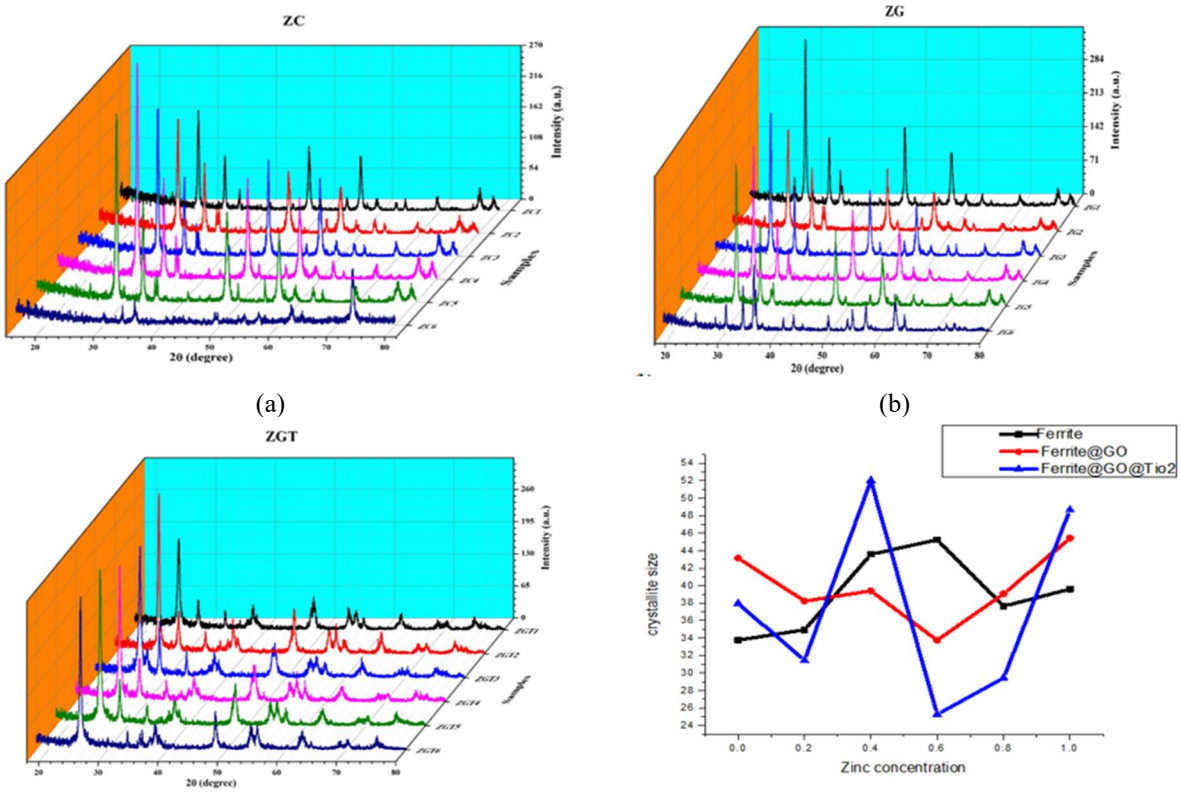


Fig.-1: XRD Patterns of (a) $Zn^{2+}_xFe^{2+}_{1-x}Ce^{3+}_yFe^{3+}_{2-y}O_4$ (b) $Zn^{2+}_xFe^{2+}_{1-x}Ce^{3+}_yFe^{3+}_{2-y}O_4$@GO, (c) $Zn^{2+}_xFe^{2+}_{1-x}Ce^{3+}_yFe^{3+}_{2-y}O_4$@GO@Titania (d) Variation of Crystallite Size with Zinc Concentration in Zinc-Cerium Ferrite ZC1-ZC6, ZG1-ZG6, ZGT1-ZGT6

Table-1: The Prepared Sample Calculated Crystal Size Using the Scherer Formula

Sample code	Ferrite composition	Crystallite size Dp (nm)
ZC1	$FeCeFeO_4$	33.77
ZC2	$Zn_{0.2}Fe_{0.8}Ce_{0.8}Fe_{1.2}O_4$	34.93
ZC3	$Zn_{0.4}Fe_{0.6}Ce_{0.6}Fe_{1.4}O_4$	43.58
ZC4	$Zn_{0.6}Fe_{0.4}Ce_{0.4}Fe_{1.6}O_4$	45.23
ZC5	$Zn_{0.8}Fe_{0.2}Ce_{0.2}Fe_{1.8}O_4$	37.65
ZC6	$Zn\ Fe_2O_4$	39.59
ZG1	$FeCeFeO_4$@GO	43.14
ZG2	$Zn_{0.2}Fe_{0.8}Ce_{0.8}Fe_{1.2}O_4$@GO	38.22
ZG3	$Zn_{0.4}Fe_{0.6}Ce_{0.6}Fe_{1.4}O_4$@GO	39.40
ZG4	$Zn_{0.6}Fe_{0.4}Ce_{0.4}Fe_{1.6}O_4$@GO	33.74
ZG5	$Zn_{0.8}Fe_{0.2}Ce_{0.2}Fe_{1.8}O_4$@GO	39.07
ZG6	$Zn\ Fe_2O_4$@GO	45.41

ZGT1	$FeCeFeO_4$@GO@TiO_2	37.96
ZGT2	$Zn_{0.2}Fe_{0.8}Ce_{0.8}Fe_{1.2}O_4$@GO@$TiO_2$	31.44
ZGT3	$Zn_{0.4}Fe_{0.6}Ce_{0.6}Fe_{1.4}O_4$@GO@$TiO_2$	52.02
ZGT4	$Zn_{0.6}Fe_{0.4}Ce_{0.4}Fe_{1.6}O_4$@GO@$TiO_2$	25.25
ZGT5	$Zn_{0.8}Fe_{0.2}Ce_{0.2}Fe_{1.8}O_4$@GO@$TiO_2$	29.44
ZGT6	Zn Fe_2O_4@GO@TiO_2	48.65

SEM Analysis

The SEM analysis micrographs of the prepared $Zn^{2+}_xFe^{2+}_{1-x}Ce^{3+}_yFe^{3+}_{2-y}O_4$ ferrite@GO@Titania ferrite powders particles are presented microstructure. These SEM images show Zn-Ce ferrite@GO@TiO_2 exhibits irregular particles, Spherical shape, and agglomeration particles from large clusters.[14]

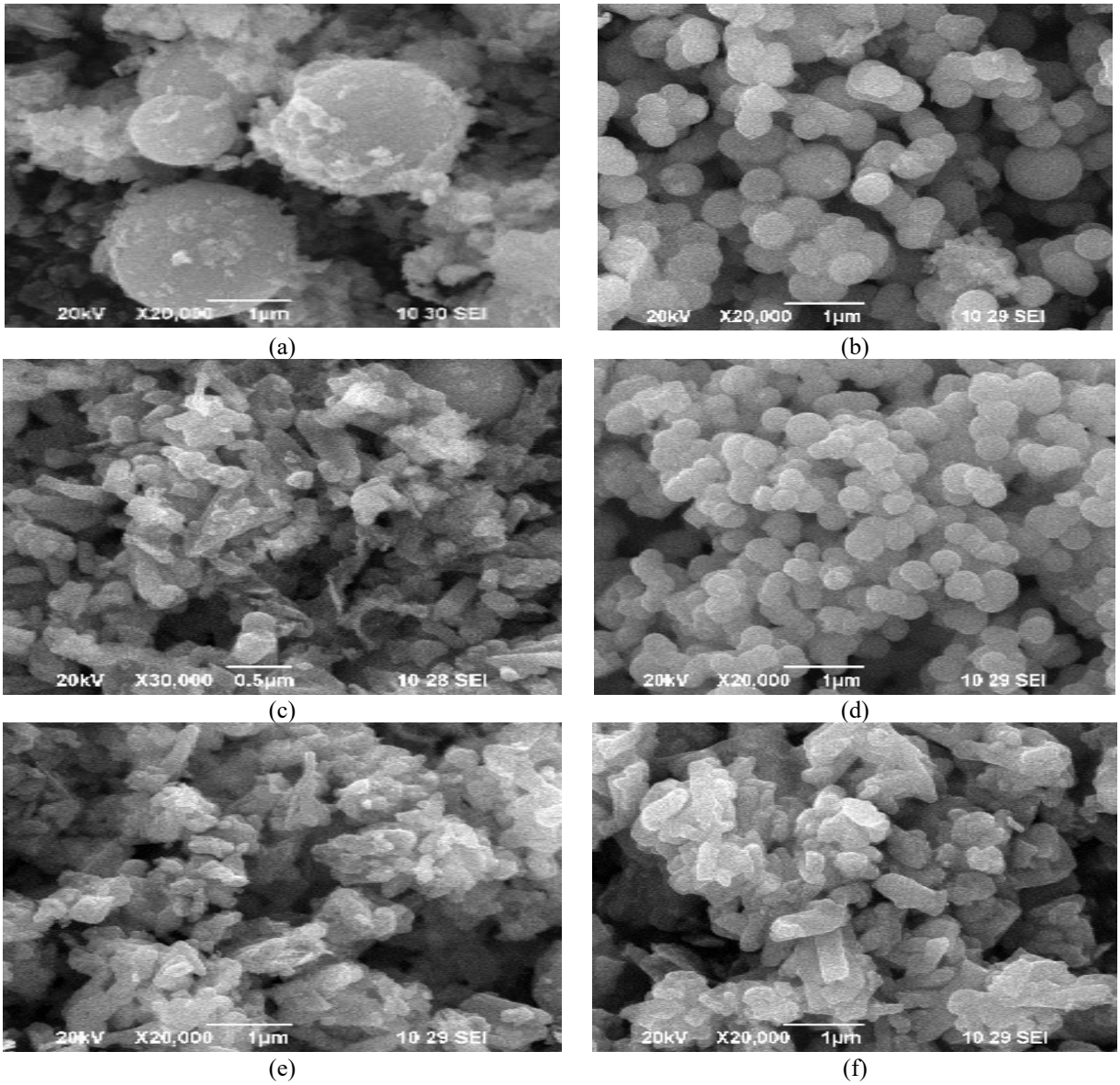


Fig.-2: The SEM Images on Synthesized Zinc-Cerium Ferrite (a-f) ZGT1-ZGT6

EDX Analysis

The chemical composition of Zn-Ce ferrite @ GO@TiO_2 ferrite is confirmed by EDX analysis to be stoichiometric, and the percentage of the elements is displayed in Table-2. Analysis of the existence of elements of Zn, Ce, Fe, Ti, C, O. EDX was performed and detected the element and their mass ratios corresponding to $Zn^{2+}_xFe^{2+}_{1-x}Ce^{3+}_yFe^{3+}_{2-y}O_4$@GO@$TiO_2$ ferrite chemical composition.[15]

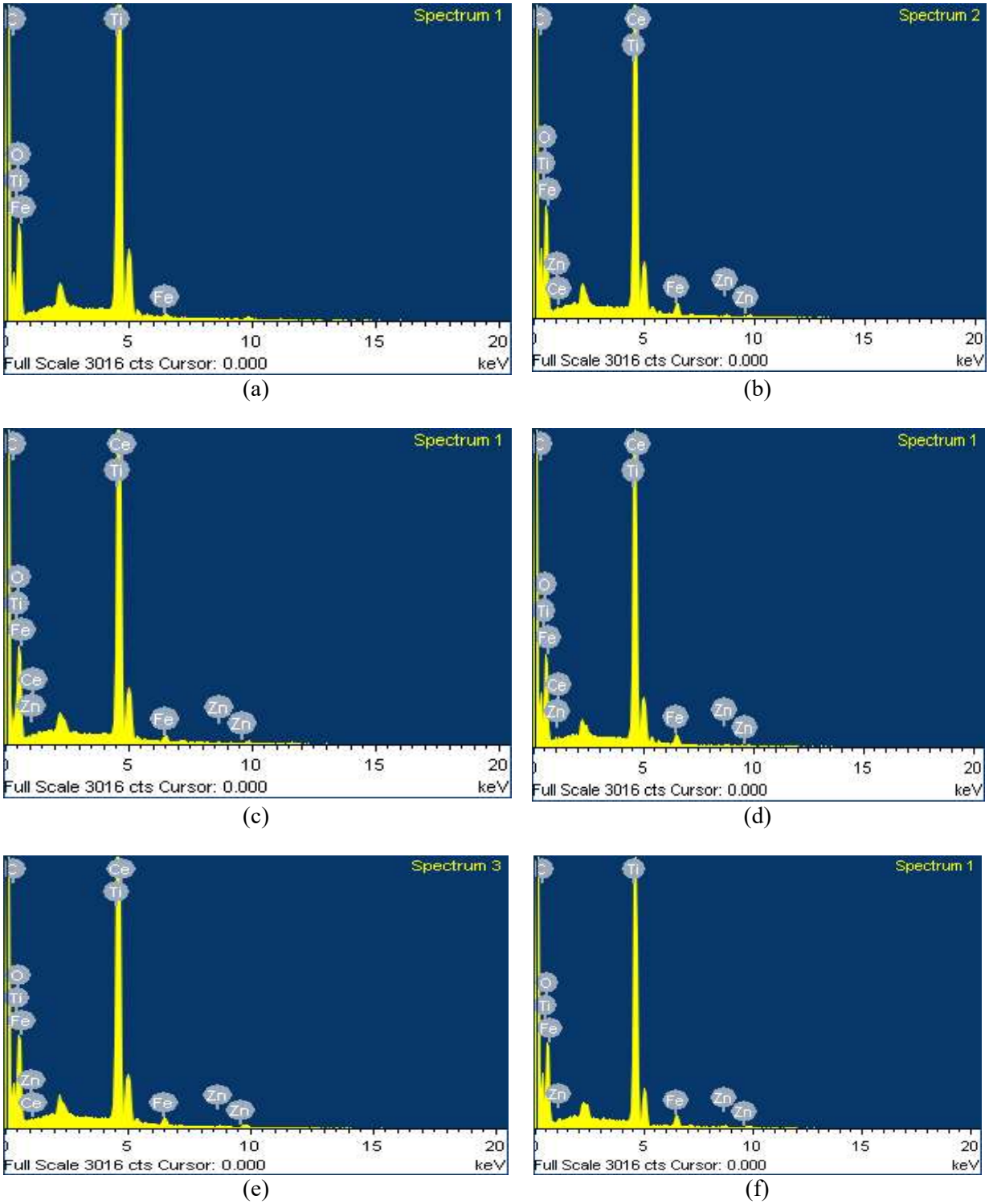


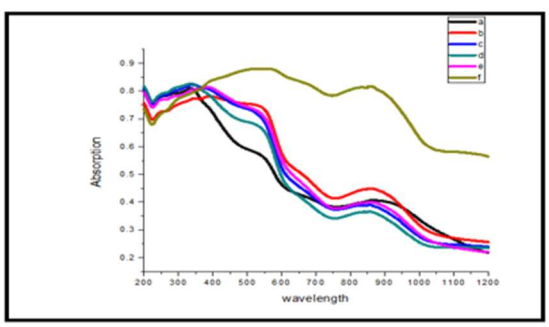
Fig.-3: EDX Images of (a-f) ZGT1-ZGT6

UV-Vis Spectroscopy

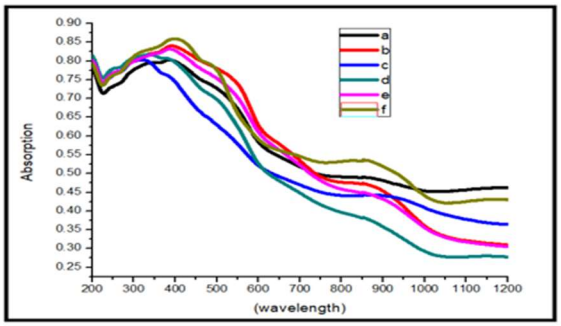
The UV-Vis Spectroscopy analysis to assess the Optical properties of synthesized zinc cerium ferrite Nano-powders and the coating of Graphene oxide, Titania, can be seen in Fig.-4. The zinc-Cerium-Iron, Titania elements, and graphene show more absorption in the UV region and low absorption in the visible region.[16]

Table-2: The Zinc-Cerium Ferrite is the Elemental Composition of Synthesized ZGT1-ZGT6

Sample Code	Ferrite Composition	Zn (%) Atomic weight	Ce (%) Atomic weight	Fe (%) Atomic weight	C (%) Atomic weight	O (%) Atomic weight	Ti (%) Atomic weight
ZGT1	$FeCeFeO_4$	---	0.20	0.29	17.48	62.94	19.09
ZGT2	$Zn_{0.2}Fe_{0.8}Ce_{0.8}Fe_{1.2}O_4$	0.02	0.20	0.60	24.43	60.69	14.05
ZGT3	$Zn_{0.4}Fe_{0.6}Ce_{0.6}Fe_{1.4}O_4$	0.10	0.05	0.52	8.69	71.98	18.66
ZGT4	$Zn_{0.6}Fe_{0.4}Ce_{0.4}Fe_{1.6}O_4$	0.03	0.22	0.66	23.94	60.59	14.56
ZGT5	$Zn_{0.8}Fe_{0.2}Ce_{0.2}Fe_{1.8}O_4$	0.07	0.18	0.58	18.83	63.40	16.93
ZGT6	$Zn\ Fe_2O_4$	0.20	---	0.71	24.15	60.90	14.04



(a)



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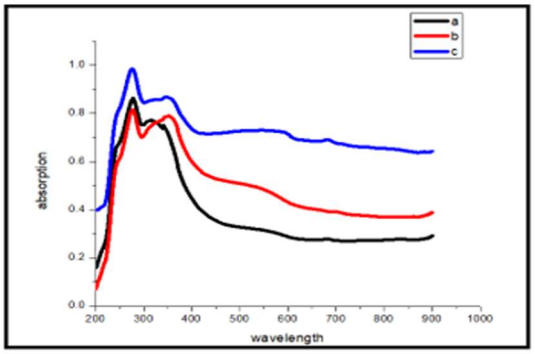


(c)

Fig.-4: The UV-visible spectrum Shows Images of (A) (a-f) ZC1-ZC6. (B) (a-f) ZG1-ZG6. (C) (a-c) ZGT1, ZGT3, ZGT6

Fourier Transform Infrared Spectroscopy (FTIR) Studies

FT-IR spectra of all catalytic material on zinc cerium ferrite@GO@Titania are shown in Fig.-5. The absorption peak values in the 1637 and 3367 cm^{-1} range correspond to the OH groups. The metal cerium, zinc, and iron values were measured at 465, 516, and 653 cm^{-1} range. Peak measurements of Graphene oxide were 1012, 1053, and 2939 cm^{-1}. The Ti-OH bending on stretching mode 1637, 1638 cm^{-1} appears. Carbon residual vibration appears 1400, 2939 cm-1 obtained. The metal oxide range 1012, 1053,1045cm^{-1} is obtained.[17]

Anti-Bacterial Activity

The Zinc cerium ferrite@GO@Titania, analysis of antibacterial activity against Escherichia coli and Staphylococcus aureus is shown in Fig.-6. The various ratio of Zinc Cerium substituted ferrite@GO@Titania was fixed at 1 gram/Litre. The result shows that structure, shape, and chemical composition are crucial in the rate of bacterial death as Escherichia coli bacteria and Staphylococcus aureus bacteria differ in Nature.[18] Tests on antibacterial activity to use pathogens Spread over plates of mueller-hinton agar. Agar is covered with the required amount of drug concentration, and a sterile cork border with a 6 mm diameter is used. At 37°C, the agar on the test plates was incubated for 24 hours as the Activity

against the test Pathogen with Staphylococcus aureus, Escherichia coli. The zone result of Inhibition is expressed in mm to obtain Positive control: Ciproflaxin - 20 µg. ZGT1 shows the highest inhibition against s. aureus among ZGT1-ZGT6 nanocomposite.

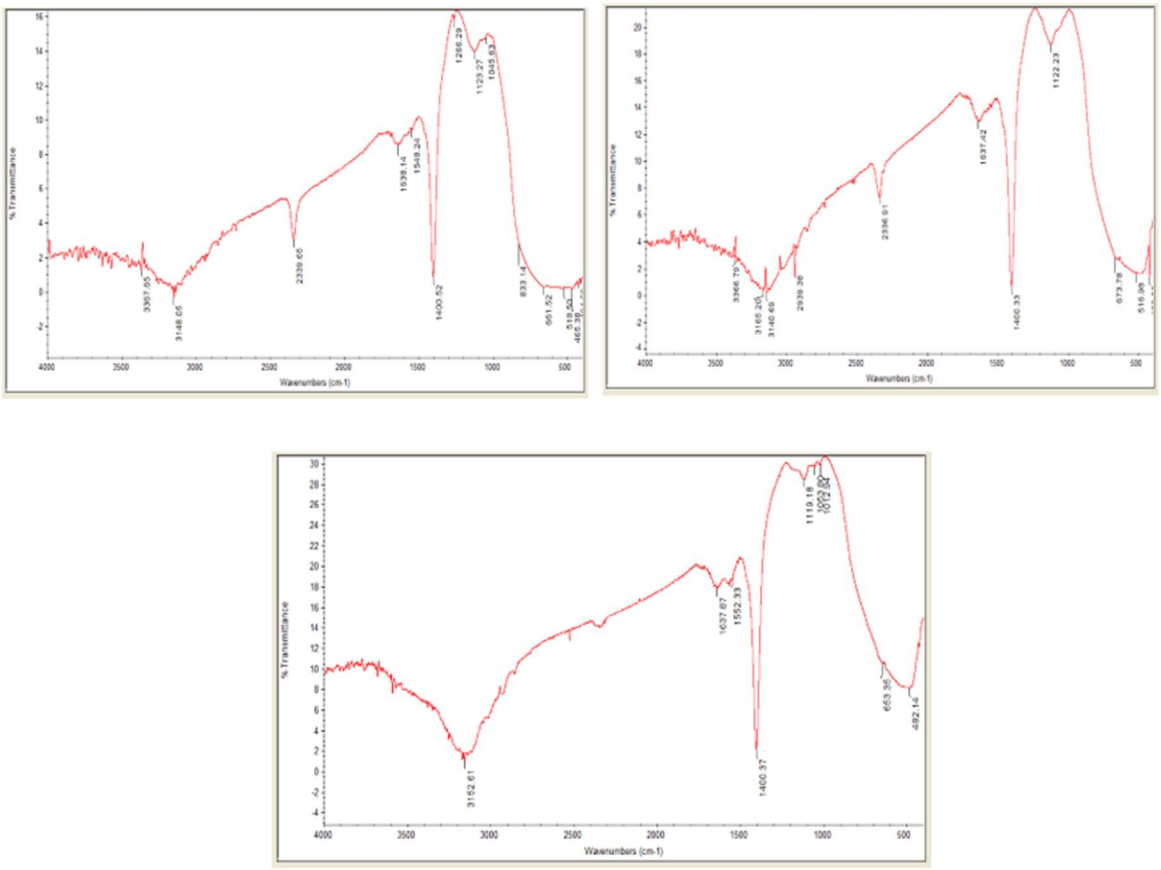


Fig.-5: Fourier Transform Infrared Spectroscopy Study on (a) ZGT1. (b) ZGT3 (c) ZGT, clockwise

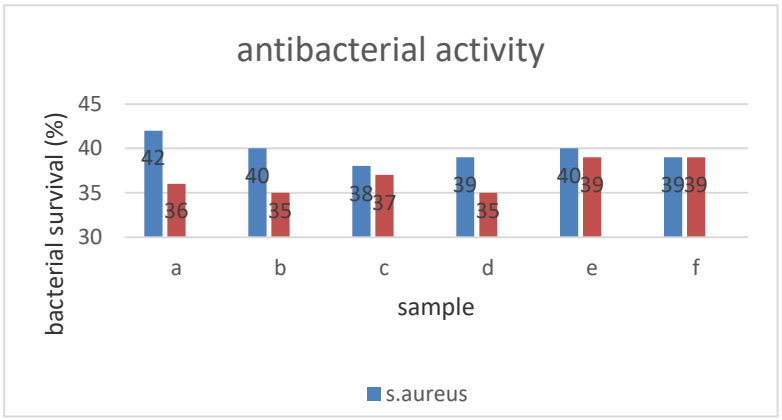
Anti-Fungal Activity

To prepare the sample, adding yeast in Mueller -Hinton Agar (MHA) with glucose-supplemented Agar plates, a sterile cotton swab should ideally be dipped into the corrected suspension within 15 minutes of altering the turbidity of the inoculums suspension. Once the MHA plate has dried, the swab should be turned several times and pressed firmly inside the plate 60-degree distribution two additional times, and the sample, by various ratios using positive Control Amphotericin B, DMSO as a negative control. The Plates were incubated at 35^0 C for 48 hours after being left at room temperature for 30 min to allow for diffusion. The anti-candidal efficacy of zinc cerium ferrite@GO@Titania was Agar-based effective Growth cultures. The nanomaterials were generated at a concentration of 1 mg/mL; the investigated activity used Yeast in the inoculated media. The anti-candidal activity of Candida albicans on ferrite has good antifungal activity, and ZGT3 holds great potential in biomedical applications.[19]

Anti-Oxidant Activity

The DPPH radical scavenging test is used at various sample concentrations as the antioxidant assay. To take 50 µl of 0.659ml on DPPH mixed in Methanol solution, add water to the Tubes that were Incubated at 25 ^{0}C for 20 minutes. The report recorded at 510nm as an absorbance value. The significance of biomaterials has received good attention due to the effect of oxidative stress on solving inflammation, chronic disease, and other problems. Our study shows excellent results for 1,1,-Diphenyl-2-picryhydrazyl free Radical Scavenging method on the antioxidant property shown in figure 8 of new zinc cerium ferrite@GO@TiO_2.[20]

(A)



(B)

Fig.-6: (A) Antibacterial Activity on Images of (a) ZGT1 Use Bacteria Staphylococcus Aureus and Escherichia Coli. (B) Antibacterial Activity Against Escherichia Coli and Staphylococcus Aureus (a-f) ZGT1-ZGT6.

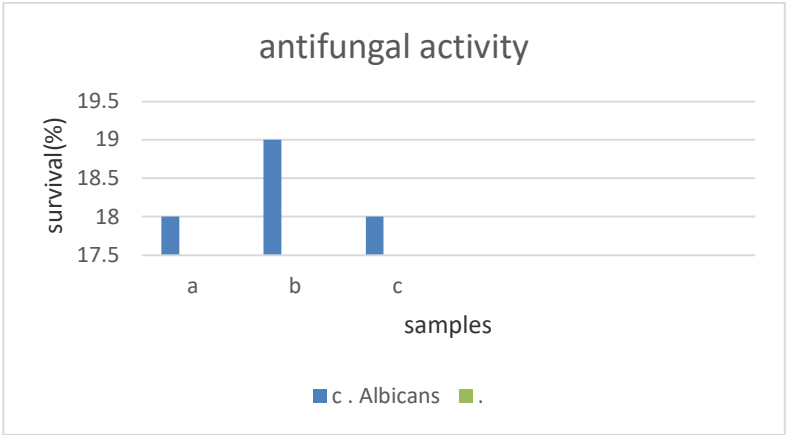
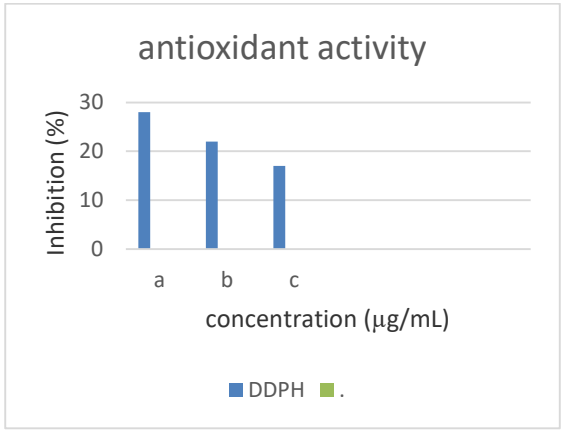


Fig.-7: Antifungal Activity Studyon Images of (a) ZGT1 (b) ZGT3(c) ZGT6

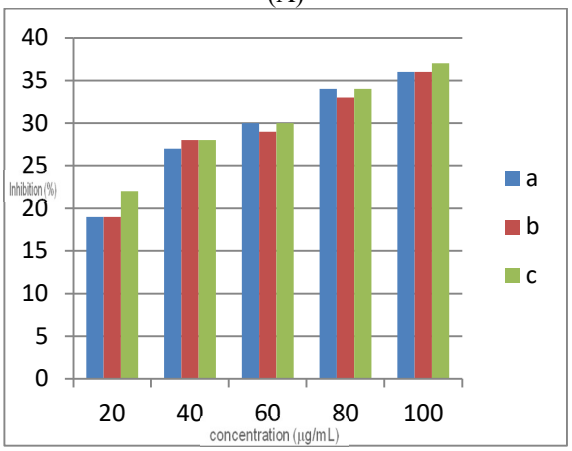
Cyclic Voltammeter Activity

For cyclic voltammetry (CV), chemically deposited ZGT1, ZGT3, and ZGT6 electrodes were employed, and their performance was evaluated using an electrochemical cell containing a working electrode of nanocomposite, a counter electrode of platinum, and a reference electrode of SCE. Specific capacitance is calculated by dividing the dipped electrode's mass by the electrode's area dipped in the electrolyte. Figure-9 depicts the change of voltammetric current for ZGT1, ZGT3, and ZGT6 electrodes at a scan rate of 5

mVs^{-1}. Cyclic Stability is a crucial parameter for assessing a capacitor's longevity, efficiency, and stability. The Cycling measurement of Zinc cerium ferrite@GO@Titania studied CV tests for above 250 cycles at scan rate are shown in Fig.-9.[21]



(A)



(B)

Fig.-8: antioxidant Activity Study on Images (A) Average Antioxidant Activity Value of (a) ZGT1 (b) ZGT3(c) ZGT6. (B) Different Concentration Verses Inhibition of (a) ZGT1 (b) ZGT3(c) ZGT6 Nano-particles by 1,1,-Diphenyl-2-picryhydrazyl Free Radical Scavenging.

Voltammetric currents are observed to grow with scan rate, mimicking the behavior of an ideal capacitor. At a scan rate of 5 mVs^{-1}, the specific capacitance was 366 Fg^{-1}, while interfacial capacitance was measured to be 0.110 Fcm^{-2}. The drop in specific capacitance could be attributed to electrode material loss during cycling. The specific capacitance loss of 9.4% after 250 cycles indicates that the nanocomposite electrode is electrochemically stable. It is hoped that the globular-like nanostructure may find use in other sectors, such as electrochemical sensors and catalysis.

CONCLUSION

Fabrication of Zinc-Cerium-Ferrite nanocomposite was achieved using simple preparation techniques. Powder XRD studies show the formation of zinc cerium-ferrite (ZC1-ZC6) samples; all diffraction planes agreed with the α-Fe_2O_3 hematite phase (rhombohedral). Graphene oxide and Titania coatings were done using modified Hummers' and solvothermal methods. The average crystallite sizes, ranging from 25-52 nm, were obtained. SEM image shows irregularly shaped globular-like morphology. The nanostructure provides a high surface area, which is helpful for better applications such as biological and electrochemical. The highest inhibition against S. aureus was shown by ZGT1 of all samples prepared.

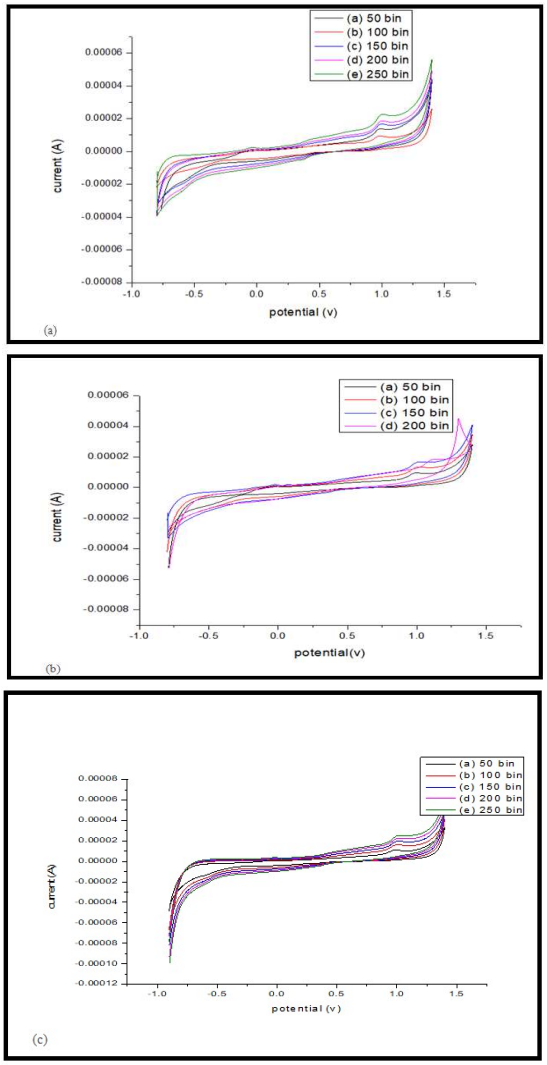


Fig.-9: Cyclic Voltammeter Analysis Images (a) ZGT1 (b) ZGT3(c) ZGT6at Different Current Verses Potential

ZGT3 exhibited good antifungal activity using Candida albicans. ZGT1-ZGT6 shows promising results on antioxidant activity compared to simple ferrites and other GO and Titania-coated ferrites. We suggested a new Zinc-Cerium-Ferrite@GO@TiO_2 nanocomposite with improved electrochemical properties from the effect of highly surfaced nanostructures with minimal loss after 250 cycles and enhanced specific capacitance.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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