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*Annona Muricata*Inspired Synthesis of CeO_2 Nanoparticles and their Antimicrobial Activity

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Abstract

CeO_2 nanoparticles (NPs) have shown promising results as therapeutic agents in biology and medical sciences. In this study, CeO_2-NPshave been synthesized through green synthetic approach by applying natural matrices(fruit of *Annona muricata)* as stabilizing agents in order to prepare biocompatible CeO_2-NPs, thereby solving the challenges regarding safety, and providing the appropriate properties for their effective use in biomedical field.The synthesized CeO_2 nanoparticles are characterized by XRD, FTIR, UV-DRS, FESEM, EDAX, PL and antimicrobial analysis. UV-DRS analysis shows that formation of CeO_2 nanoparticles with maximum absorption at 318 nm.The antibacterial activities of synthesized CeO_2 NPs were carried out against the human pathogenic microorganism by agar-well diffusion method.

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Keywords: Biosynthesis;CeO_2;UV-DRS;PL and Antimicrobial activity;

1. Introduction

Green nanotechnology is a mushrooming area of research in the scientific world. The green approach methodsare largely unexplored and under-exploited to our knowledge. There are several biological techniques are available, the use of fruit extract for the synthesis of CeO_2 -NPsis potentially advantageous over microorganisms or plant extracts

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mediated synthesis due to the simplicity, less bio-hazard and complicated process of maintaining cell culture[1-6]. Moreover, the use of fruit extract for the synthesis of CeO_2-NPs is the new facelift towards green nanotechnology, because of its eco-friendly, economical and rapid approach.

1.2 Preparation of Extracts

The fruit of annona muricata (*Soursop or Mulatha*) was taken. Skin from the fruit was peeled off and cut into small pieces. The seeds were removed and put into a sterile beaker. It was stirred well to get the fruit extract.

1.3 Synthesis of CeO_2 -NPs using fruit extract

0.5 M of Cerium (III) nitrate hexahydrate was taken into a beaker and 50 mL of distilled water was added to it. This solution was stirred using a magnetic stirrer until a homogeneous solution was formed. To this aqueous solution 50 mL of fruit extract was added. The reaction mixture was stirred for 30 minutes continuously. The solution was heated on a hot plate at 80°C till the supernant got evaporated. The obtained product was pounded into fine powder and calcinated at 600 °C for 2 h.

2. Results and discussion

2.1 X-Ray diffraction

Fig.1 shows the XRD pattern of as prepared CeO_2 -NPswith 50 mL of fruit extract (annona muricata). The structure is cubic (facecentered), cyrstalline in nature and the diffraction data are in good agreement with the JCPDS file No: 81-0792.The peaks are very broad, polycrystalline in nature and observed at (111), (200), (220), (311), (400), (331) corresponding to 2θ = 28.50°, 32.88°, 47.33°, 56.34°, 69.46°, 76.72°.

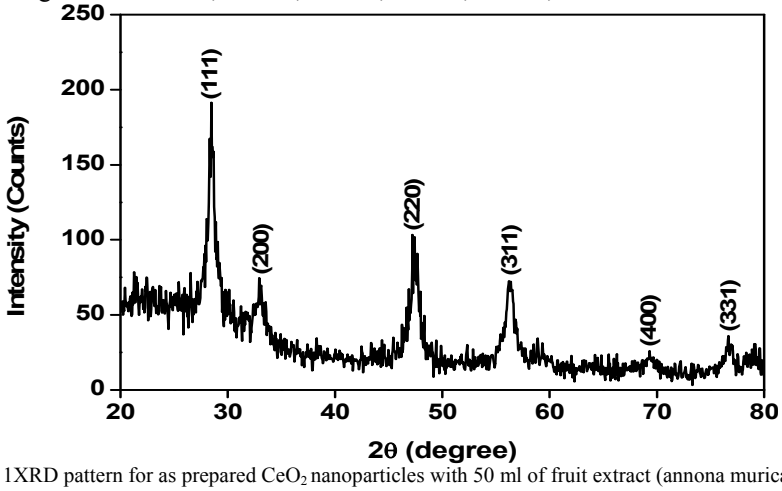

Fig. 1XRD pattern for as prepared CeO_2 nanoparticles with 50 ml of fruit extract (annona muricata)

The d-spacing values obtained from XRD data of as-prepared for CeO_2 -NPswith 50 ml of fruit extract (annona muricata) before calcination are identified with the JCPDS file No: 81-0792 and theirh, k and l values and relative intensity values were tabulated in Table 1.

Table 1. d-spacing values for as prepared CeO_2 nanoparticles using fruit extract (annona muricata)

S. No.	2θ(degree)	d-spacing (Å)		(h k l)	Relative intensity(%)
		Observed	JCPDS		
1	28.5069	3.1312	3.1248	(1 1 1)	100.00
2	32.8816	2.7239	2.7062	(2 0 0)	23.27
3	47.3347	1.9205	1.9135	(2 2 0)	58.43
4	56.3415	1.6329	1.6319	(3 1 1)	42.84
5	69.4600	1.3532	1.3531	(4 0 0)	7.11
6	76.7252	1.2421	1.2416	(3 3 1)	15.46

Figure 2 shows the XRD pattern of CeO_2-NPsusing fruit extract (annona muricata) calcinated at 600°C. The peaks are very broad, polycrystalline in nature and observed at (111), (200), (220), (311), (222), (400), (331) corresponding to 2θ = 28.36°, 32.93°, 47.36°, 56.30°, 69.43°, 76.67°, 79.04°.

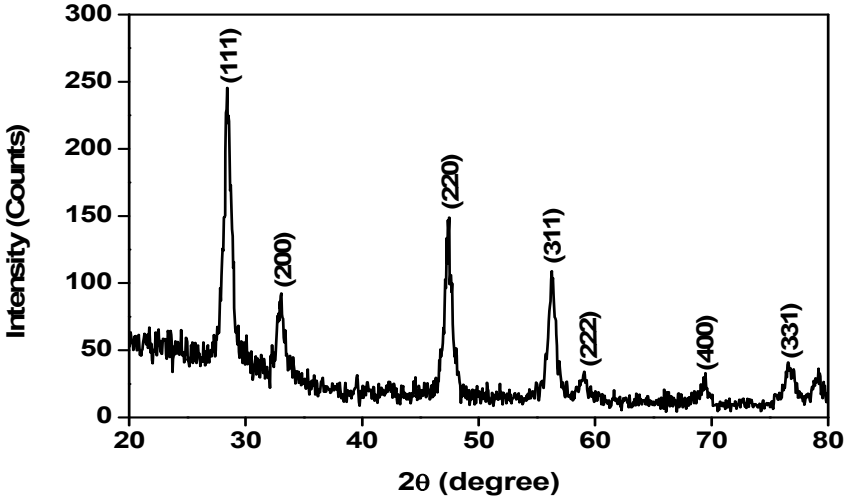

Fig. 2 XRD pattern for CeO_2 nanoparticles with 50 ml of fruit extract (annona muricata) calcinated at 600ºC

The d-spacing values obtained from XRD data of CeO_2 -NPswith 50 ml of fruit extract (annona muricata) calcinated at 600 °C are identified with the JCPDS file No: 81-0792and their respective h k l values and relative intensity values were tabulated in Table 2.

Table 2. d-spacing values for CeO_2 nanoparticles using fruit extract (annona muricata) calcinated at 600 ºC

S. No.	2θ(degree)	d-spacing (Å)		(h k l)	Relative intensity (%)
		Observed	JCPDS		
1	28.3629	3.14676	3.1248	(1 1 1)	100.00
2	32.9377	2.71941	2.7062	(2 0 0)	27.32
3	47.3691	1.91918	1.9135	(2 2 0)	63.37
4	56.3086	1.63387	1.6319	(3 1 1)	47.16
5	69.4391	1.35357	1.3531	(4 0 0)	8.15
6	76.6775	1.24283	1.2416	(3 3 1)	14.91
7	79.0463	1.21142	1.2102	(4 2 0)	10.47

2.2 Ultraviolet - Diffuse Reflectance spectroscopy

The absorbance spectrum of as-prepared CeO_2 -NPs with 50 mL of fruit extract (annona muricata) with a maximum of 0.9 at 320 nm is shown in Fig.3 (a) calcinations at 600 °C with a maximum of 0.9 at 318 nm is shown in Fig.3 (b).

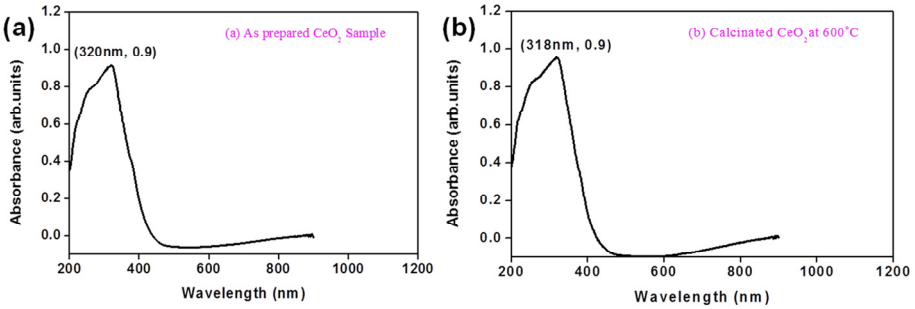

Fig. 3 Optical absorbance spectra for as preparedCeO_2using fruit extract (a) as prepared and (b) calcinated at 600 ºC

Ttau'c plot for CeO_2 -NPswith 50 mL of fruit extract (annona muricata) before and after calcinations with $(\alpha h\nu)^2$ versus photon energy (hν) with band gap values of 3.35 eV and 3.31 eV were calculated as shown in Fig.4(a) and Fig.4(b) respectively. The observed band gap values are found to decrease, which may be due to the calcinations of sample.

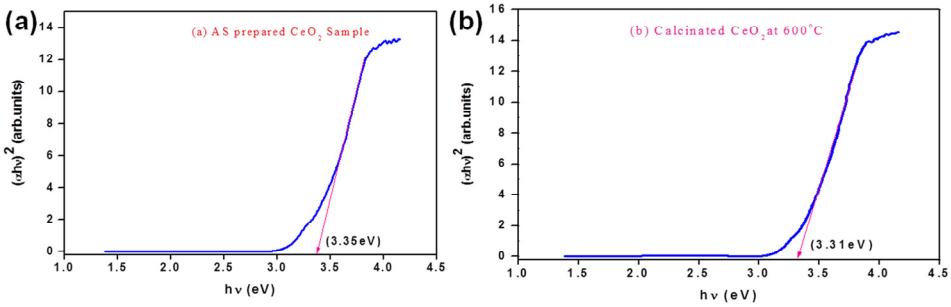

Fig. 4(a) Tauc plot for CeO_2 with 50 ml offruit extract before calcinations and (b) calcined at 600 ºC

2.3 FESEM analysis

Figure 5 represents FESEM images of CeO_2-NPswith 50 mL of fruit extract (annona muricata) with different magnifications. It shows that all samples were nanofibre structures.

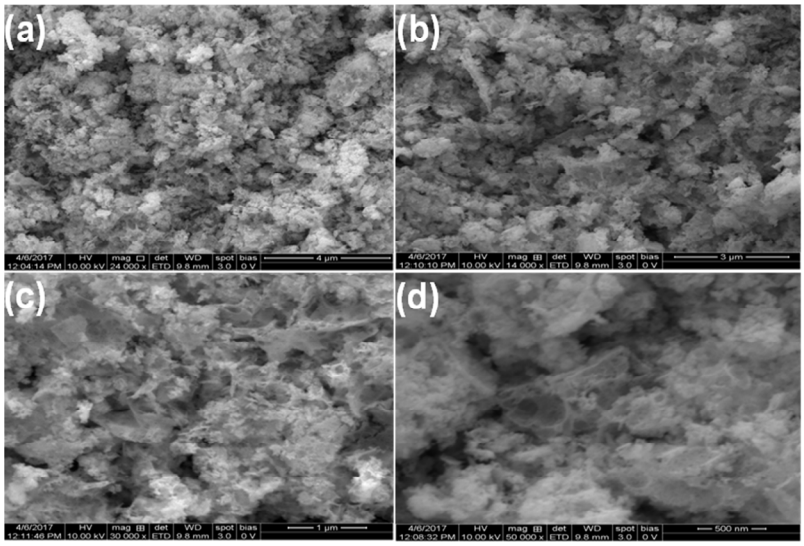

Fig. 5 FESEM image of CeO_2 nanoparticles calcinated at 600 °C with a magnificationat a) 4 µm, b) 3 µm, c) 1 µm, d) 500 nm

2.4 EDAX Analysis

The chemical compositions of as prepared CeO_2-NPs were investigated by EDX analysis as shown in Fig. 6. It shows that presence of Cerium (Ce) and Oxygen (O) as the main elements. There are noimpurities presence in the samples.

2.5 Photoluminescence Spectral analysis

Figure 7 shows the photoluminescence (PL) emission and maximum excitation peak of wavelength 409 nm for CeO_2-NPs with 50 mL of fruit extract (annona muricata) calcinated at 600 ºC.

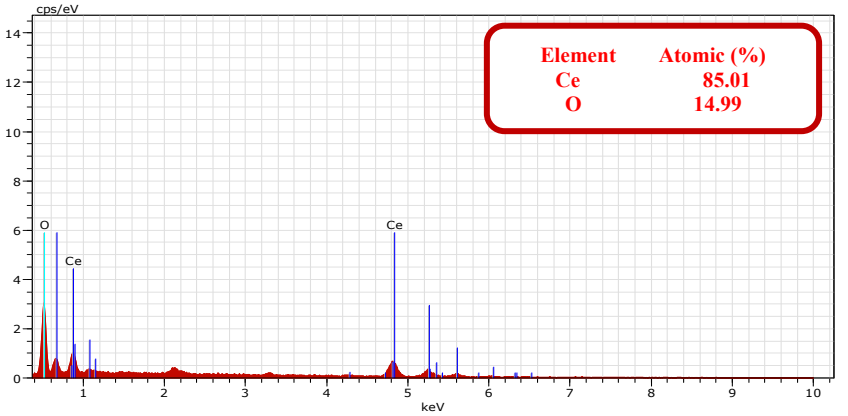

Fig. 6 EDAX spectra for CeO_2 nanoparticles with 50 ml of fruit extract calcinated at 600 °C

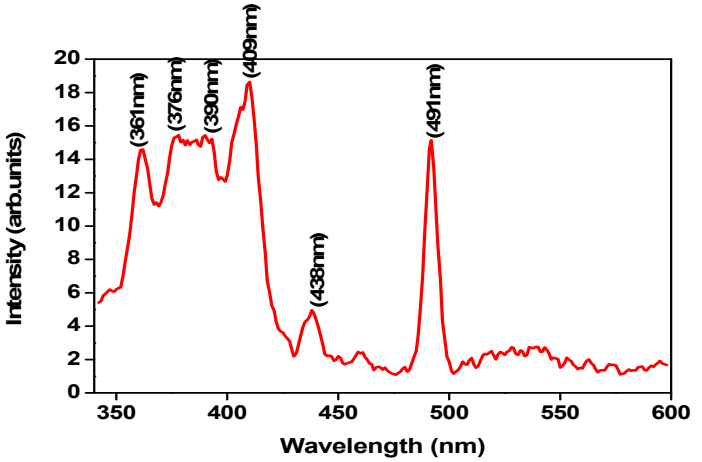

Fig. 7 PL excitation spectrum of CeO_2 with 50 ml of fruit extracts, calcinated at 600 ºC

2.6 FTIR analysis

The FTIR spectrum of CeO_2 -NPswith 50 mL of fruit extract asprepared and after calcinations are shown in Figure8(a) and Figure 8(b). The vibrational bands at the region at 2970 cm^{-1} and 2800 cm^{-1} in Figure 8(a) are narrowed in Figure 8(b). In Figure 8(b), some new bands are appeared in the region from 1500 cm^{-1} to 750 cm^{-1}. Both the spectrum confirmed that the chemical changes have been occurred during calcinations. During the calcinations, particle sizes werealso found to be decreased.

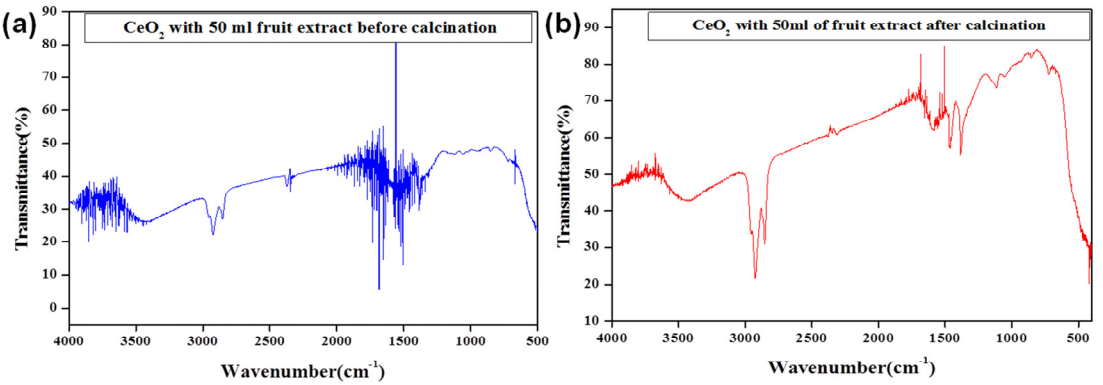

Fig. 8(a) FTIR spectrumof theCeO_2 nanoparticles (a) as preparedand (b) calcinated at 600° C

2.7 Antimicrobial activities

Antibacterial activities of the biosynthesized CeO_2-NPsonGram-positive(Enterococcusfaecalis, staphylococcus aureus) and Gram-negative (Klebsiella pneumonia, Escherichia coli) bacterial strains were studied. Figure 9 shows the observed mean diameter inhibition zones for pure and bio synthesized CeO_2 NPs.The size of the zone of inhibition observed each disc loaded with test samples, indicating the antibacterial activity of samples.

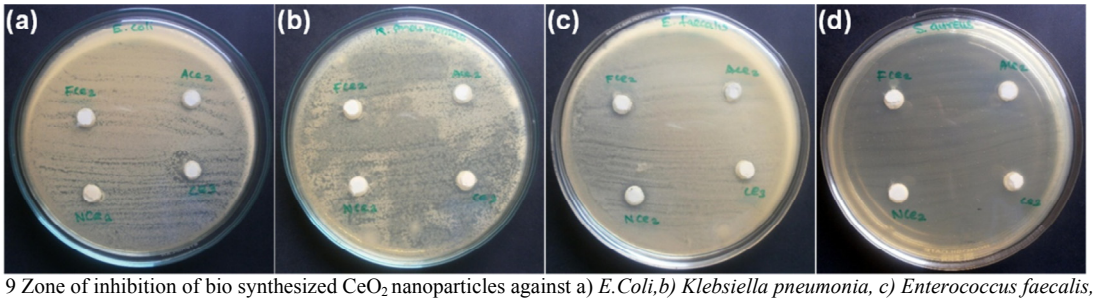

Fig. 9 Zone of inhibition of bio synthesized CeO_2 nanoparticles against a) *E.Coli,b) Klebsiella pneumonia, c) Enterococcus faecalis, d) Staphylococcus aures*

For bio synthesized (Annona Muricata) CeO_2NPs, the zones of inhibition areobserved to be 8 mm for Enterococcus faecalis and for Staphylococcus aureus bacterial strains it is around 9 mm (Table 3).

Table 3 Zone of inhibition of bio synthesized CeO_2 nanoparticles

S. No	Name of Samples	Escherichia coli	Klebsiella pneumoniae	Enterococcus faecalis	Staphylococcus aureus
1	CeO_2	No inhibition	No inhibition	8	9

3. Conclusion

The green synthesis technique has been adopted to prepare CeO_2-NPs using *Annona Muricata* fruit extracts, which can be better alternative to chemical synthesis without using any hazardous chemical, reducing agent and capping agent. The XRD result confirmed the formation of face centered cubic phase structure of CeO_2 NPs. FESEM images showed that the synthesized CeO_2 NPs were of fibre-like morphology. The UV-DRS analysis showedablue shift, which could be due to the quantum confinement effect. The maximum zone of inhibition was observed in the CeO_2 NPs against as *E. faecalis and S. Aureus*compared to *E.coli.,and K. pneumonia,*as tested by agar-well diffusion method, which is promising for further applications towards antibacterial activities against various pathogens.

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