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Green Synthesis, Characterization and Photocatalytic Applications of CeO2 Nanoparticles using Leaf Extract of *Psidium guajava*

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ABSTRACT
G – CeO2 NPs had been effectively synthesized the usage of a skilled methodology the usage of Psidium guajava plant leaf extract. XRD, EDAX, UV-Vis, and SEM are used to signify the G – CeO2 NPs that have been synthesized. The X-ray diffraction pattern confirms the formation of the cubic fluorite shape with the Fm3 house group. The crystalline dimension of G – CeO2 NPs used to be decided the usage of the Debye-Scherer method. Diffraction research has been used to have a look at the frequent crystal dimension of the synthesized NPs. The crystallite measurement of G – CeO2 NPs will increase from 12 nm as cerium oxide awareness increases. The floor Plasmon resonance top was once determined to be 311 nm in the UV-Vis spectra, and the bandgap used to be discovered to be 3.62 eV. The SEM photo demonstrates the formation of G – CeO2 NPs that are especially spherical and uniform. The EDAX spectrum exhibits the purity and whole chemical composition of G – CeO2 NPs. The fundamental photocatalytic traits of synthesized G – CeO2 NPs had been evaluated by using the MB dye degradation below UV – Vis irradiation are presented.
KEYWORDS: Nanoparticle, CeO2, Green synthesis, *Psidium guajava*

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INTRODUCTION

Nanotechnology has sparked enormous activity in each and every area of science and technology, and it is now considered as one of the most promising lookup areas. It has several functions in electronics, imaging, industry, and scientific treatment. It has especially been used through healthcare for situation diagnosis, treatment, delivery, and formulations of new drugs [1-4]. It makes use of nanoparticles, which are constructions with sizes ranging from 1 to a 100 nm (NPS). These nano scale entities have special phytochemical homes and have been used in physics biology and chemistry experiments Exploration of herbal assets (plant or plant part) is the most promising and eco-friendly choice to the bodily or chemical nanoparticle synthesis process [5]. The workable and promise of plant structures in biologically assisted synthesis of metal nanoparticles in the name of green synthesis is a key issue in nanoscience research [6].

CeO2 NPs have been commonly exploited due to the fact of their awesome floor chemistry, excessive balance and biocompatibility[7]. It is primarily used in sensor fabrication. Cells, catalysis, therapeutics agents, drug shipping careers, and anti-parasitic ointments [8]. Presently, CeO2 NPs are typically synthesized by way of two methods, such as bodily and chemical. CeO2 NPs have been the most broadly used rare-earth oxides for organic applications, with the majority of them involving the consumption of mammalian cells [9-11]. The CeO2 NPs are successfully used in most cancers remedy and infection via controlling the reactive oxygen species levels [12, 13].

Guajava (Myrtaceae) is extensively used in Mexico to deal with gastrointestinal and respiratory disorders, as properly as an anti-inflammatory medicine. Its roots, bark, leaves, and immature fruits are extensively used to deal with gastroenteritis, diarrhea, and dysentery. They are historically used to deal with wounds, ulcers, and rheumatoid arthritis; however they are additionally chewed to relieve toothache [14]. A febrifuge made from new shoots is used, and a combination of leaves and bark is used to expel the placenta after childbirth [15].

Due to the plausible makes use of nanostructure cerium oxides in a range of applications, a whole lot effort has been put into creating new artificial routes for producing them in latest years. Cerium oxide has several purposes at the nanoscale, together with oxygen reservation capacity, conductivity, excessive UV absorption, hardness, catalysis, gasoline cells, and sensors. Powder XRD, EDAX, SEM, and UV-analysis have been used to characterize the nanoparticles

CeO_2 nanoparticle photocatalyst is broadly used in renewable power and environmental clean-up. The photocatalytic cure to sunlight, and its augmentation thru coupling with electrocatalytic degradation, gives a lower-priced and environmentally pleasant approach for definitely getting rid of refractory pollution from industrial wastewater, such as surfactants, pharmaceuticals, pesticides, material dyes, and heavy metals. One of the most usually used photocatalysts in pollutant degradation is CeO_2 nanoparticles. CeO_2 nanoparticles showcase promising photocatalytic activity [16].

MATERIALS AND METHODS

Chemicals Used

Cerium Nitrate $Ce(NO_3)_3.6H_2O$, used to be bought from Sigma Aldrich. All reagents had been industrial grade and had been used except in addition purification. Ultrapure grade water is used in the experiment.

Plant Material Collection

Psidium guajava leaves had been accrued from Pudukkottai district, Tamil Nadu, India and recognized in the Rapinat Herbarium and Centre for Molecular Systematics, St. Joseph's College (Autonomous), Tiruchirappalli. The leaves had been air dried for 10 days in shadow, and then stored in the warm air oven at 60 oC for 24 to 48 h. The leaves had been grinded to a high-quality powder for in addition use.

Figure 1. ***Psidium guajava***

Aqueous extract of Psidium guajava leaves

10 g of finely chopped Psidium guajava leaves have been weighed, then 100 ml of double-distilled water was once brought and boiled at 50 – 60 ˚C for 15 minutes, the acquired extract used to be filtered the usage of Whatman -1 filter paper and the filtrate used to be accumulated in 250 ml Erlenmeyer flask.

Synthesis of CeO2 Nanoparticles

Cerium Nitrate Hexahydrate $Ce(NO_3)_3.6H_2O$, distilled water, and leaf extracts of Psidium guajava are used for the preparation G - CeO_2 NPs. G - CeO_2 NPs have been organized through an experienced synthesis technique the usage of metal precursors and Psidium guajava plant extract as reducing and capping agents. 0.1 M Ce $(NO_3)_3.6H_2O$ solution was added into 100 ml of Psidium guajava leaves extract and it was stirred constantly at 80 oC for 5 h. A yellow color precipitate was obtained further the precipitate was dried at 80 ˚C for 2 h. The obtained G - CeO_2 Powder was annealed at 400 ˚C for 5 h.

Characterization Studies

UV-Visible Spectroscopy

Ultraviolet-visible spectroscopy refers to absorption spectroscopy in the UV-Visible spectral region using UV-1601 PC Shimadzu spectrophotometer model. This means it uses light in the visible and adjacent near-UV and Near-Infrared (NIR)) ranges. The absorption in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronictransitions.

X-Ray Diffraction Method

The phase formation of bio-reduced CeO_2 NPs was studied with the help of XRD. The diffraction data of thoroughly dried thin films of nanoparticles on glass slides were recorded on D8 Advanced Brucker X-ray diffractometer with CuKα(1.54Ao) source.

EDAX and SEM

The morphological and elemental analyses were carried out using SEM and EDAX spectrum. The energy-dispersive x-ray spectroscopy (EDX) is an observational method designed for elemental detection. Elemental composition analysis of synthesized CeO_2-NPs was done using the energy-dispersiveX-ray spectroscopy model: INCA equipped with scanning electron microscopy model Hitachi S - 4500 SEM machine.

Photocatalytic activity

The photocatalytic activity of synthesized G - CeO2 NPs was evaluated by the MB dye degradation under UV-light irradiation. Then 1.0 mg of photocatalyst synthesized G - CeO2 NPs was added in 100 mL (1x10-5 M) of MB dye aqueous solution was stirred in the dark condition for 10 min until equilibrium condition attains followed by continuous stirring. Afterward, the suspension was kept under UV light and readings were taken for each 10 min up to 80 min. The suspension was changed from blue color to colorless. The final solution was analyzed by using the absorbance spectra SHIMADZU 3600 UV-vis NIR sectrophotometer. The percentage of MO dye absorbed on the catalyst surface was calculated by following below equation;

$$\text{Photocatalytic degradation (\%)} = \frac{A_0 - A_t}{A_0} X\ 100$$

Where A0 - initial in absorption and At is absorption after various time intervals (min).

RESULTS AND DISCUSSION

XRD analysis for G - CeO2 NPs

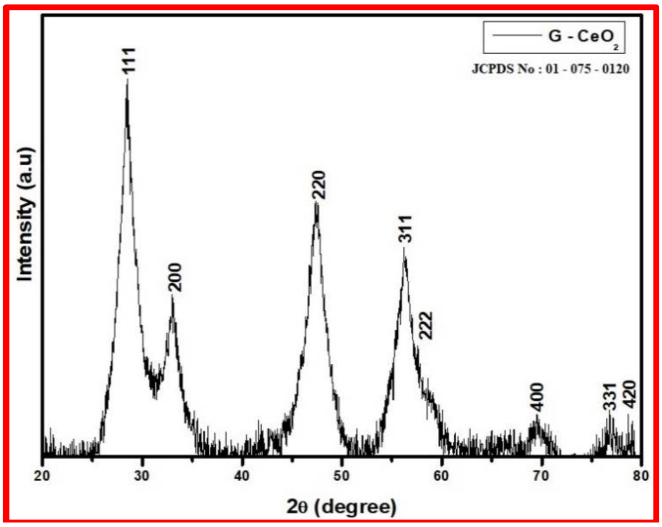

Figure-2: XRD pattern of synthesized G - CeO_2 NPs

The crystalline behaviour of as prepared G - CeO2 NPs was characterised using XRD in the diffraction angle (2θ) ranges of 10o to 80o with such a scanning rate of 5o per minute, as shown in Figure-1a. The obtained results show that the maximum intensity peak was observed at 111 degrees, and other intensity peaks were observed at 200, 220, 311, 222, 400, and 331 degrees crystal planes. The identified peaks are in good agreement with the JCPDS file (01-075-0120) and with previous reports17. It clearly shows the formation of polycrystalline G - CeO2 with cubic fluorite structure. The average crystallite size (D in nm) of the G - CeO2 NPs was found to be 12 nm using the Debye-Scherrer formula, D=K / B cos; Where K is a constant (0.90), is the X-ray wavelength (=0.15406 Ao), and is the diffraction angle for the X-ray.

Morphological study

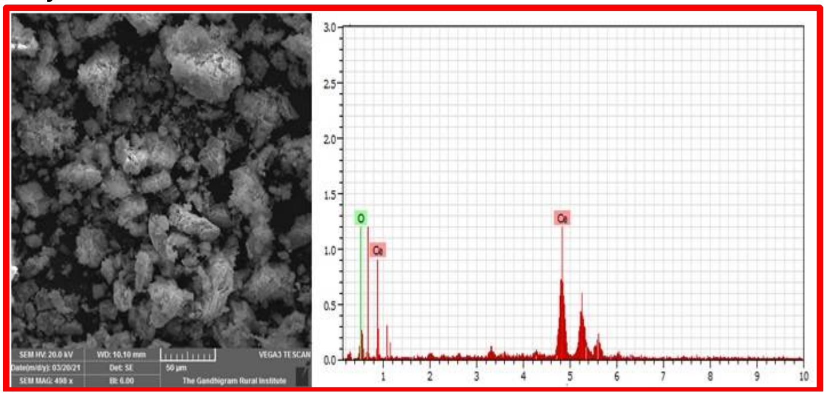

Figure-3: Morphological and Elemental analysis of G - CeO2 NPs

The scanning electron microscope (SEM) is a powerful magnification tool for detecting the surface morphology of nanoparticles. Powder EDAX analysis was used for structural characterization. Figure-2 depicts the obtained SEM image of the as-prepared G - CeO2 nanoparticles as well as a quantitative and qualitative analysis of elements that may be involved in the formation of G - CeO2 NPs18, 19. It is clear that the surface of G - CeO2 is made up of spherical-shaped particles with a uniform distribution. Aside from that, a small number of agglomerations were found in the SEM images. The obtained morphology also corresponded well with the literature20-22. Because of the larger agglomerations, it was difficult to calculate an exact value of particle size. The average particle size was discovered to be around 4 nm. The absence of any additional peak in the EDAX spectrum indicates the formation of G - CeO2 NPs with the 91.98% of Ce and 8.02% of O.

Optical Measurement of G - CeO2 NPs

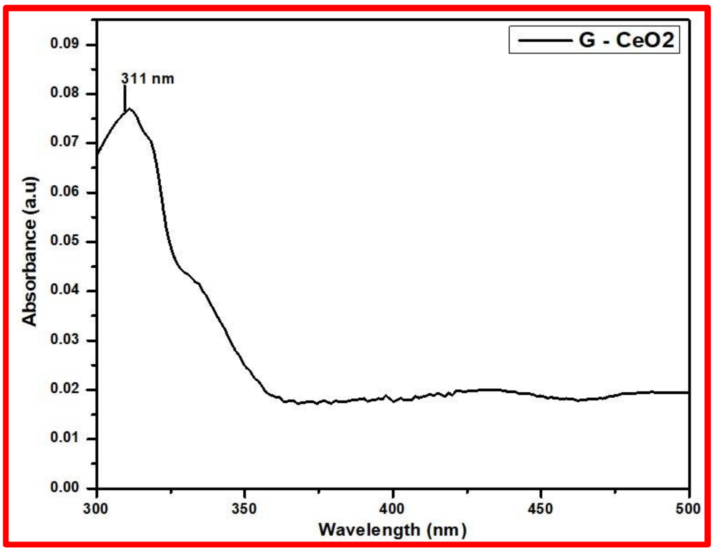

Figure. 4: UV-Visible Spectrum of G - CeO2 NPs

The most common technique for determining nanoparticle formation is absorption spectral analysis. Metal nanoparticles were typically analysed in the wavelength range of 300–800 nm, and the formation of G - CeO2 NPs can be detected commonly from absorption measurements in the wavelength ranges of 300–500 nm. The UV-Vis absorption spectrum shown in Figure-5 reveals that the absorption threshold edge was determined to be 311 nm. The UV-Visible spectra revealed no other peak associated with impurities or defects, confirming that the synthesized nanoparticles are G - CeO2. For G - CeO2 NPs23, 24, the band gap energy is 3.62 eV. The UV-visible spectra show that the smaller G - CeO2 NPs have better optical properties.

The optical absorption coefficient (α) was calculated from transmittance using the following relation (Eg =3.62 eV). α = 1/ d log (1/T); Where, T denotes the transmittance and d is the thickness. The study has an absorption coefficient (α) obeying the following relation for high photon energies (hν).

$$\propto = \frac{A(hv - Eg)^2}{hv}$$

Where α, Eg, and A are the absorption coefficient, bandgap and constant respectively. The fundamental absorption corresponding to the optical transition of the electrons from the valence band to the conduction band can be used to determine the nature and value of the optical bandgap Eg of the nanoparticles.A plot of$(\alpha hv)^2$vs. (eV) is used to evaluate the direct optical bandgap of the material and is shown in Figure-6. The obtained Eg value shows that blue shift occur on the G - CeO2 NPs. The attained bandgap value is determined by extrapolating the linear portion of the curve and the bandgap was found to be 3.62 eV.

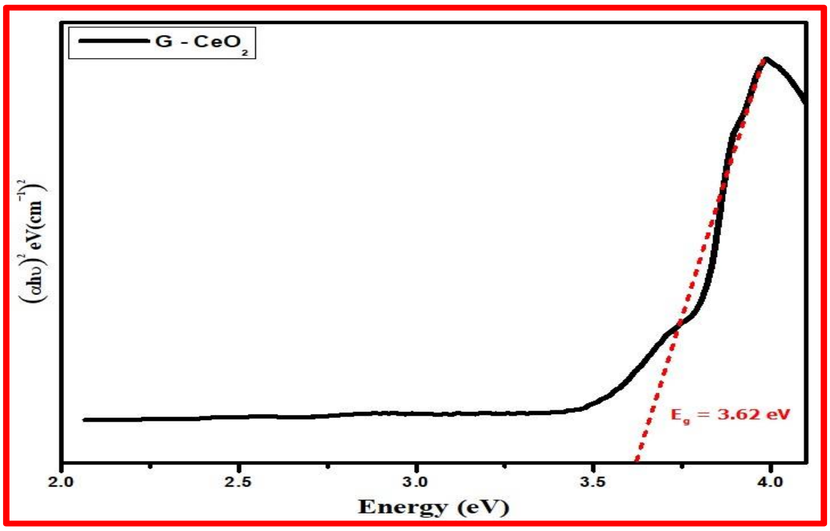

Figure- 5: Direct Optical Bandgap of the G - CeO2 NPs

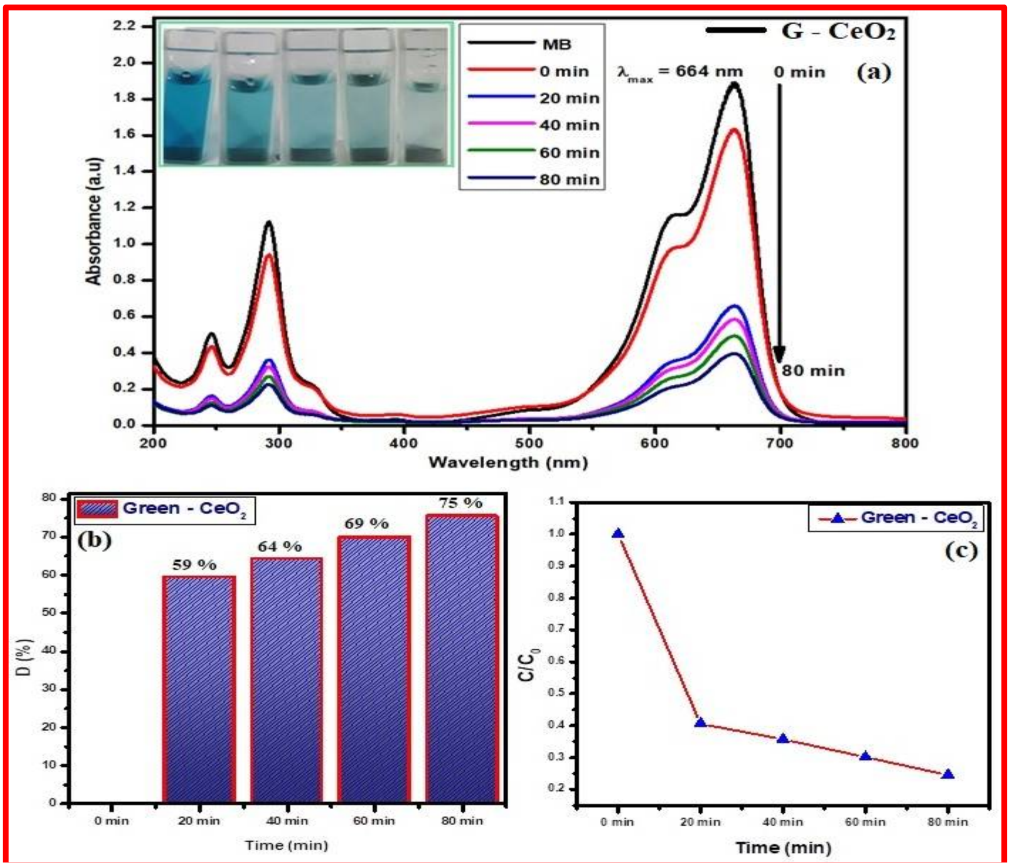

Figure 7. Catalytic efficiency of synthesized nanoparticle

APPLICATION

Photocatalytic activity

The catalytic efficiency of synthesized G - CeO2 NPs in the degradation of organic methylthioninium chloride, also known as Methylene Blue, was investigated (MB). MB dye is one of the most common hazardous dyes. This heterocyclic aromatic compound is commonly used as a day indicator in biochemistry and has a number of medical applications due to its redox properties25. Despite the widespread use of MB as a human therapeutic agent, its negative environmental impact has raised serious concerns. As a result, removing MB dye from effluent is critical for environmental protection. The photocatalytic activity of the synthesised G - CeO2 NPs was investigated in this study using MB dye disintegration as an activator and UV-light irradiation. The removal efficiency rate of MB dye was also monitored as a function of time at regular intervals (0, 20, 40, 60, and 80 min).As shown in Fig. 4a, the time of choice for mineralization of MB organic pollutant is 80 minutes, and the rate of discoloration from changes in the intensity of the absorption peak at 664 nm was noted. The photocatalytic decay rates of the MB solutions in the presence of the synthesized G - CeO2 NPs are shown in Figure 4b as a function of changes in absorption intensity. Because of their outstanding photocatalytic properties, semiconductor photocatalysts are very likely to be considered as a strong candidate for organic contaminate degradation. Under UV-light irradiation, our findings show higher efficiency than chemically produced G - CeO2 NPs toward the same pollutant.

CONCLUSION

The green method was used to successfully synthesize ultrafine CeO2 NPs from Psidium guajava leaves extract. The cubic phase of the G - CeO2 nanoparticles was confirmed by an XRD pattern and the particle crystallite size was determined to be 12 nm (Scherrer method). The SEM images of G - CeO2 nanoparticles show that the particles are spherical with few agglomerations. The EDAX results showed that the CeO2 NPs are 91.98 % Cerium and 8.02 % Oxygen. The presence of a strong absorption band at 311 nm indicates that G - CeO2 nanoparticles have superior optical properties. The Eg value demonstrated that a blue shift occurs on G - CeO2 NPs with a band-gap of 3.62 eV. Photodegradation of methylene blue under UV-Visible light irradiation was used to investigate the photocatalytic activities of the prepared nanoparticles. The photodegradation process was monitored using a UV–Vis spectrophotometer at the maximum absorption wavelength of MB (664 nm). The results show thatG - CeO2 NPs photodegrade Methylene Blue effectively.

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