Facile synthesis of ultrafine CeO_2 nanoparticles by the thermal treatment of $[Ce(DNPH)_2(HSA)_2]$

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Abstract:

Ultrafine CeO_2 nanoparticles obtained from the inorganic cerium complex $[Ce(DNPH)_2(HSA)_2]$, have been subjected to structural and morphological evaluation, which has revealed interesting results. $[Ce(DNPH)_2(HSA)_2]$, prepared using the combination of 1-hexane sulphonic acid (HSA) and 2,4 dinitrophenyl hydrazine (DNPH), which acts as the ligand, has yielded the desired CeO_2 nanoparticles on thermal decomposition. These particles have been characterized using SEM, XRD and EDX techniques.

Keywords:

$[Ce(DNPH)_2(HSA)_2]$, CeO_2, 1-hexane sulphonic acid, 2,4 dinitrophenyl hydrazine, SEM, XRD, EDX.

Introduction:

Size-induced structural distortions associated with changes in cell parameters have been observed, for example, in nanoparticles of Al_2O_3, NiO, Fe_2O_3, ZrO_2, MoO_3, CeO_2; and Y_2O_3. As the particle size decreases, the increasing number of surface and interface atoms generates stress strain and concomitant structural perturbations. Beyond this “intrinsic" strain, there may be also "extrinsic" strain associated with a particular synthesis method which may be partially relieved by annealing or calcination [1-3].

In their bulk state, many oxides have wide band gaps and a low reactivity. A decrease in the average size of an oxide particle do in fact change the magnitude of the band gap, with strong influence in the conductivity and chemical reactivity. Surface properties are also significant, included in this subject due their importance in chemistry [2].

Among all the materials prepared on the nanoscale, transition metal oxides are noteworthy candidates from a scientific as well as a technological point of view. Transition metal oxides can exhibit unique characteristics which make them the most versatile class of materials with properties covering all aspects of solid state and material science [4-6].

Transition metal oxides, the oxides of d-block elements with partially filled d-subshell, have attracted the research community with their unique and fabulous properties such as magnetic, optical and electrochemical. The novel properties have envisaged them in many practical applications such as energy storage (e.g. supercapacitors, lithium-ion batteries, etc), non-volatile memory devices sensors, solar cells and infrared detectors. The ability to modulate the physical as well as chemical properties helps designing novel devices with tunable properties and hence enhances the industrial importance [7].

Cerium oxide is a compound from two elements cerium and oxygen, which are d block and p block elements in the periodic table respectively. Inorganic cerium oxide nanoparticles, also known as nanoceria, are exceptional antioxidants used for regeneration radical scavenging in-vitro [8-11]. Cerium oxide nanoparticles represent a recent approach in cancer therapy, possessing the “smart” capacity to selectively induce cellular

death in irradiated cancer cells, being suitable for radiation therapy [12-16]. They are widely used in chemical mechanical polishing/planarization, corrosion protection, solar cells, fuel oxidation catalysis, and automotive exhaust treatment. It has been found that they also display many bio-relevant activities-mimicking superoxide dismutase (SOD), catalase, peroxidase, oxidase, and phosphatase, and scavenging hydroxyl radicals, nitric oxide radicals, and peroxynitrite [17-21].

This work mainly focuses on the synthesis of CeO_2 nanoparticles from $[Ce(DNPH)_2(HSA)_2]$, the metal complex prepared using cerium nitrate, 1-hexane sulphonic acid sodium salt anhydrous (HSA), 2,4 dinitrophenyl hydrazine (DNPH) in a stoichiometric ratio, and their characterization.

MATERIALS AND METHODS

Commercially available chemicals (Analar or Equivalent grades) were used as received.

SYNTHESIS OF $[Ce(DNPH)_2(HSA)_2]$:

The coordination complex of cerium of the formula $[Ce(DNPH)_2(HSA)_2]$ was synthesized using 1:2:8 ratio of cerium nitrate, 1-hexane sulphonic acid and 2,4 dinitrophenyl hydrazine in the following manner. About 0.2713 g of cerium nitrate hexahydrate was weighed and transferred it into a 250 ml beaker containing 50 ml of ethanol and dissolved. Then about 0.2315 g of 1-hexane sulphonic acid was weighed and transferred it into another 250 ml beaker containing 50 ml of ethanol. To this 0.9970 g of 2,4 dinitrophenyl hydrazine was weighed, added and stirred well. Then, this mixture was poured into the 250 ml beaker containing cerium nitrate solution. A reddish orange precipitate was formed, which kept on a water bath for one hour for digestion. After digestion, the precipitate was filtered washed well with ethanol and dried in air.

ANALYTICAL METHODS

ESTIMATION OF HYDRAZINE

The hydrazine content of the precursor was determined volumetrically using standard KIO_3 (0.025 M) solution under Andrew's conditions [29].

$$IO_3^- + N_2H_4 + 2H^+Cl^- \longrightarrow ICl + N_2 + 3H_2O$$

1 ml of 0.025 M KIO_3 0.0008013 g of hydrazine

In an iodimetry flask 100 mg of the sample dissolved in 10 ml of concentrated hydrochloric acid. 20 ml of distilled water and 5 ml of carbon tetrachloride was added. It was titrated against standard potassium iodate (0.025 M) solution from the burette. The solution was shaken well after the addition of each ml of KIO_3 solution. The end point is the disappearance of pink colour and appearance of pale yellow in the organic layer [30].

PREPARATION OF CERIUM OXIDE NANOPARTICLES

The precursor, cerium complex synthesized was converted to cerium oxide by high temperature thermal decomposition method, which is a top-down method for the synthesis of nanoparticles. The complex is heated in a muffle furnace taken in a silica crucible at a temperature of 700°C for about 2 hours after attaining the temperature. The precursor started decomposing violently. The total decomposition of precursor led to the formation of cerium oxide, which was quenched to room temperature, ground well and stored.

RESULTS AND DISCUSSION

FT-IR SPECTRAL ANALYSIS OF $[Ce(DNPH)_2(HSA)_2]$

The FT-IR spectrum of complex is given and the spectral data are presented in Table 1. In the spectrum of the complex, the band in the region of 3317 cm^{-1} is assigned to the N-H stretching of by DNPH, which proves the coordination of the amino nitrogen group to the metal atom. N-N stretching is observed at 972 $cm^{-1.}$ The band at 1489 cm^{-1} is attributed to the NO_2 asymmetric stretching and the one at 1411 cm^{-1} indicates the NO_2 symmetric stretching. These findings point out that the ligands are coordinated with the metal ion through one oxygen atom of the nitro group [37]. The asymmetric and symmetric stretching frequencies of the SO_3^- ions are seen at 1326 and 1088 cm^{-1} respectively with separation of 238 cm^{-1}, showing its monodentate linkage to the metal atom. The lower frequency bands appearing at 547 cm^{-1} and 439 cm^{-1}, can be attributed to the ν(M-O) and ν(M-N) bands, respectively [38].

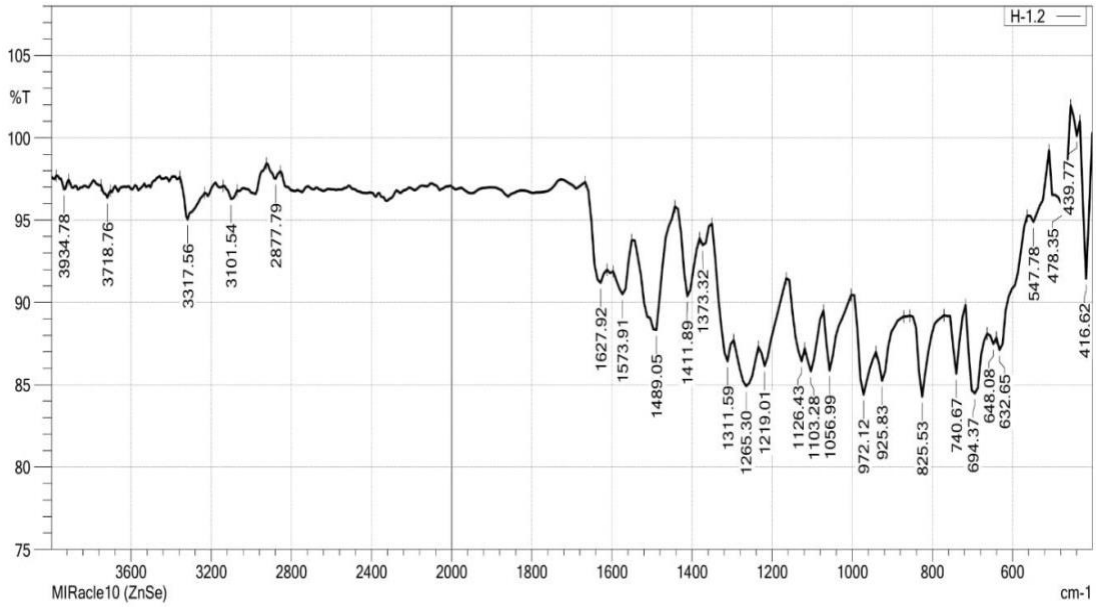


Fig. 1 – IR Spectrum of $[Ce(DNPH)_2(HSA)_2]$

Table 1 – IR Spectral data of $[Ce(DNPH)_2(HSA)_2]$

Wave number cm^{-1}	Assignment
972	ν_{N-N}
1266	$\nu_{S=O}$
3317	ν_{N-H}
1326	$\nu_{SOO^-(asymmetric)}$
1088	$\nu_{SOO^-(symmetric)}$
1489	$\nu_{NO2\,(asymmetric)}$
1411	$\nu_{NO2\,(symmetric)}$
547	M-O
439	M-N

THERMAL STUDIES

As can be observed from Fig. 2, the precursor loses weight in two steps. The first step is the dehydrazination of the precursor compound between room temperature and 245°C with a weight loss of 39%. The major weight loss of 61% on the TG curve from 280°C to 390°C is attributed to the second step involving the desulphonation of the dehydrazinated precursor, which gives CeO_2 as the final residue.

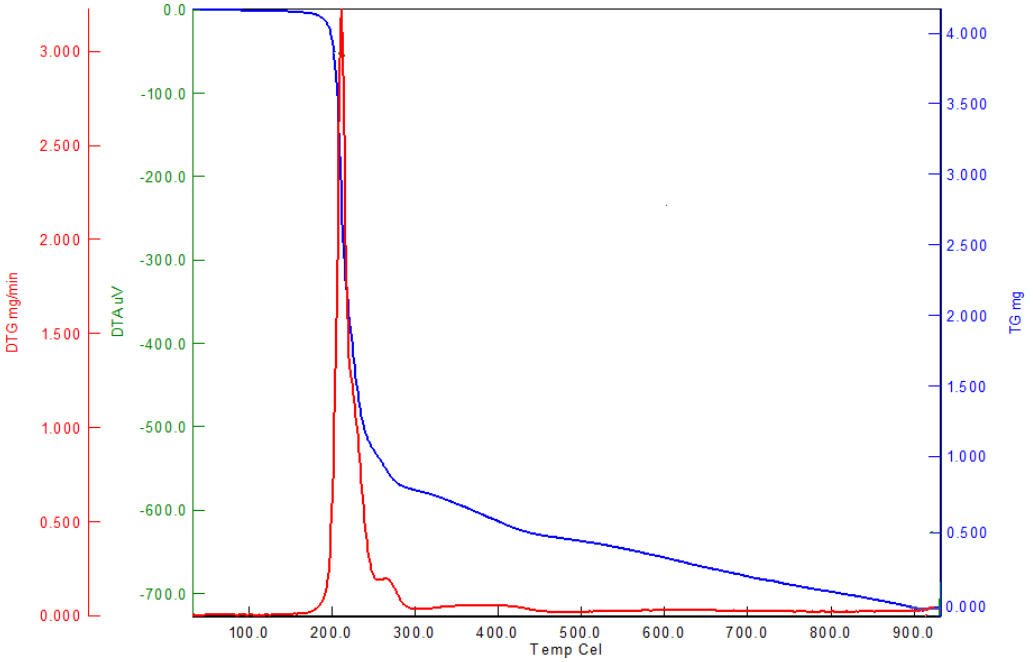
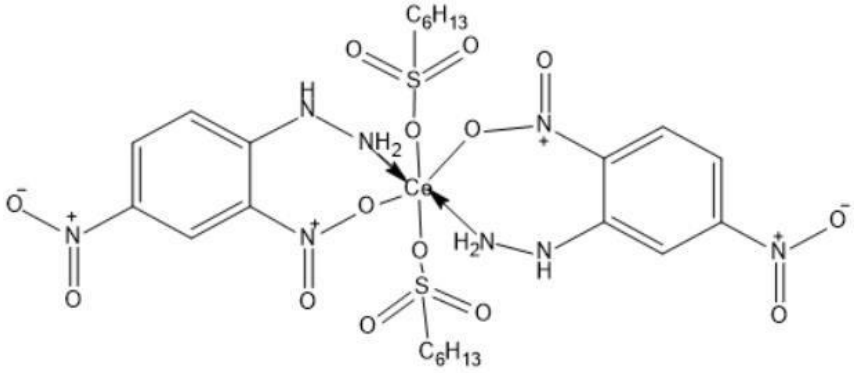


Fig. 2 – TG-DTA pattern of $[Ce(DNPH)_2(HSA)_2]$

STRUCTURE OF [Ce(DNPH)2(HSA)2]

Based on the IR spectral data and TG-DTA results, the following structure is proposed for the precursor.



XRD ANALYSIS OF CeO_2 NANOPARTICLES

Fig. 3 depicts the X-ray diffraction peaks of CeO_2 with 2θ values ranging between 20° and 90°. The powder XRD pattern recorded using a Schimadzu model XRD 6000 with CuK_α radiation (λ = 1.5417 Å). The crystallographic planes validated the material's crystalline phase and are very well aligned to specifications

(JCPDS card # 34-0394). The result shows the characteristic diffraction peaks located at 2θ = 28.70°, 32.39°, 47.28°, 56.59°, 59.14°, 77.32°, 78.89° and 88.57°, corresponding to the 111, 200, 220, 311, 222, 400, 331, 420 and 422 respectively. There really is no discernible shift in peak location, and the spikes are observed to be extremely acute and powerful. The Debye-Scherrer equation has been used to compute the regular crystallite sizes of CeO_2 particles. The crystallite size estimated is 18 nm.

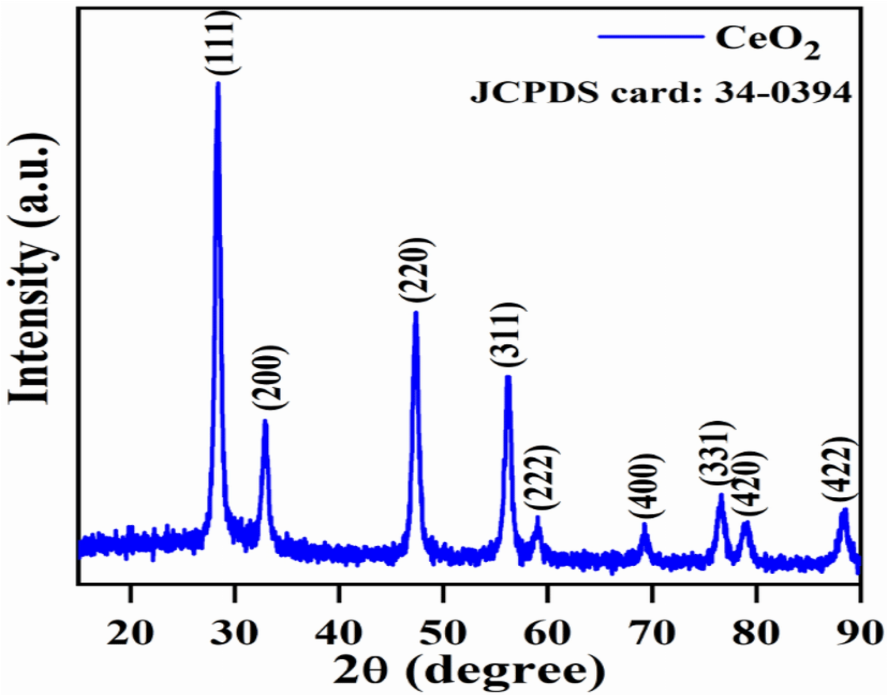


Fig. 3 – XRD pattern of CeO_2 nanoparticles

SCANNING ELECTRON MICROSCOPY (SEM)

The scanning electron micrographs of the synthesised CeO_2 nanoparticles are shown in Fig. 4. The SEM pictures clearly show nano-sized homogenous grains with the presence of a sizable number of agglomerated particles. The particles are well-defined and they appear to stick each other and agglomerate in different masses throughout the micrographs.

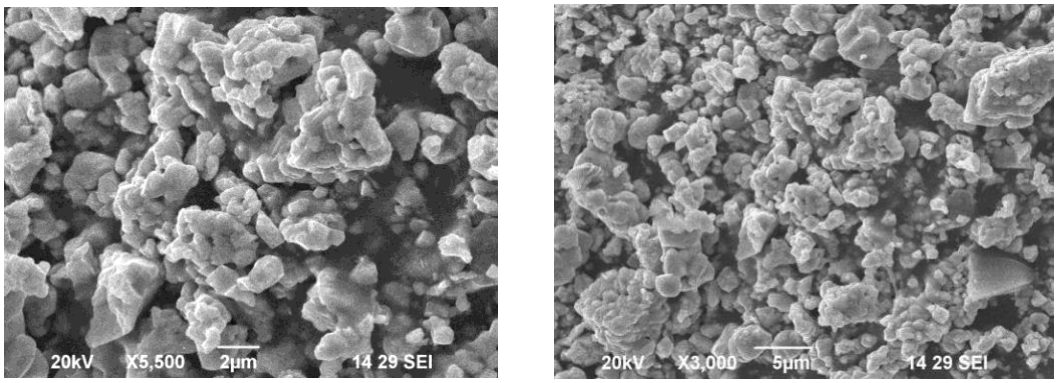


Fig. 4 – SEM images of CeO_2 nanoparticles

ENERGY DISPERSIVE X-RAY (EDX) ANALYSIS

The EDX spectrum of CeO_2 nanoparticles is shown in figure 5. The spectrum provides information about their actual chemical composition. It is evident form the spectra that no other impurity elements are present in the sample.

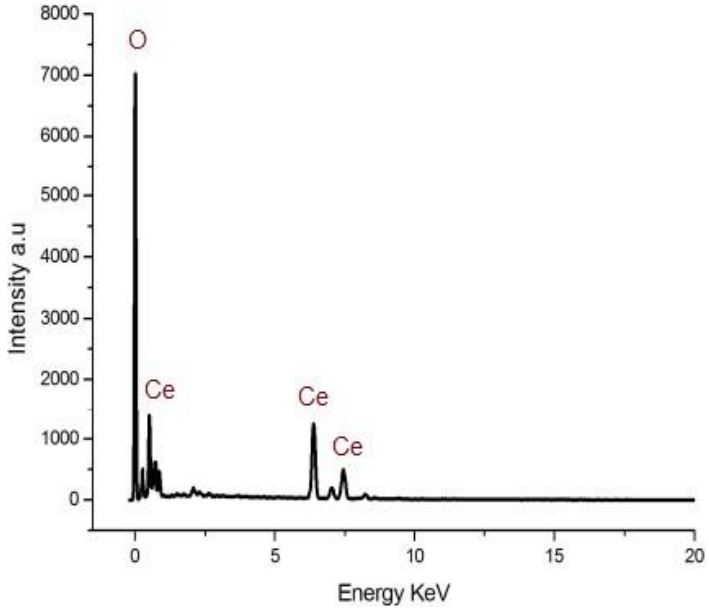


Fig. 5 – EDX Spectrum of CeO_2 nanoparticles

SUMMARY AND CONCLUSIONS

Ultrafine CeO_2 nanoparticles were effectively synthesized through a simple and efficient thermal decomposition method from the inorganic precursor $[Ce(DNPH)_2(HSA)_2]$. The FT-IR spectral study of the precursor compound revealed the monodentate coordination of the sulphonate groups present in 1-Hexane sulphonic acid (HSA) and the bidentate linkage of the 2,4 dinitro phenyl hydrazine (DNPH). TG-DTA showed that the precursor compound yielded cerium oxide as the final residue, through a two-step thermal decomposition process. CeO_2 nanoparticles were characterized by XRD, SEM and EDX techniques. Particles are found to have around 18 nm crystallite size, as estimated from XRD results.

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REFERENCES

1. Morsi RE, El-salamony RA, "Effect of cationic, anionic and non-ionic polymeric surfactants on the stability, photo-catalytic and antimicrobial activities of yttrium oxide nano fluids" Journal of Molecular Liquids, 297, 111848 (2020).
2. Ibrahim Khan , Khalid Saeed, Idrees Khan "Nanoparticles: Properties, applications and toxicities" Arabian Journal of Chemistry, 12(7), 908-931 (2019).
3. Guanying Chen, Indrajit Roy, Chunhui Yang and Paras N. Prasad "Nanochemistry and Nanomedicine for Nanoparticle-based Diagnostics and Therapy", Chem. Rev., 116, 5, 2826–2885 (2016).
4. Kalpanadevi K, Sinduja CR and Manimekalai R, "Synthesis and characterisation of $Ni_{0.25}Co_{0.75}Fe_2O_4$ nanostructures", Bulletin of the Chemical Society of Ethiopia, 30(1), 79-85 (2016).
5. lLuis Arturo García de la Rosa, Miguel Angel Méndez-Rojas, in Direct Synthesis of Metal Complexes, "Direct Synthesis of Nanomaterials: Building Bridges Between Metal Complexes and Nanomaterials", Direct Synthesis of Nanomaterials, 317-337 (2018).
6. Radwa A. El-Salamony, Sara A. El-Sharaky, Seham A. El-Temtamy, Ahmed M. AlSabagh, Hamada M. Killa, "Effect of Ruthenium promotor ratio on Ni/Y_2O_3 Based Catalysts for CO_2 Methanation Reaction", Egypt. J. Chem. Vol 64, No10, pp 5765 - 5780 (2021).
7. Soumen Das, Janet M Dowding, Kathryn E Klump, James F McGinnis, William Self & Sudipta Seal "Cerium oxide nanoparticles: applications and prospects in nano medicine", Nanomedicine (Lond), 8(9), 1483-508 (2013).
8. Yat-Ming So, Wa-Hung Leung "Recent advances in the coordination chemistry of cerium (IV) complexes", Coordination Chemistry Reviews, 340, 172-197 (2017).
9. Kshitij RB Singh, Vanya Nayak, Tanushri Sarkar and Ravindra Pratap Singh, "Cerium oxide nanoparticles: properties, biosynthesis and biomedical application", RSC Adv., 10, 27194–27214 (2020).
10. Nadeem M, Khan R, Afridi K, Nadhman A, Ullah S, Faisal S, Mabood ZU, Hano C, Abbasi BH. Green Synthesis of Cerium Oxide Nanoparticles (CeO_2 NPs) and Their Antimicrobial Applications: A Review. Int J Nanomedicine. 15, 5951-5961 (2020).
11. Tamizhdurai, P., Sakthinathan, S., Chen, SM. et al. "Environmentally friendly synthesis of CeO_2 nanoparticles for the catalytic oxidation of benzyl alcohol to benzaldehyde and selective detection of nitrite" Sci Rep 7, 46372 (2017).
12. Miao, J. J., Wang, H., Lia, Y. R., Zhub, J. M. & Zhua, J. J. "Ultrasonic-induced synthesis of CeO_2 nanotubes" J. Cryst. Growth. 281, 525–529 (2005).
13. Hirst, S. M. et al. "Anti-inflammatory Properties of Cerium Oxide Nanoparticles", Small. 24, 2848–2856 (2009).
14. Sachin Pundir, Ruby Priya, Kulwinder Singh, Harmanpreet Kaur, Prashant Choudhary, "A systematic study on synthesis of CeO_2 nanoparticles by various routes", IOP Conf. Series: Earth and Environmental Science, 1110, 012030 (2023).
15. Samiee, S. & Goharshadi, E. K. "Effects of different precursors on size and optical properties of ceria nanoparticles prepared by microwave-assisted method" Mater. Res. Bull. 47, 1089–1095 (2012).
16. Can Xu and Xiangong Qu "Cerium oxide nanoparticle: a remarkably versatile rare earth nanomaterial for biological applications" NPG Asia Mater, 6, 90 (2014).
17. Ahmed H E, Iqbal Y, Aziz M H, Atif M, Batool Z, Hanif A, Yaqub N, Farooq W A, Ahmad S, Fatehmulla

A and Ahmad H, Molecules 26, 4659 (2021).

18. Aseyd Nezhad S, Es-haghi A and Tabrizi M H, "Green synthesis of cerium oxide nanoparticle using Origanum majorana L. leaf extract, its characterization and biological activities: Green Synthesis of nanoparticle", Appl. Organomet. Chem. 34, 1 (2020).
19. Vasily V. Spiridonov, Andrey V. Sybachin, Vladislava A. Pigareva, Mikhail I. Afanasov, Sharifjon A. Musoev, Alexander V. Knotko and Sergey B. Zezin, "One-Step Low Temperature Synthesis of CeO_2 Nanoparticles Stabilized by Carboxymethylcellulose", Polymers, 15, 1437 (2023).
20. Mawlood Maajal Ali, Hadeel Salih Mahdi, Azra Parveen, and Ameer Azam "Optical properties of cerium oxide (CeO_2) nanoparticles synthesized by hydroxide mediated method" AIP Conf. Proc. 1953, 030044 (2018).
21. Atul Dhall and William Self "Cerium Oxide Nanoparticles: A Brief Review of Their Synthesis Methods and Biomedical Applications" Antioxidants (Basel), 24, 7(8), 97 (2018).