Structural and Optical Properties of Mesoporous Sm^{3+}: CeO_2 and Its Environmental Applications

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ABSTRACT

Cerium oxide (CeO_2) is one of the most interesting oxides industrially because it has been widely used as a catalyst, three-way automotive catalytic converters for purification of exhaust gases, oxygen sensors, and so forth for long periods of time. Recently, CeO_2 nanoparticles has also emerged as a fascinating and lucrative material for environmental remediation applications. The key for most of the above mentioned applications of CeO_2 based materials is its extraordinary ability to release or uptake oxygen by shifting some Ce^{4+} to Ce^{3+} ions. Better catalytic performances of CeO_2 have been reported in the presence of Ce^{3+} and oxygen vacancy defects, which are potentially potent surface sites for catalysis. Here, we present the effect of Sm^{3+} doping on structural and optical properties of mesoporous CeO_2 and its environmental applications. The XRD results showed that even as-prepared material has cubic fluorite structure of CeO_2 with no crystalline impurity phase. All the nanopowders exhibited strong absorption in the UV region and good transmittance in the visible region. Mesoporous Sm^{3+} doped CeO_2 sample could effectively photodegrade all types of cationic, anionic and nonionic dyes under natural sunlight irradiation. These high surface area mesoporous materials exhibited notable adsorption and effective removal of Cr(VI) from aqueous solutions. Further Sm^{3+} doping was found to cause unusual emissions with a dominant $^4G_{5/2} \rightarrow {}^6H_{5/2}$ transition cantered at 573 nm. Additionally, the luminescence intensities enhanced with increasing Sm^{3+} concentration from 0.5 mol% to 1 mol% with further increasing Sm^{3+} concentration leads to the decrease in luminescence intensities. The presence of increased surface hydroxyl group, mesoporosity, and surface defects have contributed towards an improved activity of mesoporous CeO_2, which appears to be potential candidates for optical, and environmental applications.

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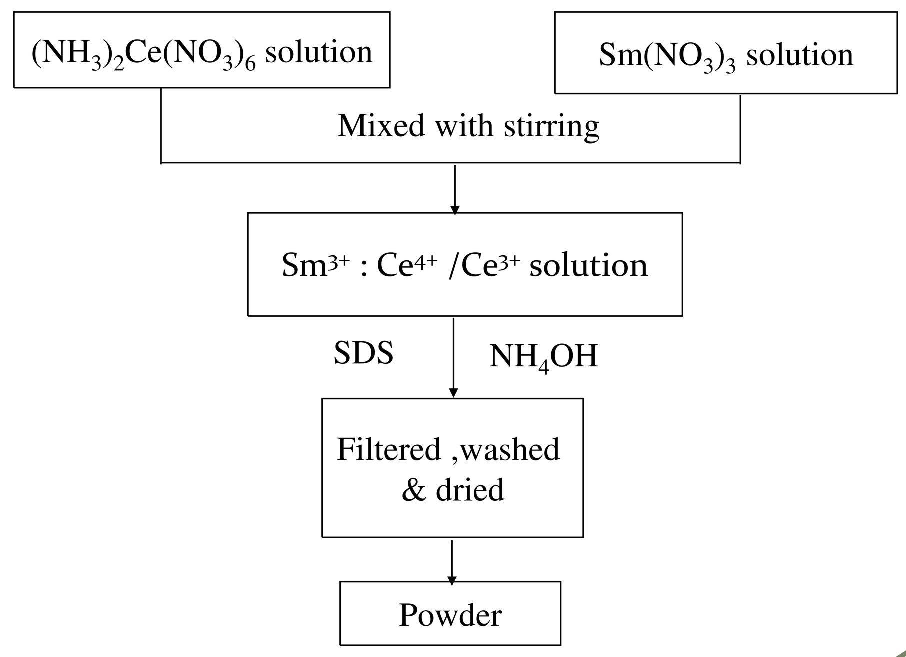
Motivation

In recent years, inorganic phosphors find its applications in cathode ray tubes (CRT), field emission devices (FED) and fluorescence applications. Rare earth doped oxide nanoparticles serve as the best phosphor material in comparison with other inorganic metal oxide nanomaterials. Among the rare earth family, cerium (Ce) is the most abundant element. With a high abundance and various unique properties nanostructured ceria (CeO_2) has attracted much attention for wide variety of technological applications as in the area of three-way catalysts (TWCs), fuel cells, solar cell, phosphors, UV absorber/blocker, shielding material, and in sunscreen cosmetics, hydrogen storage materials, developing new luminescence devices.

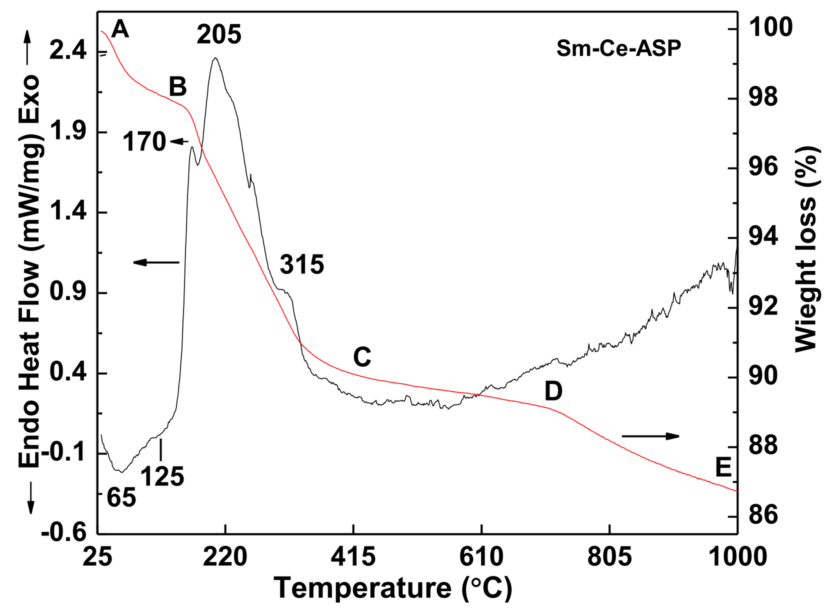
Objectives

- Development of pure and rare earth doped ceria nanopowder via facile and low cost method by using inorganic precursors.
- Convenient low temperature preparation of multifunctional efficient CeO_2 materials with higher surface area and higher crystallinity.
- Development of highly luminescent materials.
- Structural and optical characterization by using TG-DSC, XRD, BET, XPS, UV-visible, PL,FESEM and HRTEM analysis.
- Application of synthesized nanopowder in the for removal of toxic heavy metal Cr(VI) by adsorption.
- We also demonstrate a new photochemical remediation method for dye-polluted waters by using samarium doped ceria nanoparticles and natural sunlight only.

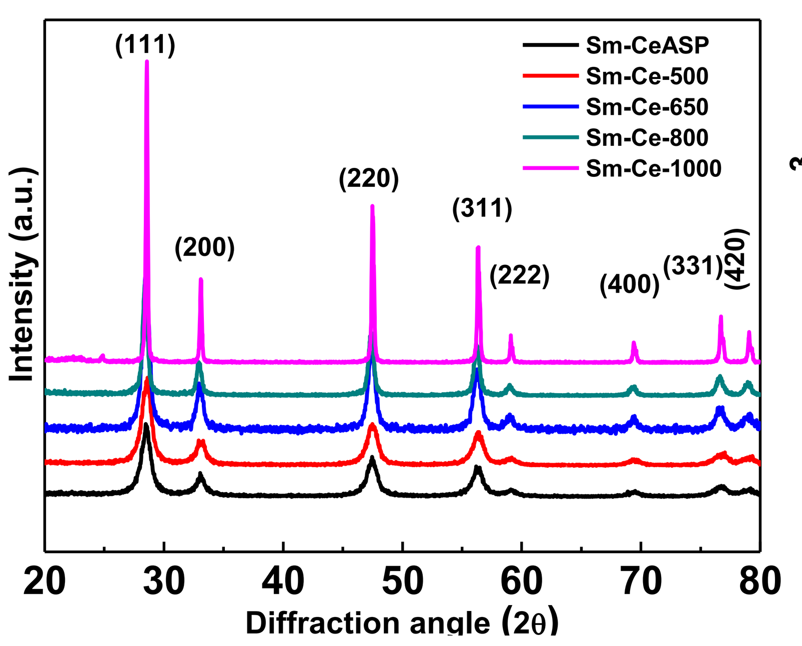
Synthesis



TG-DSC Curves



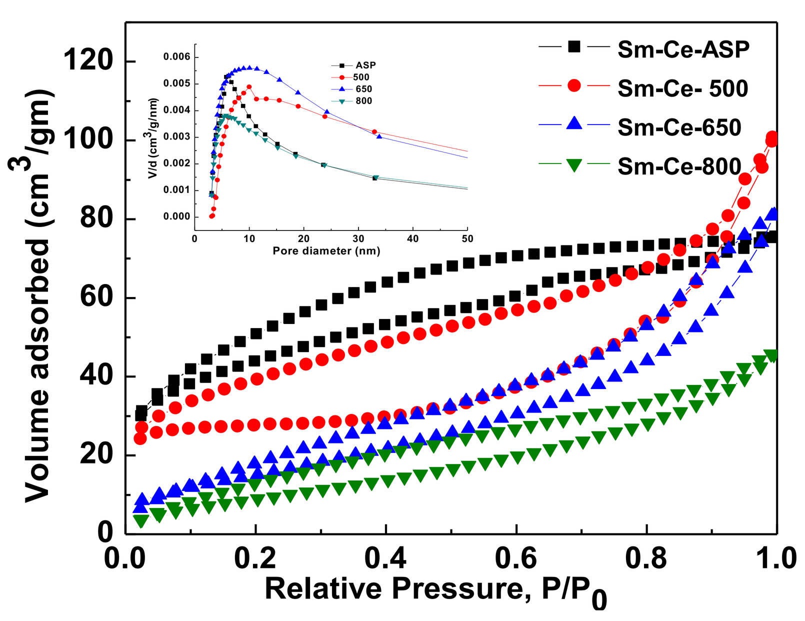
XRD Patterns



Crystallite size (nm)

Condition	ASP	500°C	650°C	800°C	1000°C
CS	9.6	9.7	13.5	19.4	51.2

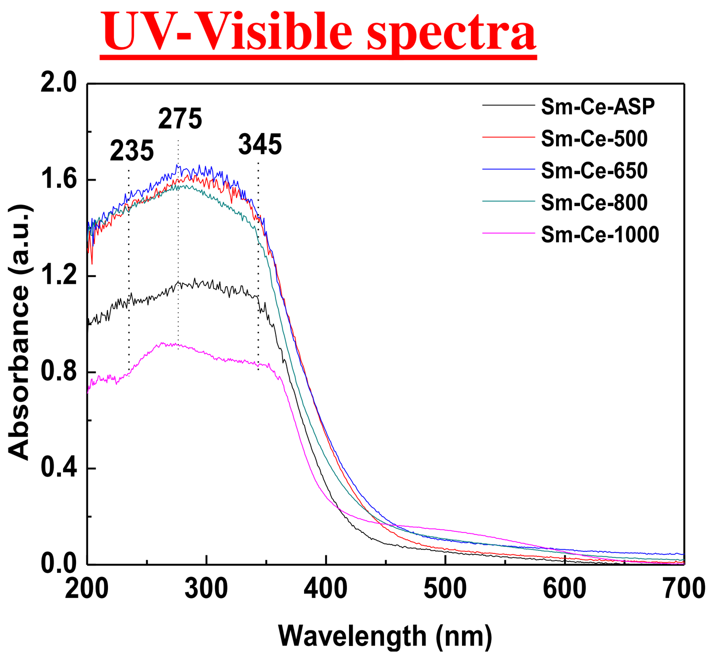
BET surface area



BET surface area (m^2/g)

Condition	ASP	500°C	650°C	800°C
SA	184	138	59	38

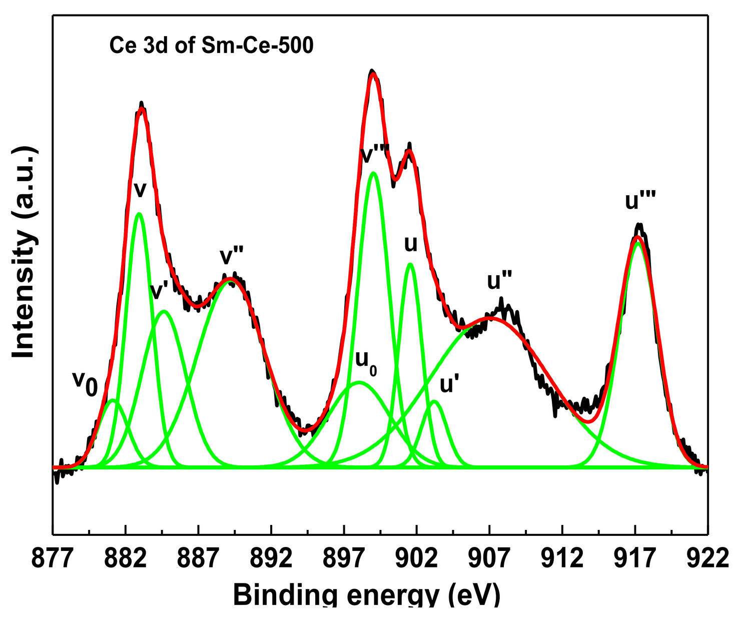
UV-Visible spectra

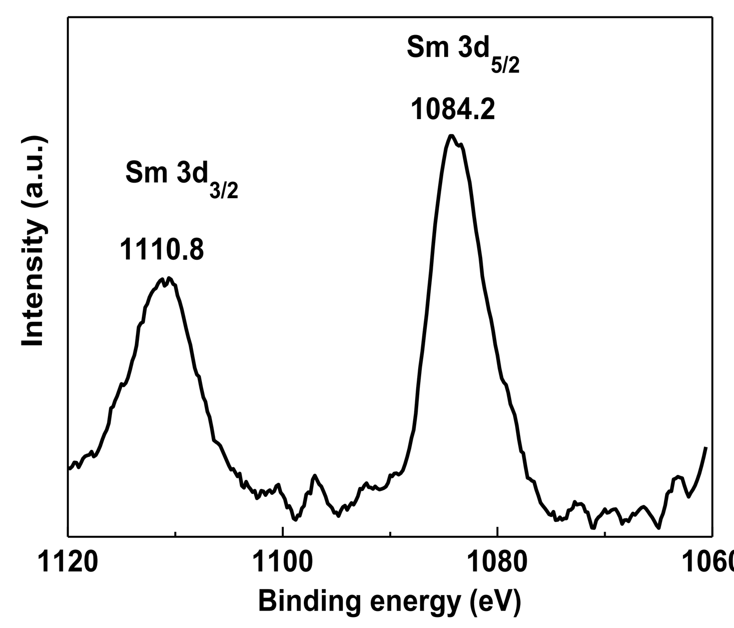


Band gap energy (eV)

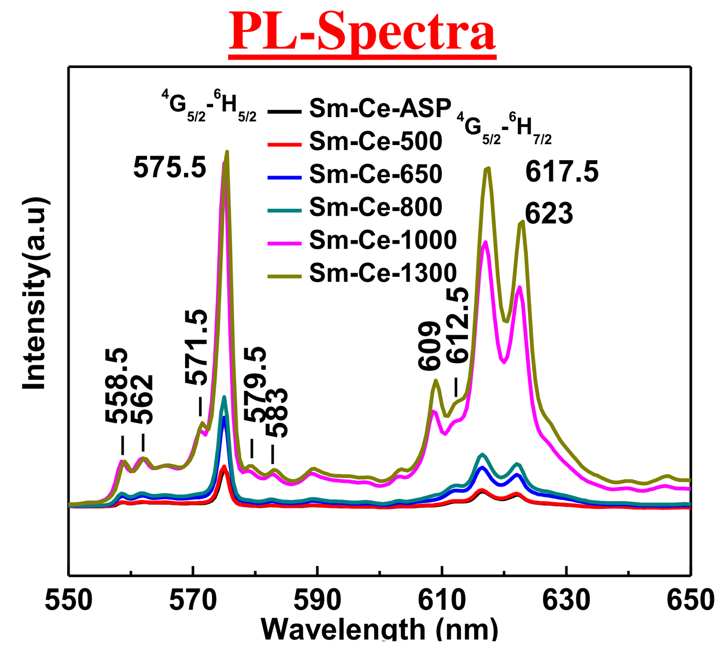
Condition	ASP	500°C	650°C	800°C
BG	2.91	2.81	2.83	2.95

XPS Spectra

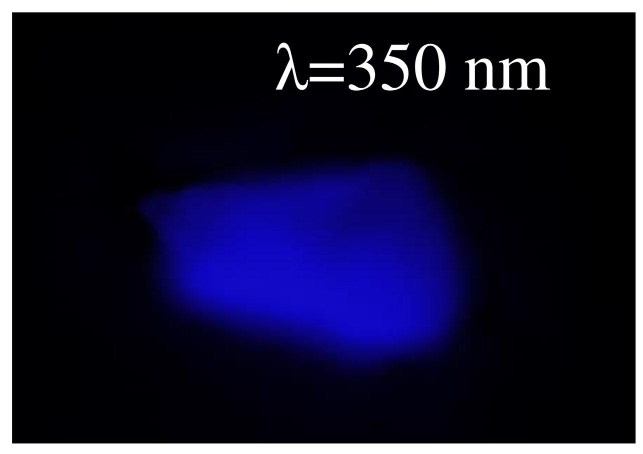


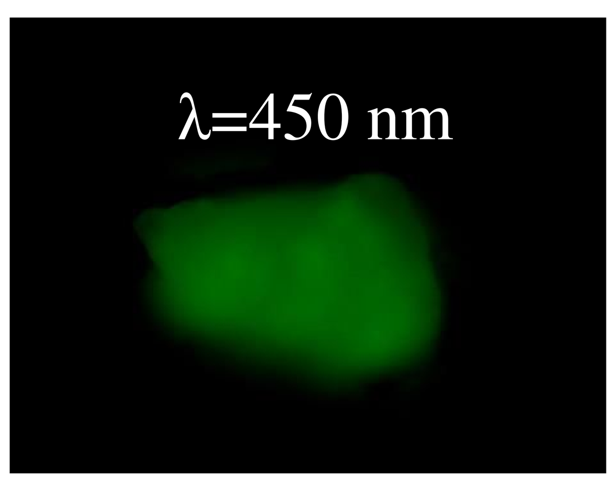


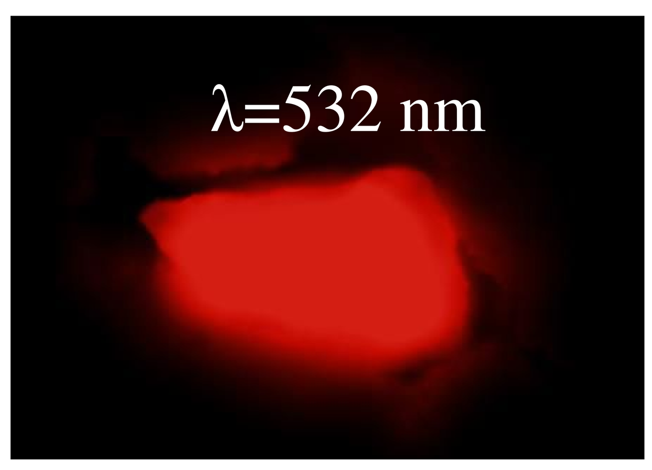
PL-Spectra



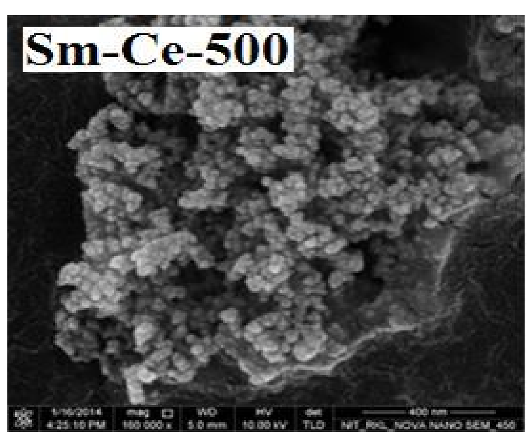
Fluorescent microscope images

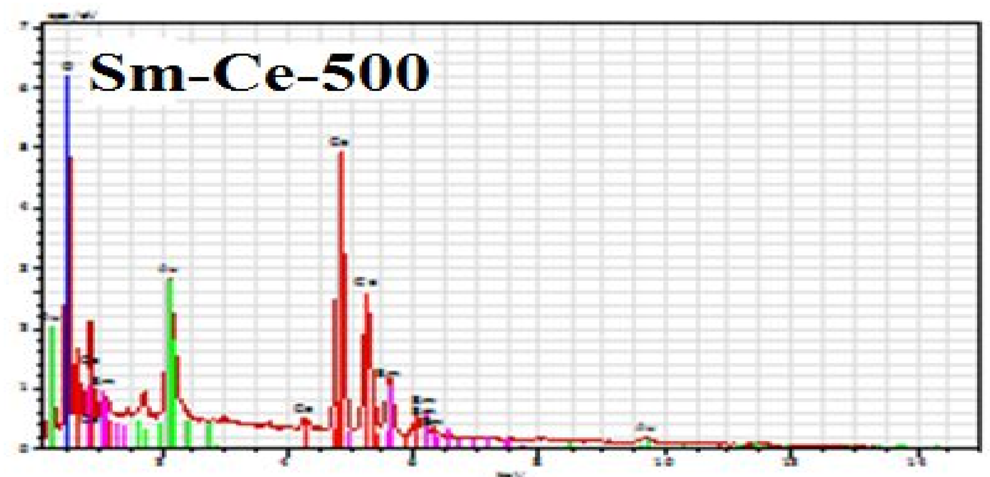




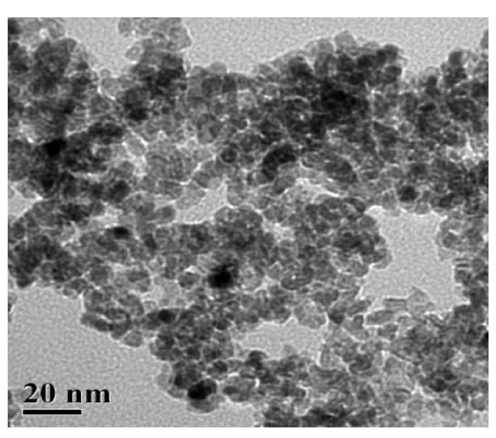


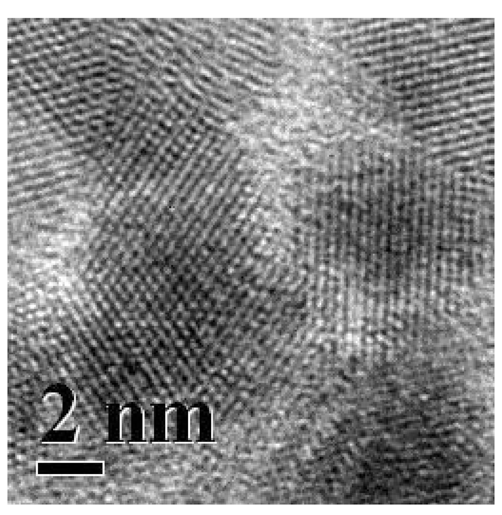
FESEM-Images

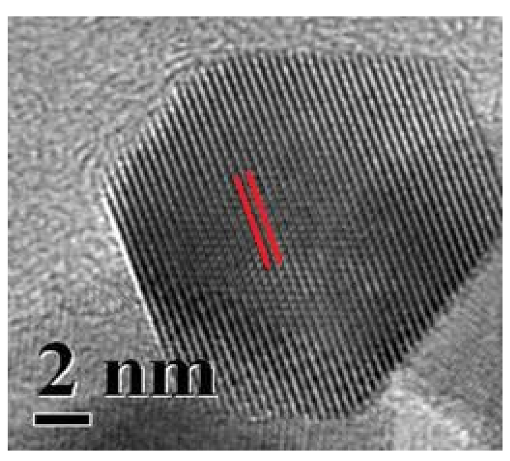




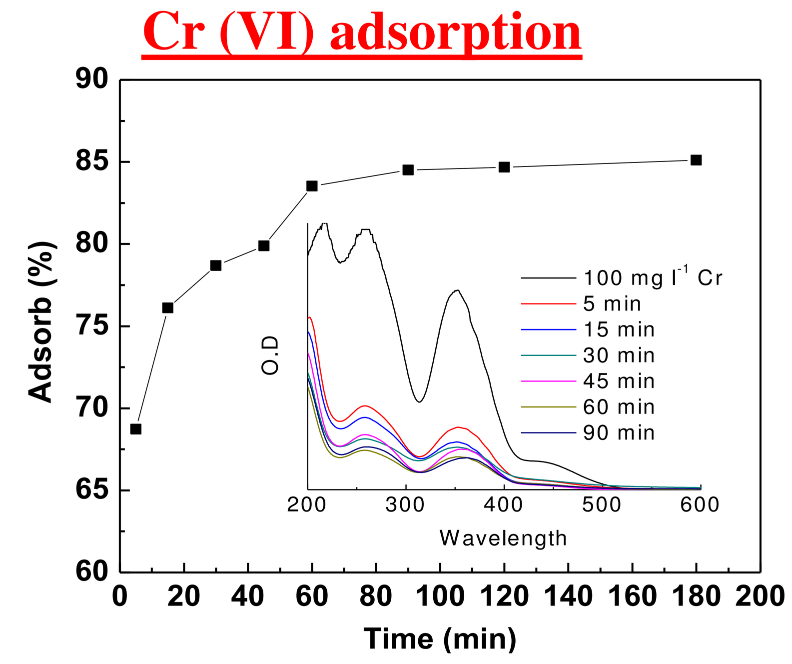
HRTEM-Images





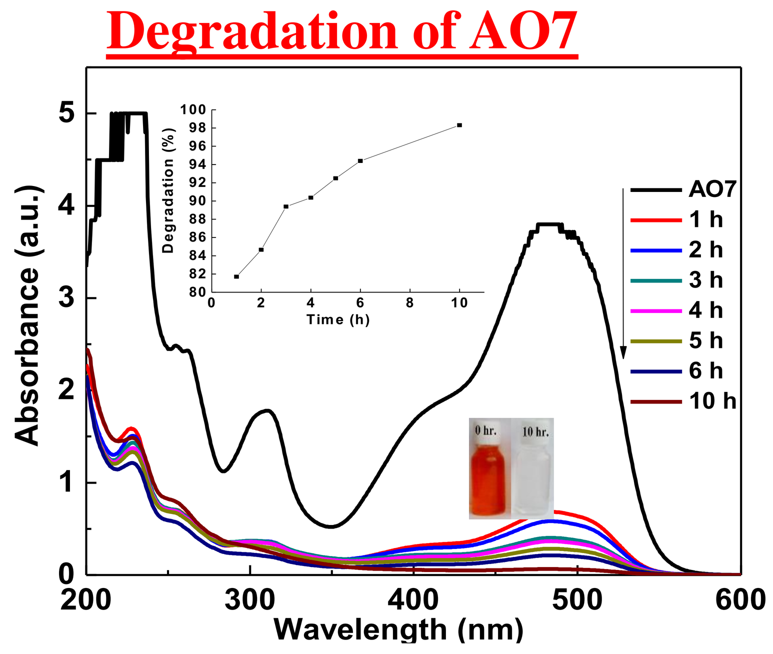


Cr (VI) adsorption



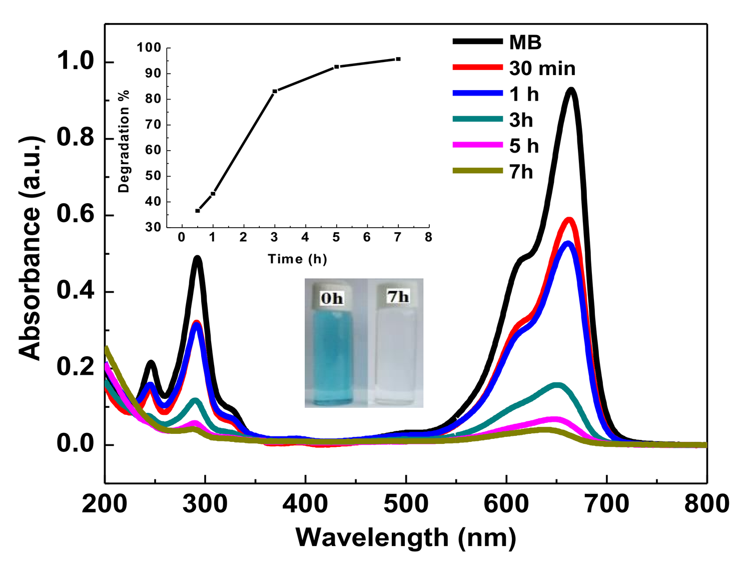
initial Cr (VI) conc 100 mg L^{-1}, amount of Sm-Ce-ASP 10g.L^{-1}. Without any further pH adjustment.

Degradation of AO7



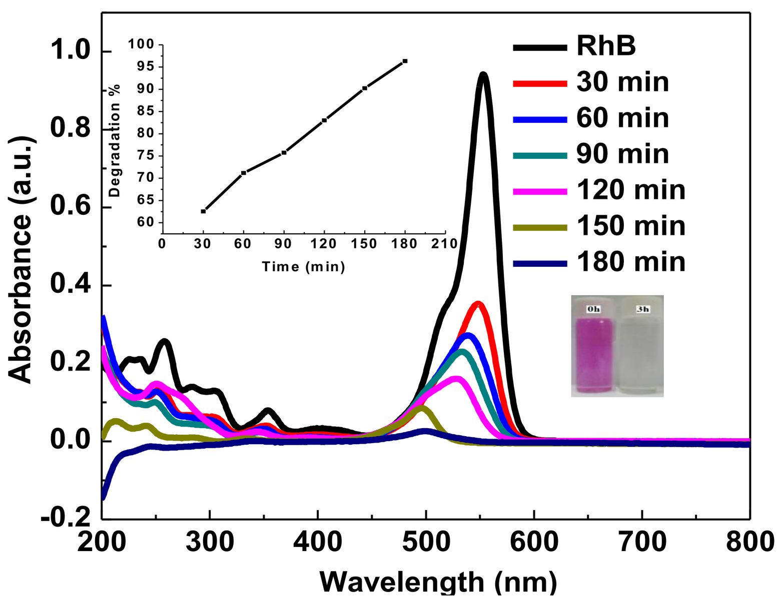
Initial AO7 conc 2X10^{-4}M, amount of Sm-Ce-500 1g.L^{-1}. under natural sunlight

Degradation of MB



Initial MB conc 2X10^{-5}, amount of Sm-Ce-500 1g.L^{-1}. under natural sunlight

Degradation of RhB



Initial RhB conc 2X10^{-5}, amount of Sm-Ce-500 1g.L^{-1}. under natural sunlight

Conclusions

- Multifunctional rare earth doped CeO_2 mesoporous materials with high crystallinity and high surface area have been successfully synthesized by a facile and low-cost method.
- Structural, spectroscopic, and electron microscopy techniques were used to characterize the prepared materials.
- The resultant Sm^{3+} doped CeO_2 exhibits excellent photocatalytic activities for degradation of toxic organic pollutant under natural sunlight irradiation in absence of any oxidising agents and over a broad range of pH values.
- CeO_2 :Sm^{3+} material having strong UV-visible absorption, and PL will have important applications in catalysis, and separation technology, and the possibility of these materials to be used as better UV blockers and nanoscale photoluminescent or nano-optoelectronic materials.

Publications

1. B. Mandal, A. Mondal, "Solar light sensitive samaria doped ceria photocatalysts: microwave synthesis, characterization and photodegradation of Acid Orange 7 at atmospheric condition and in absence of any oxidizing agents" **RSC Adv., 2015, 5, 43081–43091.**
2. B. Mandal, A. Mondal, S. S. Ray and A. Kundu "Sm doped mesoporous CeO_2 nanocrystals: aqueous solution-based surfactant assisted low temperature synthesis, characterization and their improved autocatalytic activity" **Dalton Trans., 2016, 45, 1679–1692.**