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Facile sol-gel preparation of Cd-doped cerium oxide (CeO_2) nanoparticles and their photocatalytic activities

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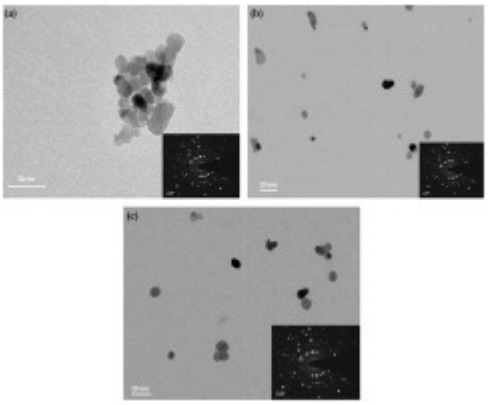
Highlights

- Nanostructured Cd-doped CeO_2 is synthesized using the facile sol-gel process.
- The structural studies reveal the cubic fluorite phase of Cd-doped CeO_2.
- The spherical/elliptical shaped particles can be seen in the SEM and TEM studies.
- The magnetic property of sample showed the ferromagnetic nature of CeO_2.
- The photocatalytic degradation of Rhodamine B and Congo red dyes are investigated.

Abstract

Nanostructured Cd-doped cerium oxide (CeO_2) is synthesized using the facile sol-gel process. The structural studies such as powder XRD, FTIR and Raman reveal the cubic fluorite phase of Cd-doped CeO_2. The SEM and TEM analyzes interpret the spherical/elliptical morphology of the Cd-doped CeO_2 nanoparticles of sizes ranging between 7 and 8 nm. The ferromagnetic nature of Cd-CeO_2 is confirmed by magnetization hysteresis loop measurements at room temperature. The Cd-CeO_2 samples show a strong absorption below 400 nm, which is much blue-shifted towards a shorter wavelength, indicating a narrow and uniform particle size distribution. From the PL studies, an intense green emission band is located at 530 nm due to the transition from the Cd donor level to the oxygen vacancies level traced in the CeO_2 band gap. The photocatalytic degradation of Rhodamine B and Congo red dyes in aqueous solution under UV irradiation in the presence of Cd^{2+} and Pd^{2+} doped CeO_2 samples are investigated on a comparative study. The high photocatalytic activity authenticates that Cd-CeO_2 nanomaterials are a kind of promising photocatalysts in remediation of water polluted by some chemically stable organic dyes.

Graphical abstract



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Introduction

On the technological front, there is a strong demand to develop new techniques to fabricate and measure the properties of nanomaterials related devices. In recent years, cerium oxide (CeO_2) nanoparticles have attracted much interest because of their unique physical and chemical properties [1]. CeO_2 nanoparticles display excellent

catalytic activity in most of the chemical reactions, due to the properties like high mobility and oxygen storage capacity within the lattice specially, cerium that readily changes between Ce^{3+} and Ce^{4+} states. Cerium oxide is a low-cost with highly effective alternative to noble metal catalysts. CeO_2 nanoparticles draw much attention because of their applicability to various areas such as optoelectronics, solid oxide fuel cells, gas sensors, and photocatalysis [2], [3], [4]. Recently, the solution-based techniques such as hydrothermal, sonochemical, precipitation, thermal decomposition and sol-gel methods [5], [6], [7], [8], [9], [10], [11], [12] have been adopted for the controlled synthesis of cerium oxide nanoparticles. Among various chemical syntheses for preparing metal oxides of large surface area, sol-gel process proves advantageous over the other methods for its better homogeneity, controlled stoichiometry, high-purity and phase-pure powders at a lower temperature. Moreover, CeO_2 nanomaterials have been studied and widely grown by different methods based on the reaction between stoichiometric metallic salts in a mixed solution without using any organic dispersant or capping agent often attributed to band tail effect related to intrinsic defects [13], [14], [15], [16].

Presently, the environmental pollution has been at the helm of affairs due to its harmful effect on human health and living organisms. Dyes from textile, paper and other industries are the prime sources of environmental contamination. Nowadays, the ejection of organic dye pollutant into the wastewater has become a serious problem and hence, drawn attention of the researches to develop photocatalytic materials that degrade these dye contents. Photocatalysis is one of the most promising techniques that can be used efficiently to achieve high removal rates of organic pollutants. It is important to find alternatives to the degradation of toxic dyes in an aqueous solution and destruction of several classes of organic dyes. Most conventional treatment processes are effective in water treatment, but they only transfer the contaminants from one medium to another or generate waste that requires further treatment and disposal. In this regard, the photocatalytic reactions on irradiated metal oxide powders have a good potential to remove the organic and inorganic waste materials from water. However, particle size, band gap, surface area, life-period of the electron-hole pair, stability, and other physical and chemical properties determine the photocatalytic efficiency of the material [17], [18], [19], [20], [21].

It is a known fact that one of the commonest ways to modify the characteristics of a material is doping the structure. Of late, the enhancement of the optical properties and photocatalytic activities of rare-earth metal oxide nanoparticles with dopants has been a subject of great interest. In the case of cubic fluorite CeO_2, particularly doped ones, has attracted attention due to its unique optical properties and competent applications in optoelectronic devices. One approach to producing strongly

luminescent nanoparticles is to injecting small quantities of dopant like transition metal elements. Accordingly, some transition metal ion dopants such as Fe, Mn, Ti, Pd and Co have been identified for the magnetic, optical and photocatalytic properties of the CeO_2 nanoparticles [22]. Sagar Vijay Kumar etal. [23] have synthesized an efficient and reusable nanostructured Zr-doped CeO_2 catalyst. Saranya etal. [24] found that Co-doped ceria nanoparticles have patronized photocatalytic activity under UV and visible light irradiation.

With the available sources of knowledge and literature, the current article seems to be the first report on the size, structural, morphological, optical and photocatalytic activities of Cd-doped CeO_2 nanoparticles via sol-gel process. The introduction of a small quantity of Cd^{2+} in the reaction system is found to have impacted greatly in controlling the size and shape. Furthermore, the photocatalytic degradation of Rhodamine B and Congo red dyes in aqueous media under UV irradiation in the presence of doped CeO_2 catalysts are investigated on a comparative study.

Section snippets

Experimental procedures

All the chemical reagents with commercial AR purity are used directly without further purification. In a typical synthesis, a transparent sol solution is prepared by controlled mixing of 0.1 M of Cerium (III) chloride heptahydrate ($CeCl_3{\cdot}7H_2O$) and cadmium chloride in 100 ml methanol under vigorous stirring, and the concentration of the Cd^{2+} ions is varied in the range of 1–3 mol % in relation to the cerium content. Further, 10 ml of an aqueous ammonia solution is added drop wise for chemical

Results and discussion

Fig. 1 (A) shows the XRD patterns of the Cd doped CeO_2 samples with 1–3% dopant concentrations. All the samples display broad diffraction peaks at the same position; they can be indexed to the cubic fluorite structure of CeO_2 and are well matched with

the data available in JCPDS (card no. 81-0792). No extra impurity peaks are observed for the Cd-doped CeO_2 nanoparticles, indicating the high purity of the final product, and the absence of the bulk transition metal phase in the doped CeO_2

Conclusions

A variety of metal ions such as Cd^{2+}, V^{2+}, Ni^{2+}, Ag^{2+} and Pd^{2+} doped CeO_2 nanoparticles has been successfully synthesized using the simple sol-gel method. Among them, the Cd^{2+} doped CeO_2 sample appears to be the best in terms of the crystallite size than the other metal ion dopants. The structural studies such as powder XRD, FTIR and Raman determine the cubic fluorite phase of Cd-doped CeO_2. The ferromagnetic nature of the Cd-CeO_2 nanomaterials is confirmed by the room temperature magnetization

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