Synthesis and characterization of CeO₂ nanoparticles by hydrothermal method

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ABSTRACT

Crystalline structure, phase and surface morphology of ceria nanostructure was discussed in detail in the recent work. Our latest work is persistent on ceria nanostructure by conventional and plant extract–mediated synthesis starting from cerium nitrate as precursors for putrefaction of pollutant in the industrial wastewater. The crystalline structure, surface morphology, phases, functional groups and size were examined by assorted characterization techniques like powder X-ray diffraction pattern (XRD), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM). Therefore, the pure phases of ceria nanostructure were investigated by XRD analysis. The surface morphology, shape and unique size of synthesized ceria established through electron microscopy were reported in detail.

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Selection and peer-review under responsibility of the scientific committee of the NANOSMATAFRICA-2018.

1. Introduction

Cerium is comparatively earth-abundant and its oxides like CeO₂ and Ce₂O₃ are recognized to have bandgaps to generate a reactive oxygen species in the visible region [1]. Ceria is a highly existing rare earth metal oxide and has attracting interest in the past decade as possible material [2]. CeO₂ nanostructure is a n-type semiconductor which is coupled with wealthy oxygen vacancies, in current research, ceria has been established to be a capable photocatalyst for the removal of industrial pollutants in the environmental owing to the redox property of the two stable oxidation state of ceria (Ce⁴⁺/Ce³⁺), strong absorption of light, stability, non-toxicity and availability [3–6]. In the present study, ceria nanostructure was synthesized by chemical conventional and plant-mediated method and characterized by various techniques [7–10].

2. Materials and methods

2.1. Materials

Ce(NO₃)₂·6H₂O, (Merck) as the oxidizing agents used without any purification. All the chemicals utilized in this work are analytical grade purchased from Merck, India. Acalypha indica plant leaf extract acted as capping agent and stabilizing agents in the synthesis of CeO₂ nanostructure process and solutions were prepared by using DD water.

2.2. Preparation of the plant extracts

Acalypha indica plant leaf extract was prepared from 20 g part of plants, which were washed to remove the dust and used in this present work as an alternative of toxic organic compounds. The leaves of the plants are isolated for grinding with help of 50 ml of double deionized water. The mixture was stirred carefully and maintained in ice cold condition for 3 h. The extract was separated by filtration and used for further reaction.
2.3. Preparation of ceria by plant extract - mediated synthesis

0.1 M cerium nitrate solution were prepared by using DD water and stirred to get homogeneous solution. The plant extract was added slowly to the cerium nitrate solution with constant stirring for 5 h and the reaction was carried out at room temperature. This mixture solution was kept in the oven for further heating at 200 °C for 5 h for removal of easily volatile compounds like water. Finally, the obtained greenish yellow porous sample was ground with help of a mortar and pestle and sintered at 500 °C for 6 h in the high temperature muffle furnace. As a result, the yellow colour ceria powder was obtained which was washed with deionized water, acetone and dried in hot air oven. The ceria sample obtained by this method was label as CE1.

2.4. Preparation of ceria by conventional method

0.1 M cerium nitrate solution were prepared by using DD water and stirred to get homogeneous solution. 0.1 M hydrazine was added to the prepared cerium nitrate solution with vital stirring via magnetic stirrer. In the reaction procedure, the pH of the solution was maintained at almost 10. The obtained pale-yellow precipitate was intense at 120 °C for 3 h in the oven. Further the obtained precipitate was filtered and sintered at 500 °C for 6 h. As a result, the yellow colour ceria powder was obtained which was washed with deionized water, acetone and dried in hot air oven. Thus, CeO₂ nanopowder was obtained was labelled as CE2.

2.5. Characterization studies

To determine the phase structure and the crystalline purity of nanocrystalline samples, Rigaku Ultima IV high tenacity diffractometer was utilized from the 2 theta values in between 10° to 80° using CuKα radiation at λ = 1.5418 Å. The superficial shape of the nanocrystallites was analyzed by Scanning Electron microscope (Joel JSM 6360 microscope with accelerated voltage 15 kV). The functional groups in the ceria samples were identified by Fourier transform infrared spectrometer (Excalibur Series FTIR).

3. Results and discussion

3.1. Crystalline structure identification by PXRD studies

The crystalline structure and phase of the synthesized samples were investigated by XRD pattern as shown in Fig. 1. PXRD pattern of both the synthesized CeO₂ nanostructures shows the most important peaks at 2θ = 28.22°, 33.02°, 47.23°, 56.39°, 59.54°, 69.61°, 76.80°, 79.07° and 88.56° with the planes (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1), (4 2 0) and (4 2 2) respectively (JCPDS No.43-0394) [5,11]. It's proved the both the samples shows cubic fluorite structure of CeO₂ [6,12]. In the diffraction pattern, the observed peaks are corresponds to cubic ceria phase and proves the absence of metal hydroxide, metallic and other oxide phase of ceria [13]. From the result, the diffraction peak of ceria nanoflower show significantly wider peaks than the other samples, which illustrates that the grain size of the materials is smaller., their mean crystallite sizes are calculated via Scherrer's equation: D = 0.89λ/(βcosθ), the crystallite size of CE1 nanosphere sample is 85.6 nm, and the CE2 nanoflower sample is 20.2 nm. For the CE2 nanoparticle sample, the XRD patterns showed extremely sharp and intense peaks, signifying its high crystalline structure [14–16].

3.2. Fourier transforms infrared spectral studies (FTIR)

The FTIR spectral studies of the ceria (CE2) nanoparticles exposed that the formation of oxides of metal nanostructures as shown in Fig. 2(a-b). A wider absorption band around 3430 cm⁻¹ is attributed to hydroxyl stretching frequency of ceria nanostructures. The band occurred at 1634 cm⁻¹ owing to the bending vibrations of water molecules adsorbed on the surface of the ceria nanoflower and band appears at 659 cm⁻¹ corresponds to metal oxygen bond stretching mode. In additional a band appears at 555 cm⁻¹ due to M–O stretching modes of nanostructures [6,17].

3.3. Scanning electron microscope (SEM)

The surface morphology of the synthesized ceria (CE1 & CE2) by conventional and plant extract - mediated synthesis was examined by scanning electron microscopy. Fig. 2(a-d) depicted the SEM images of ceria (CE1 & CE2) by conventional and plant extract - mediated synthesis [7,8,18]. The SEM image observed at high and low magnification for the CE1 sample has agglomeration of nanoparticle as shown in Fig. 3(a-b). Also, it’s clearly noted that CE2 sample is observed to be in the form of nanoparticle structure shown in the Fig. 3(c-d). The SEM analysis proved both the nanostructure are uniformly arranged due to the crystallinity of the samples. The average particle size for CE1 and CE2 was found to be 55–90 nm and falls 35–45 nm [9,10].

Fig. 1. PXRD pattern of a) CE1 and b) CE2 nanostructures of CeO₂ nanoparticles.

Fig. 2. FTIR spectra of CE2 nanoparticles.
4. Conclusion

CeO$_2$ nanoparticles were effectively developed by conventional and plant extract-mediated synthesis for putrefaction of Congo red dye in the industrial wastewater. CeO$_2$ nanoparticles were examined by various characterisation techniques to depict their crystalline nature and surface morphology. The prepared CeO$_2$ nanoparticles observed almost high agglomeration and crystallinity. The XRD investigation proves the maximum purity and crystallinity of the samples. The photocatalytic experiment with the CE2 catalyst has better effect when compared with the other CE1 samples due to the more active surface area, advanced capability in the direction of absorption of solar light, lesser size effect with prominent diffusion.

CRediT authorship contribution statement

C. Maria Magdalane: Supervision, Methodology, Writing - original draft, Data curation. K. Kaviyarasu: Visualization. B. Siddhardha: Visualization, Investigation. G. Ramalingam: Methodology, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References


Fig. 3. SEM image of (a-b) CE1 and (c-d) CE2 nanostructures of CeO$_2$ nanoparticles.