



ORIGINAL ARTICLE

Preparation of nanosized yttrium doped CeO₂ catalyst used for photocatalytic application



A. Akbari-Fakhrabadi ^{a,*}, R. Saravanan ^{b,*}, M. Jamshidijam ^{c,d},
R.V. Mangalaraja ^c, M.A. Gracia ^e

^a Advanced Materials Laboratory, Department of Mechanical Engineering, University of Chile, Beauchef 851, Santiago, Chile

^b Department of Chemical Engineering and Biotechnology, University of Chile, Beauchef 850, Santiago, Chile

^c Advanced Ceramics and Nanotechnology Laboratory, Department of Materials Engineering, University of Concepcion, Concepcion, Chile

^d Department of Materials Engineering, Islamic Azad University, Sirjan Branch, Sirjan, Iran

^e Laboratorio de Nanociencias y Nanotecnología (FCFM), Universidad Autónoma de Nuevo León, Monterrey, Nuevo León, México

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Abstract In the present work, the pure CeO₂ and yttrium doped CeO₂ nanopowders were synthesized by the nitrate-fuel self-sustaining combustion method and calcined at 700 °C for 2 h. X-ray diffraction (XRD) and high resolution electron transmission microscopy (HRTEM) results demonstrated a cubic fluorite with high purity and the crystallite sizes less than 20 nm calculated from Scherrer's formula. The BET specific surface area of yttrium doped CeO₂ samples showed high values than those of pure CeO₂. The photocatalytic activity of yttrium doped CeO₂ showed high degradation of Rhodamine B solution under visible light illumination.

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1. Introduction

Water is essential for every living organism despite the fact that the quality and quantity of fresh water on earth is incomplete in accomplishing human needs. In the past years, the developing countries have met the dangerous effects on the

* Corresponding authors.

E-mail addresses: aliakbarif@ing.uchile.cl (A. Akbari-Fakhrabadi), saravanan3.raj@gmail.com (R. Saravanan).

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environment due to the failure of pure water supply. Water contamination has led to major health risks which grow at a faster rate every year. According to a report given by the World Health Organisation (WHO), about 2.2 million people die due to water related problems every year, of these 90% are children [1]. Thus, water pollution creates major environmental issues around the globe. Nowadays, water gets polluted due to several reasons in the atmosphere such as population growth, releasing of effluents from industries and agricultural activities. In spite of so many factors that affect the quality of water, contaminants coming from the textile industries are one of the major causes for water pollution. In these industries, azodyes such as acid red 88 and methyl orange are used for dyeing purposes. These azodyes were found to have great

hazardous effects on human health and environment [2–4]. One of the best ways to reduce the contamination of water is by photocatalytic treatment [2].

In the recent years, semiconductor based photocatalysts are attractive and significantly degrade the textile effluents. The large band gap semiconductors like titanium dioxide, zinc oxide, tin oxide are mostly used as photocatalytic materials due to their versatile properties such as thermal and chemical stability, low cost and eco-friendly [5–8]. Apart from these materials, cerium oxide (CeO_2) is one of the large bandgap semiconducting materials having lot of advantages and broad applications [9]. However, the CeO_2 is restricted to degrade pollution under visible light. The natural sunlight consists of ~45% visible region. Therefore, many researchers have focused in the field of photocatalyst that aims to increase the degradation efficiency in the visible light. Many efforts have been explored to extend the absorption wavelength of CeO_2 into the visible region by using metal doping, semiconductor coupling and so on [10–11]. Doping is a simple way to reduce the bandgap and led to extended photocatalytic activity from UV to visible light. Doping metal ion into cerium oxide effectively prevents the electron hole recombination and led to achieve photocatalytic activity under visible light.

In this present study, nanosized CeO_2 and yttrium doped CeO_2 were prepared by the combustion method as a simple and economical method. The structure and size of the prepared catalyst were analyzed by XRD and HR-TEM analysis. The surface area of the prepared material was examined by BET measurement. The optical bandgap of the catalysts was calculated using UV–Vis reflectance spectrometer measurements. Finally, the prepared catalysts were used to degrade Rhodamine B solution under visible light illumination and their results are discussed in detail.

2. Materials and methods

For the preparation of pure CeO_2 and yttrium doped CeO_2 nanopowders; all the required chemicals were purchased from Sigma–Aldrich and all the aqueous solutions were prepared using double distilled water.

The pure CeO_2 and yttrium doped CeO_2 nanopowders were synthesized by the nitrate-fuel self-sustaining combustion method. As the precursor reagents, the molecular proportions of the corresponding cerium and yttrium-nitrate hexahydrates were dissolved in 100 ml of double-distilled water to form a mixed homogeneous solution. Then, the required amount of citric acid, calculated from the basic principle of propellant chemistry [12], was added as an organic fuel. The equivalence ratio, i.e. the ratio of the oxidizing valency to the fuel was maintained at unity ($\text{O/F} = 1$) and the valency of nitrogen was not considered due to its conversion to molecular nitrogen (N_2) during combustion. After making a clear homogeneous precursor solution, the reaction mixture was transferred into an alumina crucible and inserted inside a preheated furnace at a temperature of 500 °C. Once the reaction mixture reached the point of spontaneous combustion, it started burning vigorously. As a result of the chemical reaction, porous solid foam was obtained within a few minutes. The as-combusted foams were collected and converted to powders by gentle grinding, and then calcined at 700 °C for 2 h to obtain full crystalline nanopowders [13,14].

2.1. Characterization details

Crystalline nature and phase purity were examined using the powder X-ray diffraction (XRD) technique (X'Pert Pro, Philips X-ray diffractometer) with Cu K_α radiation. The crystallite sizes were determined using Scherrer's equation [15]. The surface area of the prepared powders was obtained by the Brunauer–Emmett–Teller (BET) method [16]. Microstructures of the powders were analyzed by high resolution transmission electron microscopy (HR-TEM, FEI TITAN G2 80-300) operated at 300 kV. Compositional analysis was performed by scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) linked with TEM. The optical reflectance spectrum and the photocatalytic activity of the irradiated samples were measured by a UV–Visible spectrophotometer (Perkin Elmer Lambda 11).

3. Results and discussion

As demonstrated in Fig. 1, the X-ray diffraction patterns of the pure CeO_2 and yttrium doped CeO_2 powders show a single phase with cubic fluorite crystal structure, Fm3m space group [17,18], which shows full incorporation of yttrium dopant into the ceria lattice and forming a solid solution of the Y_2O_3 – CeO_2 system [19,20]. Comparing the XRD pattern of pure CeO_2 , the yttrium doped CeO_2 nanopowders revealed that the decrease in peak intensity and FWHM shows the minimum crystallite size [21].

Calculations based on the (1 1 1) diffraction peak's broadening in the XRD patterns represent that the crystallite sizes (D_{XRD}) of pure CeO_2 and yttrium doped CeO_2 nanopowders are 19.5 and 17 nm respectively, which were defined by using Scherrer's formula [15].

$$D_{\text{XRD}} = \frac{0.9\lambda}{B_{hkl} \cos \theta_{hkl}}$$

where B_{hkl} is the full width at half maximum (FWHM) excluding the instrumental broadening.

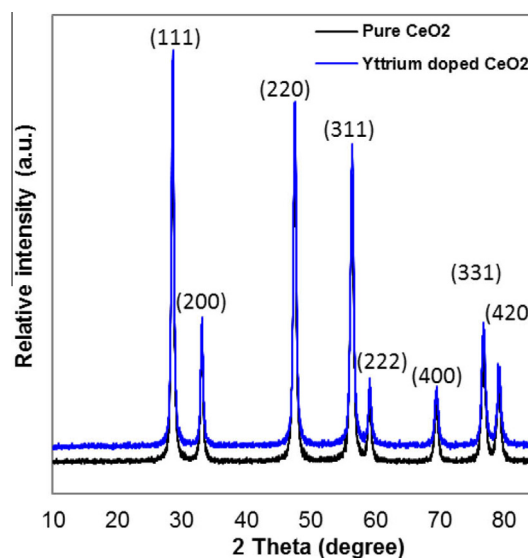


Figure 1 X-ray diffraction pattern of synthesized pure CeO_2 and yttrium doped CeO_2 nanopowders.

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