



# Synthesis and characterization cerium containing zirconium oxide ( $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ )

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## Abstract

Due to the toxicity of organic compounds like dyes environmental pollution increases day by day. So it is essential to develop a technique which can decompose these toxic compounds effectively without creating any further toxicity. In this paper, we reported synthesis and characterization of visible light active cerium zirconate via solid state calcination method at 800°C. In Solid state calcination reaction, highly photoactive powder of cerium zirconate was obtained by heating a 1:1 molar mixture of zirconyl oxychloride and ceric nitrate at 800 °c for 24 hrs. The prepared photocatalysts were then characterized by XRD and UV-Vis diffuse reflectance analyses. The XRD spectra of as prepared sample can be indexed and matches with the  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  (ICDD file 00-038-1436) having tetragonal structure with space group P42/nmc. The highest intensity of the (111) peak suggests that nano particles of CZ-SSR are growing along the (200) plane, providing active surface area for photocatalysis.

## Introduction

Titanium Dioxide ( $\text{TiO}_2$ ) is most commonly used photocatalytic material for the degradation of organics and dyes present in water, because it has excellent physical or chemical properties and has ability to decompose organic species<sup>1</sup> but  $\text{TiO}_2$  works under UV light due to its wide band gap and hence main part of solar spectrum cannot be used effectively. Several modifications of  $\text{TiO}_2$  have been carried out to observe the changes in the photocatalytic activity. Thus,  $\text{TiO}_2$  needs to be modified by doping other element to reduce its wide band gap and extend the optical absorption range to long wavelength. By reducing the recombination rate of electrons-holes, decreasing  $\text{TiO}_2$  grain size and increasing specific surface area of  $\text{TiO}_2$ , the photo-catalytic activity can be enhanced<sup>2</sup>. Recently, the modified composites of  $\text{TiO}_2$  with other oxides, particularly with  $\text{ZrO}_2$  has been used, which have much better photocatalytic activities for decomposition of organic pollutants than  $\text{TiO}_2$  under the same reaction conditions<sup>3</sup>. Yang and Ferreira (1998) also found that doping with a certain amount of Zr could improve the surface area of  $\text{TiO}_2$  powder<sup>4</sup>. Meanwhile, they found that the augment of the surface area could increase the ability of surface to adsorb  $\text{O}_2$  and  $-\text{OH}$ , and then increase the opportunity to accept electron. Over catalyst doped with Zr, some  $\text{Zr}^{4+}$  are adsorbed on the particle





surface, which boosts the surface potential to certain extent, and helps the free electrons diffuse from the interior to the surface, improving the photo-catalytic activity of catalyst.

Nowadays,  $\text{CeO}_2\text{-ZrO}_2$  is one of the important catalytic supports due to its use in the three way catalysts<sup>5</sup>. It is applied in these systems due to its high oxygen storage capacity. The incorporation of zirconium into the ceria lattice creates a higher concentration of defects improving, the  $\text{O}^{2-}$  mobility, such mobility would explain the excellent ability to store and release oxygen<sup>6</sup>.  $\text{CeO}_2$  is a fluorite type semiconductor crystal with bulk bandgap estimated to be 3.16 eV. That means a photo-irradiation with wavelength lower than 388 nm would be capable of exciting the photocatalytic activity in bulk ceria compounds. Actually, though not yet been intensively studied and used as photocatalysts,  $\text{CeO}_2$  and  $\text{CeO}_2$ -based materials have already been exploited widely in various catalytic systems. The unique capability of exchanging lattice oxygen and environmental oxygen species due to their non-stoichiometric switch between  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  ionic states renders them effective catalysts as catalytic converters in automobiles, electrolytes in solid oxide fuel cells, gas sensors, etc<sup>7-11</sup>.

The ion exchange reactivity and oxygen storage capacity is highly limited for pure ceria system due to the equilibrium ratio between  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  ions in room temperature. To improve their free radical scavenging activity and protective power on living systems, scientists have selected zirconium to substitute cerium to achieve the enhancement<sup>12</sup>.

However, to our knowledge, Zhong et al, has been studied effect of metal doping into  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  on photocatalytic activity of  $\text{TiO}_2/\text{Ce}_{0.45}\text{Zr}_{0.45}\text{M}_{0.1}\text{O}_x$  ( $\text{M} = \text{Y, La, Mn}$ )<sup>13</sup>. The catalytic activities of binary composite photo-catalysts  $\text{CeO}_2/\text{TiO}_2$ ,  $\text{ZrO}_2/\text{TiO}_2$  and the ternary composite photo-catalysts  $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-CeO}_2/\text{TiO}_2$ ,  $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-ZrO}_2/\text{TiO}_2$  were significantly higher than un-doped  $\text{TiO}_2$ <sup>14</sup>. Fe-substituted  $\text{CeVO}_4$  synthesized by solution combustion method has higher photocatalytic activity for degradation of dyes as compared to commercial Degussa P-25  $\text{TiO}_2$  and  $\text{CeVO}_4$ <sup>15</sup>. Monophasic  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  Solid solution synthesized by microwave induced combustion method has been used for various applications<sup>16</sup>. Omata et al, has been studied photocatalytic degradation of methylene blue aqueous solution over a pyrochlore-related  $k\text{-CeZrO}_4$  phase under irradiation with Xe discharge light within 8hrs.<sup>17</sup>. Hence the objective of this work is to synthesize  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  by Solid state method used under visible light for free radical scavenging application .

## Experimental Section:

### Synthesis of Photocatalyst:

All the reagents used during experiment are of A R grade. Deionized water was used throughout the experiments. In solid state calcination reaction, highly photoactive powder of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  was obtained by heating a 1:1 molar mixture of zirconyl oxychloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) and ceric nitrate ( $\text{Ce}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ ) at 800°C for 24 hrs. Both the fine powder reagent were mixed in mortar and grinded finely and then heated in oven at 100°C for 24 hrs. During heating at 800°C in muffle

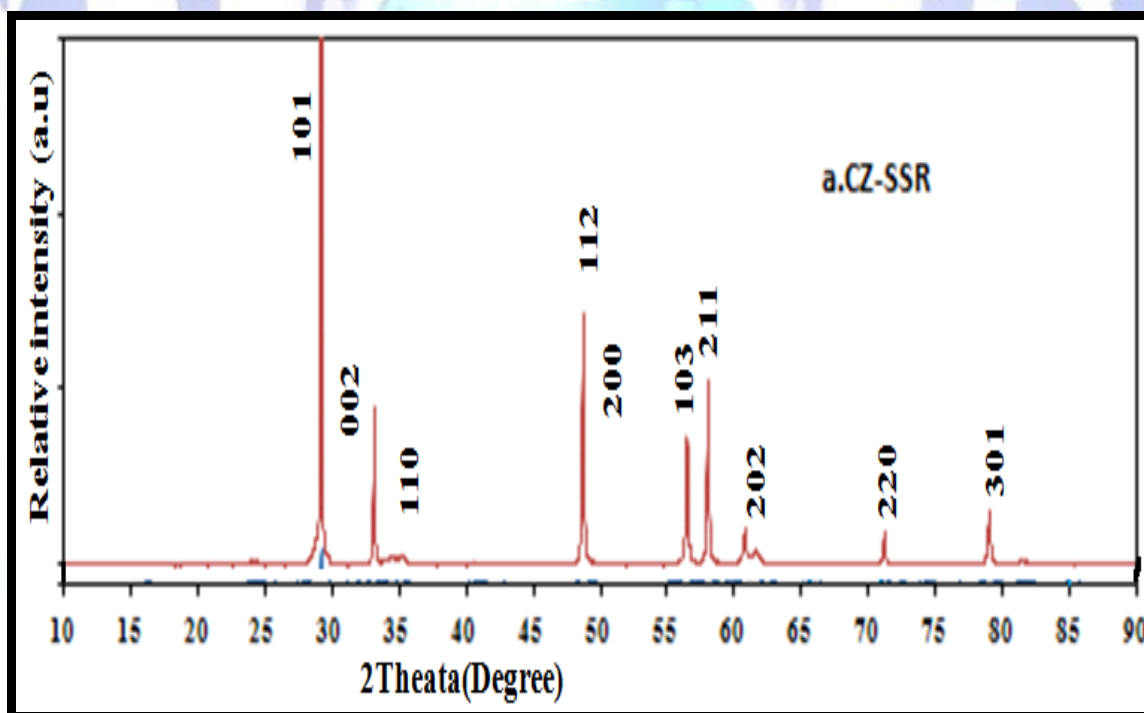


furnace, repeated grinding of the powder is carried out for the high agglomeration and compositional in homogeneity of the powders.

The  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  sample synthesized by solid state calcination reaction was labeled as CZ-SSR. The crystalline phase structure was determined by Bruker D8 Advance X-ray diffractometer (XRD) using Cu K- radiation. Optical Properties of synthesized material were studied by using UV- VIS diffuse reflectance spectroscopy (UV-1800, Shimadzu ).

## Result and Discussion:

**XRD Analysis:** The crystalline nature of the synthesized  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  photocatalyst was studied by powder X-ray diffraction (XRD) as shown in Figure 1. The XRD spectra of as prepared sample can be indexed and matches with the  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  (ICDD file 00-038-1436) having tetragonal structure with space group **P42/nmc**. The highest intensity of the (111) peak suggests that nano particles of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  are growing along the (200) plane, providing active surface area for photocatalysis. The XRD patterns of the mesoporous  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  nano particles show that the (111), (200) and (220) peaks and the broadening of XRD peaks clearly indicates the nanocrystalline nature of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ .

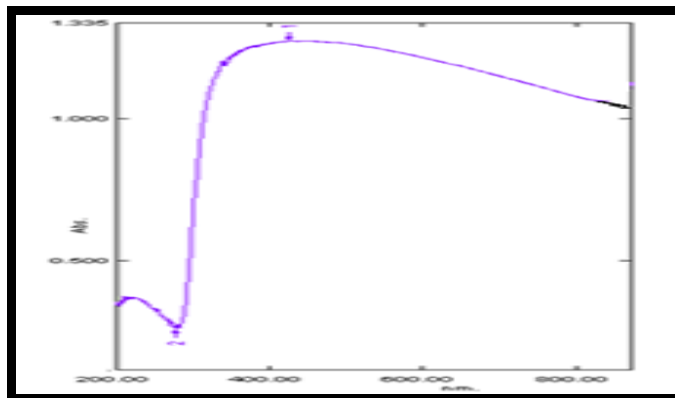


**Figure 4.1:** The XRD patterns of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ .

**UV-Visible diffuse reflectance study:** The UV-Vis diffuse reflective properties of synthesized material strongly influence photocatalytic activity. Diffuse reflectance spectra of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  that materials absorb in 400nm-600nm range. DRS spectra of synthesizes material  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  in Figure 2. This result is in good consentient with the result of photocatalytic activity.  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  absorb at 443nm which shows that catalyst is visible light active. The band gap of the samples was determined by the equation  $E_g = 1239.8/\lambda$ , where  $E_g$  the band gap (eV) is and  $\lambda$  (nm) is the



wavelength of the absorption edges in the spectrum<sup>34</sup>. The band gap energies of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  was estimated using UV-visible absorption spectra at  $\lambda$  onset 443nm found to be about 2.79. This  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  can absorb in visible light.



**Figure 2:** DRS of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$

## Conclusions:

$\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  was successfully synthesized via solid state calcination method and its crystalline nature was studied by XRD and their optical absorption spectra were recorded. The low band gap of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  (2.79 eV) make it visible light active. The band gap energies of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  was estimated using UV-visible absorption spectra at  $\lambda$  onset 443nm found to be about 2.79. Thus  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  can absorb in visible light and can work in presence of solar spectrum.

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