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Zirconium Oxide Doped with Hafnium Oxide by Hydrothermal Method

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Abstract

Zirconium oxide doped with Hafnium oxide were prepared by hydrothermal method and characterized by using X-ray diffractometer, morphological studies are studied by using Scanning Electron Microscopy and CV studies and its parameters value were reported here. XRD is good agreement with the JCPDS file no: 06-0318 and its size was nearly 58 nm. The calculated lattice parameter values were well matched with this file number. Cube shaped size of the annealed sample was observed by scanning electron microscopy. CV studies inferred that with increasing of the photocurrent at higher voltage, the current increases.

Keywords: CV studies; SEM; XRD; Hafnium oxide

Abbreviations: RGO: Reduced Graphene Oxide; CZ: Charged Zirconium Phosphates; JCPDS: Joint Committee on Powder Diffraction Standards; XRD: X-ray Powder Diffraction; FWHM: Full Width at Half Maximum; SEM: Scanning Electron Microscopy; CV: Current Voltage.

Introduction

Research into future alternatives has been and still being conducted aiming to solve the complex problems of this recent time, e.g., rising energy requirements of a rapidly and constantly growing world population and global environmental pollution. Therefore, options for a long-term environmental friendly energy supply have to be developed leading to the use of renewable sources (water, sun, wind, biomass, geothermal, hydrogen) and fuel cells. Renewable could shield a nation from the negative effect in the energy supply, price and related environment concerns. There is strong scientific evidence that the average temperature of the earth's surface is rising. This is a result of the increased concentration of carbon dioxide and other GHGs in the atmosphere as released by burning fossil fuels. This global warming will eventually lead to substantial changes in the world's climate, which

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will, in turn, have a major impact on human life and the built environment. Therefore, effort has to be made to reduce fossil energy use and to promote green energies, particularly in the building sector. Energy use reductions can be achieved by minimizing the energy demand, by rational energy use, by recovering heat and the use of more green energies. This study was a step towards achieving that goal. The adoption of green or sustainable approaches to the way in which society is run is seen as an important strategy in finding a solution to the energy problem. The key factors to reducing and controlling CO_2, which is the major contributor to global warming, are the use of alternative approaches to energy generation and the exploration of how these alternatives are used today and may be used in the future as green energy sources. Even with modest assumptions about the availability of land, comprehensive fuel-wood farming programmes offer significant energy, economic and environmental benefits. Deposition by using semiconducting oxides is and its solar cells fabrications are essential one for this era.

Zirconium dioxide (ZrO_2), sometimes known as zirconia is a white crystalline oxide of zirconium. Its most naturally occurring form, with a monoclinic crystalline structure, is the mineral baddeleyite. The main use of zirconia is in the production of ceramics. Stabilized zirconia is used in oxygen sensors and fuel cell membranes because it has the ability to allow oxygen ions to move freely through the crystal structure at high temperatures. This high ionic conductivity (and a low electronic conductivity) makes it one of the most useful electro ceramics. Zirconium dioxide is also used as the solid electrolyte in electro chromic devices [1]. Because of its very high melting point, hafnium is also used as a refractory material in the insulation of such devices as thermocouples, where it can operate at temperatures up to 2500°C. Multilayered films of hafnium dioxide, silica, and other materials have been developed for use in passive cooling of buildings. The films reflect sunlight and radiate heat at wavelengths that pass through Earth's atmosphere, and can have temperatures several degrees cooler than surrounding materials under the same conditions [2].

Reported the use of zirconia abutments has increased because of aesthetics, but sometimes customization was necessary and its effect was unclear. This study evaluated the marginal fit and torque loss of customized and non-customized aesthetic zirconia abutments associated with Morse taper implants before and after thermo mechanical cycling [3]. Reported to develop an efficient V-based catalyst for oxidative dehydrogenation, of ethane by CO_2, MCM-41was modified with various metal oxides (Mg, Al, Zr) and then, impregnated with aqueous solution of NH_4VO_3 and then tested in dehydrogenation of ethane with CO_2 at different temperatures. A series of zirconia supported molybdenum oxide materials with Mo loadings of 7, 12, and 19 wt% were synthesized using incipient wetness impregnation, the anisole hydrodeoxygenation performance of the catalysts was evaluated at gas phase conditions in a fixed bed tubular reactor in plug flow regime. A predominant selectivity towards hydrodeoxygenation and methyl transfer reactions rather than to hydrogenation was observed, irrespective of the Mo loading and further treatment, yet interesting differences in activity were observed [4].

In order to construct Reduced Graphene oxide (RGO) contained 3D ordered chiral architecture and exploit the anisotropic properties of RGO to develop functional soft matter, a brand new nanosurfactant which is two dimensional charged zirconium phosphates (CZ) nanoplatelet is firstly designed and applied to disperse RGO in liquid phase and ordered soft matter. The rheological behavior analysis shows the RGO suspensions can change from unhomogeneous non-Newtonian nanofluids to homogeneous Newtonian nanofluids after being exfoliated by CZ nanoplatelets [5].

Indeed, it is worthwhile to note that the evolutions observed on the specific surface areas recorded on ZrO_2 doped with HfO_2 and well match with the evolutions of the crystallite size with JCPDS 06-0318 file number of Hafnium oxide. Clearly, the loss in specific surface area more accentuated for ZrO_2 than for HfO_2 at increasing annealing temperature, is consistent with a faster particle growth on ZrO_2 doped with HfO_2 underlined in Table 1. Hence ZrO_2 incorporation to Hafnium improves the thermal stability by decreasing the rate of the crystallite growth process then preserving the specific surface area. After calcinations at 300 °C, the sintering is very important for all samples. The specific surfaces areas are in the same margin error and do not exceed 1 $m^2.g^{-1}$ [6].

Sample	JCPDS file (2θ)	Observed (2θ)	d-spacing JCPDS	Observed d-spacing	FWHM	Crystal size (nm)
HfO_2	28.336	28.00	3.1500	3.0250	0.1432	58

Table 1: Structural studies of ZrO_2 doped with HfO_2.

The proposed biosensor shows a wide linear range, low detection limit, good reproducibility and acceptable stability, providing a biocompatible platform for bio sensing and bio catalysis. It is reported that a good manipulation of ZrO_2 morphological tuning, porous structure control, and crystallinity development is required in order to enhance the light harvesting capability, prolong the lifetime of photo induced electron-hole pairs, and facilitate the reactant accessibility to surface active sites. As ZrO_2 doped with HfO_2 is used in a wide variety of applications in addition to photo catalysis, the fabrication of identical ZrO_2 nanoscale structures has been recently attracted a great deal of interest. Nan crystalline ZrO_2 with various attractive morphologies has been effectively prepared by different synthesis methods like hydrothermal synthesis, sol-gel synthesis, precipitation, and thermal decomposition [7].

Doping with hydro thermal synthesis is an effective and facile method to modify the structural, optical and morphological properties of the base materials and this will also expand the applications of base materials. Morphological and structural properties of the ZrO_2 changes by hafnium doping were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM) and CV studies. Cyclic voltammetry was performed with an electrochemical workstation (RST5000, China) at a scanning rate of 10 mV s^{-1}shifting from −0.95 V to −1.65 V at room temperature (25±1◦C). Tafel plot also was performed on RST5000. The shifting range of Tafel plot E_{corr} was ±300 mV, and the scanning rate of Tafel plot was 1.0 mV s^{-1}

Experimental

Analytical grade Hafnium carbide source material was dissolved in 75 mL of ultra-pure water (0.5g was added). And the solution was stirred at room temperature for 20 minutes. 0.2 g of $NaBH_4$ pellet was dissolved in ultra-pure water, and this solution was added with source material drop by drop while the beaker was placed on a magnetic stirrer for about 30mins. At last do pant of 0.1 g of Zirconium nitrate was added after 30 minutes a yellow precipitant was obtained, and the pH was noted as 11.5, possibly due to dissolved oxygen present in air. The fine powder was under the autoclave with Teflon lining and kept at 180°C for 10 hours. After autoclaving and cooling, the yellow precipitate was separated by centrifugation for 6 minutes at 7500 rpm. The collected powder was washed with ultra-pure water and ethanol and dried at 80°C for 6 hours. The collected powder was calcined at 250°C for 1 hour for further characterization. The different molar concentrations of $NaBH_4$ (4mmol) were prepared [8].

Results and Discussion

The collected powder was characterized by using an X-ray diffractometer to study the structural properties of the sample. The XRD patterns of an as-synthesized sample are shown in Figure 1. JCPDS file no: 06-0318 is in good agreement with the results, and its diffractions are equal to (111), (022), (531), and (131) planes. It has a cubic nanostructure and its lattice parameter is a= 5.5425 Å. By using Debye Scherrer's formula, the average grain size was calculated [9].

$$D = \alpha \lambda / \beta \cos\theta \quad (1)$$

Where D is the average grain size, α is a geometric factor (here, α = 0.9), λ is the wavelength of X- rays used for the measurements (λ =1.54056Å), β is the FWHM of the diffraction peaks, which can be measured from the XRD peaks, and θ is the diffraction angle. The crystal structure was monoclinic 5.12, 5.18 and 5.25 are the lattice parameter of the system according to JCPDS file number 06-0318. Calculated value was nearly equal to 5.21, 5.14 and 5.27 which was well agreement with the standard values of JCPDS.

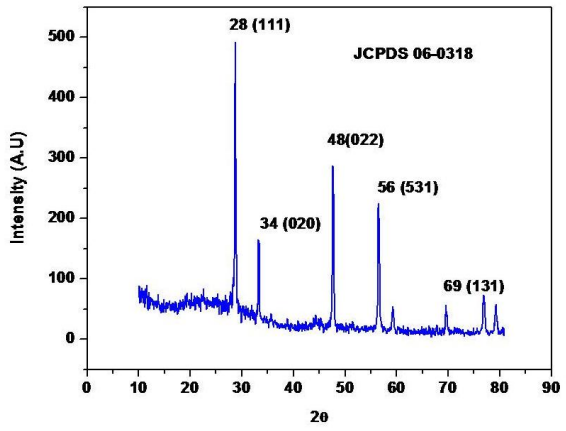

Figure 1: XRD Analysis of ZrO_2 doped with HfO_2.

The morphological studies of ZrO_2 doped with HfO_2 sample was reported in the Figure 2. There is some agglomeration due to doping concentrations of ZrO_2, which develops thicker and longer nanoparticles. Another reason for the agglomeration concerns the reaction time of its hydrothermal synthesis. It can be concluded that this proportion of source material of ZrO_2 doped with HfO_2 dehydrates constantly and oxidizes gradually with the help of $NaBH_4$ concentration. Current Voltage (C-V) characteristics.

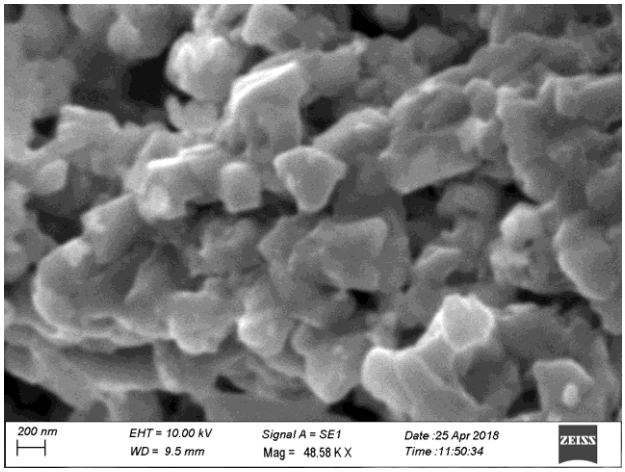

Figure 2: SEM Analysis of ZrO_2 doped with HfO_2.
SEM Analysis of ZrO_2 doped with HfO_2.

Figure 3 shows the current voltage (I-V) characteristics in the range of -1.5 to +1.5 V of the device under dark and UV light (365 nm, 6 mW/cm^2) conditions. Figure represents its semi-logarithmic representation, which reveals that the device requires an external voltage for the separation of photo-generated charge carriers [9]. Under UV illumination with a pulse frequency of 1 KHz, the device responded with the moderate photocurrent value, which was subsequently increased with the increase of the bias voltage. The systematic increase of photocurrent, in both positive and negative voltages, provides multiple options to use the device with different voltages and light intensities [9]. One may choose higher voltage for accurate and precise photo detection. Although, it is worth noting here, that with increasing of the photocurrent at higher voltage, the dark current increases simultaneously, which in turn reduces the potential difference performance i.e. detectivity (Jones) shown in Figure 3 and Table 2.

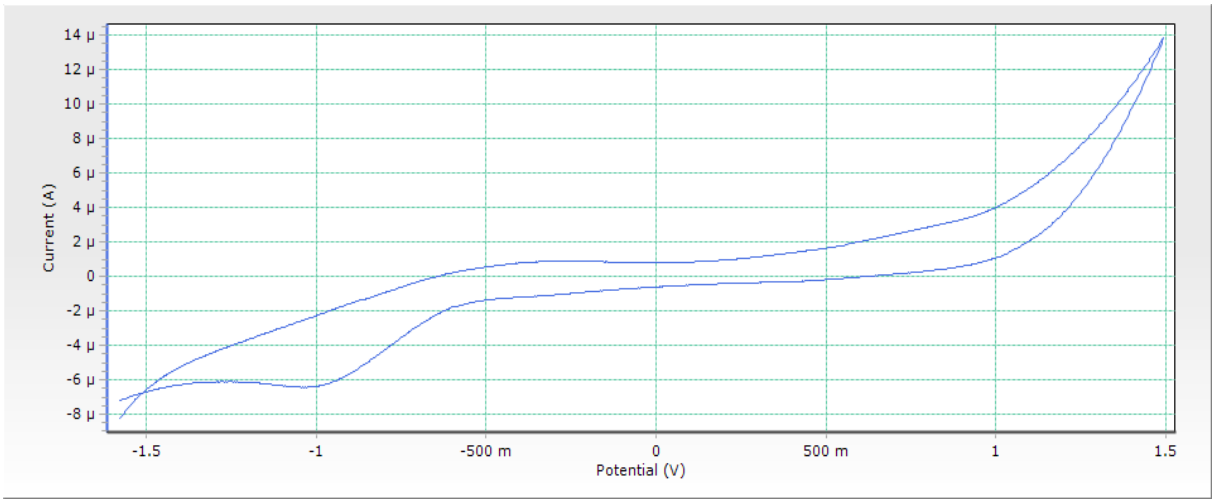

Figure 3: CV Studies of ZrO_2 doped with HfO_2.

X1	Y1	X2	Y2	Peak I	Peak E	Area
1.134 V	5.818 µA	013.064 mV	5.818 µA	-657.578 nA	-1.035 V	3.713 µC

Table 2: CV studies and its parameters value.

It is well known that ZrO_2 has three polymorphs, monoclinic, tetragonal, and cubic; when it is doped with HfO_2 it has the structure of Monoclinic. Preparation methods play an important role in determining the final crystal structure of ZrO_2 doped with HfO_2. Monoclinic surface properties on different ZrO_2 doped with HfO_2 polymorphs have been extensively studied.

Conclusions

Nanosize crystalline porous ZrO_2 doped with HfO_2 nanoparticles with pure monoclinic, tetragonal, and cubic phases were synthesized by different preparation methods. The photo catalytic performance of the three ZrO_2 samples for the degradation of methyl orange was evaluated. The pronounced photo catalytic activity for ZrO_2 doped with HfO_2 was mainly attributed to combining effects of factors including the presence of small amount of oxygen-deficient zirconium oxide phase, high crystallinity, broad pore size distribution, and high density of surface hydroxyl groups.

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