Hydrothermal synthesis, characterization and dielectric properties of zirconia nanoparticles

Abstract

Simple hydrothermal method has been used to synthesize zirconia (ZrO\textsubscript{2}) nanoparticles in alkaline medium. The powder X-ray diffraction technique (PXRD), electron microscopic studies (SEM and TEM) and BET surface area studies were done to characterize the as-synthesized nanoparticles. The crystalline nature and phase analysis of the ZrO\textsubscript{2} nanoparticles was determined by X-ray diffraction studies which revealed that the as-synthesized powder is pure monoclinic zirconia (m-ZrO\textsubscript{2}). The particle size was estimated by TEM and HREM studies, which comes out to be about 25nm. The surface area of as-prepared ZrO\textsubscript{2} nanoparticles was found to be 186m\textsuperscript{2}/g with DA pore radius of 11.9Å by using BET surface area studies. The dielectric constant and dielectric loss of the nanoparticles were found to be 7.5 and 0.0094 for as-synthesized nanoparticles at 500kHz frequency at room temperature.

Introduction

The solid materials have wide applications in many fields owing to defects in their crystal structure. The material when manipulated up to nano size then it exhibits properties very different as compared to micro size particles of the same material. Nano sized transition metal oxides have been considered gifted materials having their applications in industry, medicine and in various other fields. The metal oxide nanoparticles have attracted special attention to design nano structures for a variety of applications because of their enhanced physical and chemical properties.\textsuperscript{1} The oxide nanoparticles are used to design energy efficient lithium ion batteries,\textsuperscript{2,3} light emitting diodes,\textsuperscript{4,5} solar cells,\textsuperscript{6,7} fuel cells,\textsuperscript{8,9} and transistors,\textsuperscript{10,11} hydrogen storage devices,\textsuperscript{12,13} air purification,\textsuperscript{14} water purification,\textsuperscript{15} gas sensing,\textsuperscript{16} temperature and humidity sensing studies,\textsuperscript{17} drug delivery and bio imaging studies.\textsuperscript{18-19}

The nano sized ZrO\textsubscript{2} is very interesting and valuable material for its fundamental and application based properties. ZrO\textsubscript{2} is known to exist in three crystalline forms monoclinic, tetragonal and cubic structures. Thermodynamically most stable form of ZrO\textsubscript{2} is monoclinic. The cubical form of ZrO\textsubscript{2} is stable at high temperature (above 2370\degree C), tetragonal form is stable between 1170- 2370\degree C whereas monoclinic ZrO\textsubscript{2} is stable below 1170\degree C.\textsuperscript{20} ZrO\textsubscript{2} is well known refractory oxide and a potential candidate as high k-gate dielectric material. To select any material as gate oxide applications, the first and very important requirement is high dielectric constant value. The material possessing too high dielectric constant value, such as for TiO\textsubscript{2} (~ 80), fringing fields from the drain through the gate dielectric are observed which may degrade the source to channel potential barrier and may lead to poor sub-threshold device functioning.\textsuperscript{13-21} Pure zirconia has been known to exhibit anionic vacancies defects predominantly. The nano sized zirconia owing to large surface area has high number of oxygen vacancies at grain surfaces.\textsuperscript{22} Therefore solid ZrO\textsubscript{2} can conduct electricity up to some extent and it is considered as p-type semiconductor. The band gap value of ZrO\textsubscript{2} depends upon synthesis temperature, particle size and crystalline structure. The value of band gap for tetragonal form has been reported more than that monoclinic which in turn has higher band gap value than that of cubic form.\textsuperscript{23} A number of binary oxides such as TiO\textsubscript{2}, Y\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2} and some perovskites materials such as SrTiO\textsubscript{3}, BaZrO\textsubscript{3}, Ba\textsubscript{1-x}Sr\textsubscript{x}ZrO\textsubscript{2} and Ba\textsubscript{1-x}Sr\textsubscript{x}ZrO\textsubscript{3} have been studied as dielectric oxide material for complementary metal oxide semiconductor (CMOS) devices\textsuperscript{24-27} but ZrO\textsubscript{2} have been investigated extensively as potential candidate for dynamic random access memory devices (DRAM) owing to its moderately high dielectric constant (k=20) and higher thermal stability.\textsuperscript{28} Numerous chemical methods have been reported to synthesize pure ZrO\textsubscript{2}, such as thermal decomposition,\textsuperscript{29} sol-gel methods,\textsuperscript{30} reverse micellar method\textsuperscript{31,32} and hydrothermal techniques.\textsuperscript{32} In this paper we have synthesized the single phase ZrO\textsubscript{2} nanoparticles to check their applications as dielectric material as a function of frequency and temperature. The as-prepared nanoparticles were extensively characterized using PXRD, SEM, TEM and BET surface area studies.

Experimental section

The chemicals hydrated zirconium oxy nitrate (Alpha Aesar, 99.9%), sodium hydroxide (Merck, 99%) were used as such without further purification. The double distilled water was used throughout the experiment.

The synthesis of ZrO\textsubscript{2} nanoparticles have been processed using typical hydrothermal method. 0.1M ZrO(NO\textsubscript{3})\textsubscript{2}.xH\textsubscript{2}O and 0.2M NaOH were prepared in double distilled water. Equal volumes (25ml of each solutions) were mixed in order to form a 1: 2 molar ratio solution of ZrO(NO\textsubscript{3})\textsubscript{2}.xH\textsubscript{2}O and NaOH. The solution obtained were transferred in to the hydrothermal flask and placed in oven for heating at 150\degree C for 4hours. To collect the precipitates, the solution was centrifuged for 5 minutes at 8000rpm and washed with acetone several times. The precipitates were then dried in vacuum oven at 110\degree C for 90 minutes and graded to obtain fine powder of ZrO\textsubscript{2} nanoparticles.

Characterization

The crystalline structure of as-synthesized nanoparticles was determined with the help of Rigaku ultima IV X-ray Diffractometer with Cu target and (\lambda )=1.5416Å. Powder X-ray diffraction patterns were recorded in 10-80\degree 20 scanning range with scanning rate of 0.05\degree per second. The morphology of the nanoparticles was determined by scanning electron microscope FEI SEM (Model: Nova Nano SEM)

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The surface morphology of the as-acquired zirconia nanoparticles was investigated by scanning electron microscopy as shown in Figure 2. SEM image clearly indicates that the zirconia nanoparticles have smooth surface with small particle size. The agglomeration of nanoparticles is also visible in the SEM images.

The shape and size of the as-prepared nanoparticles have been estimated from transmission electron microscopic (TEM) studies. The TEM micrographs of zirconia nanoparticles are shown in Figure 3A. The micrograph shows that the particles are uniform in size and the small spheres tend to form cubic shape. The average size estimated from these micrographs was found to be 25nm. The transmission electron micrograph is in good agreement with the SEM image. Figure 3B represent HRTEM image of as-synthesized monoclinic ZrO$_2$ nanoparticles. The HRTEM micrograph visualizes well-resolved lattice fringes at a distance of 2.84 ± 0.04Å which can be accredited to the inter-planar spacing corresponding to (111) plane.$^{33}$ The parallel fringes were found to be equidistant authenticate single phase nanocrystalline grains of monoclinic ZrO$_2$. The selected-area electron diffraction (SAED) pattern of zirconia nanoparticles is shown in figure 3c which demonstrates the different lattice planes of m-ZrO$_2$ (111), (111), (122) and (131) in the SAED pattern which are in good agreement with the XRD pattern.

The specific surface area of the as-acquired nanoparticles was determined by the Brunauer-Emmet-Teller (BET) gas adsorption method$^{34}$ and the pore radius and pore volume was calculated using Barrett-Joyner-Halenda (BJH) method.$^{35}$ Figure 4 shows the BET plots of zirconia nanoparticles. The specific surface area calculated using the multipoint BET equation was found to be 186m$^2$.g$^{-1}$. The pore size distribution plot of as-synthesized nanoparticles is shown in Figure 5 and 6. The pore radius of these nanoparticles was calculated using BJH method as well as DA method and presented in Table 1 with the corresponding pore volumes.

The dielectric properties of as synthesized nanoparticles were studied as a function of frequency after sintering the pellets at 1000°C for 10 hours. The dielectric constant is estimated by using the formula $^{36}$

$$
\varepsilon' = \frac{C \delta}{A \varepsilon_0}
$$

Where $C$ is capacitance of pellet, $\delta$ the thickness of pellet, $A$ the cross-sectional area of the flat surface of the pellet and $\varepsilon_0$ the permittivity for free space.
The dielectric characteristics including the dielectric constant and loss factor were determined with variation of frequency in a range from 20KHz to 1MHz at room temperature as shown in Figure 7. Figure 7 shows that the dielectric constant decreases with increase in frequency. On account of space polarization effect, the zirconia nanoparticle shows high dielectric constant at lower frequency region. However, at higher frequency region the polarization effect reduces which raises the decrease in dielectric constant. The room temperature dielectric constant and dielectric loss values were found to be 7.5 and 0.0094 for the as synthesized nanoparticles at 500kHz.

Table 1 BET surface area, BJH and DA pore radius parameters of as-synthesized nanoparticles

| Nanoparticles | BET surface area \( [\text{m}^2\text{g}^{-1}] \) | BJH pore radius [Å] | DA pore radius [Å] | Pore volume \( \text{cm}^3\text{g}^{-1} \) |
|---------------|---------------------------------|----------------------|---------------------|-------------------------------|
| \( \text{ZrO}_2 \) | 186                             | 30.9                 | 11.9                | 0.247                         |

Figure 3 (a) Transmission electron micrograph, (b) HRTEM image and (c) SAED pattern of \( \text{ZrO}_2 \) nanoparticles.

Figure 4 BET plot of \( \text{ZrO}_2 \) nanoparticles.

Figure 5 BJH pore radius plot of \( \text{ZrO}_2 \) nanoparticles.

Figure 6 DA pore radius plot of \( \text{ZrO}_2 \) nanoparticles.

Figure 7 Dielectric constant and dielectric loss of \( \text{ZrO}_2 \) nanoparticles at room temperature.
Conclusion

Zirconia nanoparticles were synthesized by the simple hydrothermal method in alkaline medium at 150°C. X-ray diffraction, HRTEM and SAED analysis confirms that the synthesized nanoparticles are pure monoclinic phase of ZrO$_2$. The diameters/particle size of the m-ZrO$_2$ nanoparticles fell into range of 25nm with the specific surface area of 186m$^2$.t. The SEM image is in accordance with the TEM micrograph. The dielectric properties of m-ZrO$_2$ nanoparticles make them a suitable material for the storage devices and electronic devices. These nanoparticles can also be used for photonic applications, gas sensors and solid oxide fuel cells.

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Conflict of interest

The author declares no conflict of interest.

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