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Full Length Article

Microwave assisted synthesis of cubic Zirconia nanoparticles and study of optical and photoluminescence properties

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ABSTRACT

Synthesis of pure ZrO_2 nanoparticles in its cubic phase is a challenging task for the researchers. ZrO_2 is a promising material and has received considerable attention recently due to superior properties that provide significant advantages in various applications like display systems and lighting. This paper discusses a better method of synthesis of pure ZrO_2 nano crystals in cubic phase, free from impurities that alter the luminescence emissions. Studies on structural, optical and photoluminescence properties are reported. The structural studies show that as formed ZrO_2 nanoparticles are in cubic phase. The crystallinity and phase formation of the samples were studied by XRD, the crystallinity increases as the calcination temperature increases. The samples are mesoporous and pore size decreases with increase in the calcination temperature as studied by BET. The optical energy band gap (E_g) was calculated and found to be 5.21 eV for the as formed sample. As calcination temperature increases the increase in the optical band gap is observed. The PL spectra show an intense violet emission band peak centered at 387 nm, due to the presence of the oxygen vacancies in the ZrO_2 matrix. The crystallinity, particle size and the phase formation was further confirmed by HRTEM.

1. Introduction

The study on ZrO_2 nanoparticles has attracted much interest due to their multifunctional characteristics and its wide application. ZrO_2 occurs as naturally as the mineral Baddeleyite. The wide interest of ZrO_2 is that, it exhibit three different phases at different temperature range. The monoclinic phase formed is thermodynamically stable at a temperature range of 1100 °C, the tetragonal phase is stable at the temperature range of 1100–2370 °C and the cubic phase is stable at 2370 °C. In recent years ZrO_2 is a promising material due to potential application in the field of photonics. The ZrO_2 have novel application in various fields such as Solid Oxide Fuel Cell [1], Biological applications [2], Ceramic application [3], Optoelectronic [4], Dielectric application [5], Oxygen storage [6], , Humidity sensors [7], Catalysis [8,9] and so on.

The phase formation and the morphology of the nanoparticles depends on the method of synthesis. There are several methods employed for the synthesis of ZrO_2 nanoparticles. The most conventional methods for the synthesis of ZrO_2 nanomaterials are Precipitation method, Sol-gel method [10,11] Combustion process [12,13], Ultra sonication [14], hydrothermal method [15], Microwave assisted hydrothermal method [16], Co-precipitation [17]. In recent years Microwave method of synthesizing nanomaterials has become one of the most important methods. Microwave method is very rapid, very short time is enough to complete the reaction [18], low power consumption [19,20]. The microwave method favors kinetic processes whereas the conventional methods favor thermodynamic process. Researchers have found that the Microwave combustion synthesis is a fast method for the synthesis of metal oxide nanoparticles [18,21]. Hence, combustion route is one of the extensively used technique for the synthesis of the ZrO_2 nanoparticles. It is one of the ideal techniques for the synthesis of the nanomaterials with high purity, size controlled and controlled morphology [22] and in single step the desired phase of the nanoparticles can be synthesized. This paper presents the synthesis of highly porous and morphologically controlled cubic ZrO_2 nanostructures and study of optical and photoluminescence properties.

2. Experimental section

2.1. Materials

Zirconyl nitrate monohydrate (99.9%), L-Serine amino acid (99.8%) purchased from Sigma-Aldrich and Hemidea respectively. De-ionised water was used for the synthesis of ZrO_2 nanoparticles

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in order to avoid the introduction of the impurities during the synthetic process.

2.2. Synthesis of ZrO_2 nanoparticles

Mesoporous cubic ZrO_2 nanoparticles were synthesized by using 2.3123 g of zirconyl nitrate monohydrate ($ZrO(NO_3)_2.H_2O$) and 0.8083g L-Serine amino acid were dissolved in minimum quantity of de-ionised water in a 250 mL borosil glass beaker. The F/O ratio was maintained to be unity to ensure complete combustion. The excess water was evaporated to get a highly viscous transparent gel. This viscous transparent gel was transferred in to a domestic microwave oven (SAMSUNG CE73JD/XTL model, 50 Hz, 100–800 W power output). The gel was exposed to microwave irradiation for 60 seconds maintained at 800 W power output. Initially the solution was vigorously boiled and underwent dehydration followed by catching of the fire leading to the liberation of the enormous amount of the gases like CO_2, N_2 and water vapors and finally led to the formation of the highly swelling, porous and voluminous puffy white powder of the ZrO_2.

The theoretically balanced chemical equation of the combustion involving the formation of the ZrO_2 nanoparticles using L-Serine as a fuel is depicted by the following chemical reaction.

$$13ZrO(NO_3)_2 + 10C_3H_7NO_3 \rightarrow 13ZrO_2 + 30CO_2 + 18N_2 + 35H_2O$$

These samples prepared through microwave assisted combustion method were further calcined at 400 °C, 600 °C and 800 °C. The samples of ZrO_2 nanoparticles prepared by microwave method as formed is labeled as MCZ-0, while the samples calcined at 400 °C, 600 °C and 800 °C are labelled as MCZ-1, MCZ-2 and MCZ-3 respectively.

2.3. Characterization techniques

The ZrO_2 nanoparticles synthesized from microwave combustion method are characterized by various analytical techniques. The X-ray diffraction (XRD) of powder samples was measured using X-ray powder diffractometer (Bruker D8 Diffractometer, source Cu-Kα, $\lambda = 1.5418$ Å) operated in reflection mode. Fourier Transform Infrared (FTIR) spectra was recorded (Perkin-Elmer spectrometer) with KBr pellet technique. The morphology of the ZrO_2 nanoparticles were studied by FESEM with EDX (GEMINI, Ultra 55). BET surface area was measured using NOVA-1000 Ver.3.70 in N_2 adsorption apparatus. The absorption spectra of the samples was recorded using UV–visible spectrophotometer (Systronics PC based double beam spectrophotometer-2202). The particle size and shape of ZrO_2 nanoparticles were recorded using HRTEM. The phase formed was reconfirmed by using SAED pattern from TEM (JOEL/TEM 2100). Photoluminescence (PL) measurements was carried out using Jobin Yvon spectrofluorimeter (Fluorolog-3) equipped with a 450 W xenon lamp as an excitation source at room temperature.

3. Results and discussions

The XRD pattern was recorded for the ZrO_2 nanoparticles prepared by combustion method. The XRD pattern reveals the fact that the synthetic method plays an important role in the phase formation as well as the crystallite size of the ZrO_2 nanoparticles. XRD pattern shows that only cubic [23] phase was formed for the ZrO_2 nanoparticles synthesized from Microwave combustion method as shown in Fig. 1. The crystallite size of the ZrO_2 nanoparticles was calculated by using Scherer's equation, $D = K\lambda/\beta\cos\theta$, where the shape factor, $K = 0.94$, $\lambda = 1.5418$ Å represents the wavelength of CuK_α radiation, β is the full width of half maxima of

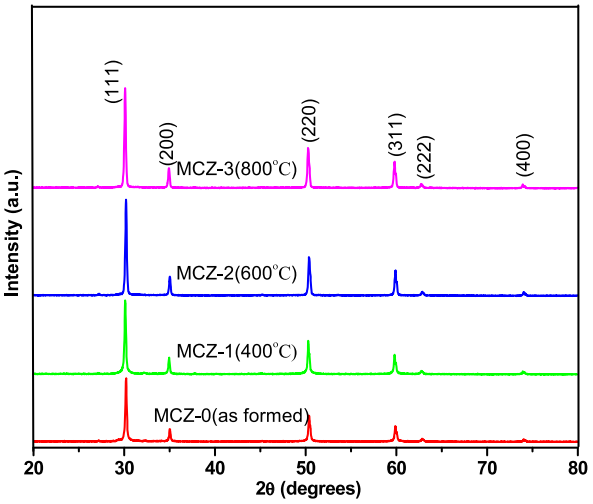

Fig. 1. XRD of ZrO_2 nanoparticles synthesized by microwave method.

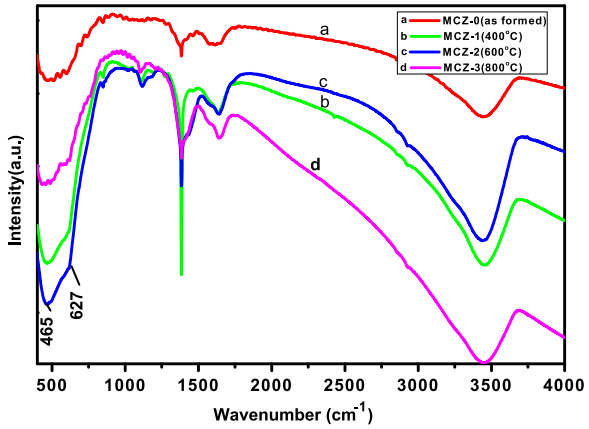

Fig. 2. FTIR of ZrO_2 nanoparticles synthesized by microwave method.

the diffraction peak and 'θ' represents the half angle of the diffraction peak. The particle size was found to be in the range of 60–65 nm for the as prepared sample (MCZ-0) [24,25].

The average crystallite size of the MCZ-1, MCZ-2 and MCZ-3 is found to be 70 nm, 76 nm and 77 nm respectively. The crystallite size was found to increase with the calcination temperature. The XRD pattern obtained for the ZrO_2 was indexed as (111) (200) (220) (311) and (222) and match with the cubic phase (ICSD No. 00-049-1642), space group (Fm3m) number 225.

FTIR spectroscopy was used to study the formation of ZrO_2 nanoparticles. Fig. 2 shows that the broad vibration band at 3430–3460 cm^{-1} is associated with the OH stretching frequencies and a weak band at 1645 cm^{-1} is the OH bending frequency of adsorbed water molecules. The vibrations 1385–1445 cm^{-1} indicates the presence of the adsorbed CO_2 [26]. The band at 465 cm^{-1} to 627 cm^{-1} are due Zr–O stretching frequencies and indicates the formation of cubic ZrO_2 nanoparticles [27].

In order to examine the morphology and the elemental composition, the samples are subjected to SEM with EDX analysis. The SEM images of the nanoparticles synthesized by microwave method and calcined at different temperatures are shown in Fig. 3. As formed sample (MCZ-0) is highly porous in nature. The majority of the crystallites are hexagonal in shape and the particles are more or less uniform. As the calcination temperature increases the porosity decreases and the crystals are densely packed due to the densification.