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Full Paper

Synthesis of mesoporous β-Ga_2O_3 nanorods by sol-gel method in aqueous medium using γ-irradiated gallium chloride precursor

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Abstract

Mesoporous structures β-Ga_2O_3 nanorods have been synthesized by sol-gel method using gelatin, water and γ-Irradiated gallium chloride with 10^2 kGy total γ-ray absorbed dose as starting materials. The transparent gel containing gallium ions was calcined at 600° C for 4 hours to form β-Ga_2O_3 nanorods. The as- synthesized β-Ga_2O_3 nanorods were characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier – transform infrared spectroscopy (FT-IR). From x-ray diffraction patterns, the purity and crystallinity nature of the as-synthesized nanoparticles were tested. Based on the infrared spectra of the as-synthesized nanoparticles, the IR bands attributed to ν_{Ga-O} and lattice vibration of β-Ga_2O_3 were recorded in the wavenumber range of (400- 4400 cm^{-1}). TEM image of the as-synthesized nanoproducts displays the formation of β-Ga_2O_3 nanorods. The role of γ-Irradiation on the synthesis of β-Ga_2O_3 nanorods was evaluated and discussed.

Keywords: Mesoporous structure, Ga_2O_3 nanorods, Gamma irradiation.

1. Introduction

Monoclinic gallium oxide (β-Ga_2O_3) is chemically and physically stable compound with a wide band gap of 4.9 e.V., which can promote the mobility of the photogenerated electrons and enhance the charge separation [1, 2].

As a result, β-Ga_2O_3 shows exceptional performance in the photocatyltic oxidation of volatile organic compounds (VOCs) into harmless compounds such as carbon dioxide and water [3]. Several routes have been proposed for the synthesis of β-Ga_2O_3 nanorods including sol-gel method [4], thermal decomposition [5], carbon thermal reduction [6] and hydrothermal method [7]. Radiation-induced synthesis of nanostructured materials plays an important role in investigation and production of well- shaped and monodispersed nanoparticles. Methods based on the interaction of high energy charged particles and γ-rays, are widely used in making ion-track membrane polymeric [8], nanocomposites and metal oxide nanoparticles. Irradiation effects on the preparation of β-Ga_2O_3 nanoparticles were scanty reported [9]. The overall goal of the present study is to investigate the effect of γ-irradiation on size, shape, and morphology of β-Ga_2O_3 nanoparticles synthesized by a sol-gel method in an aqueous medium. The as-synthesized β-Ga_2O_3 nanoparticles is found to exhibit mesoporous nature.

2. Materials and methods

2.1. Synthesis of Ga_2O_3 nanoparticles

Anhydrous $GaCl_3$ was purchased from Sigma-Aldrich and used without any further purification. In a typical experiment, 1.76 gm of γ-irradiated $GaCl_3$ (1 mmol) with 10^2 kGy total absorbed γ-ray dose was added to 3 g of gelatin (powder-gel) strength ~ 300 g Bloom, Type A). Few drops of water were added dropwise until a hard transparent solid resin containing gallium ions was formed. The resin was transferred into a muffle furnace; the temperature was raised at a heating rate of 10 °C min^{-1} to 600 °C, and kept constant for four hours. At the end of the calcination process, the as-synthesized product was cooled to the room temperature and collected into a clean and dry container and subjected to characterization.

2.2. Instrumentations

X-ray powder diffraction patterns (XRD) were recorded on Siemens D 5000 X-ray diffractometer with CuKα radiation (λ=1.54 Å). TG measurements were recorded on Perkin-Elemer TG A7 thermogravimetric analyzer in the temperature range of 30-1000 °C. The sample weight was 10.0 ± 0.1 mg with a heating rate of 10 °C/min.

FT-IR measurements were recorded as KBr pellets in the range of 200- 4000 cm^{-1} on Perkin- Elemer FT- IR spectrophotometer (spectrum 1000). SEM and TEM images were captured using the models (SEM, JSM-6360 ASEM, JEOL, Japan) and (TEM, JEM-2100F, JEOL, Japan) electron microscopes. The optical absorption spectra of CdO nanoparticles dispersed in cyclohexane are recorded on Shimadzu 2101 UV double-beam spectrophotometer using quartz cells of path length 1 cm.

For irradiation, samples were encapsulated under vacuum in glass vials and exposed to successively increasing doses of radiation at a constant intensity. A Co-60 γ-ray source model gamma cell 220 from MDS (Nordion, Canada) was used for irradiation of the samples. The source was calibrated against a Fricke ferrous sulfate dosimeter and the absorbed doses in the irradiated samples were calculated by applying appropriate corrections on the basis of photon mass attenuation and the energy absorption coefficients for the sample and the dosimeter solutions [10]. The dose rate was 9.83 kGy h^{-1} and the transient dose was estimated to be 12.07 Gy. All of the irradiations were conducted at 25 °C. After irradiation, the samples were stored at room temperature for 24 h before analysis.

3. Results and discussion

3.1. Characterization of β-Ga_2O_3 nanoparticles

Figure1 shows XRD patterns of as-synthesized β-Ga_2O_3 nanoparticles. The Figure demonstrates a stable phase of β-Ga_2O_3 (with cell parameters, a = 12.22, b = 3.04 Å, c= 5.79, β = 103.7° and space group of C2/ m (***JCPDS Card 06- 0180***). Two minor peaks recorded at 2θ 34.2° and 60.8° belong respectively to 110 and 220 reflections of monoclinic gallium metal (Ga^0) with space group A2/a ***(JCPDS Card No-04-007-2074***) were observed in XRD pattern of β-Ga_2O_3 nanorods attributed to reduction of Ga^{3+} to Ga^0 as result of γ-irradiation . The sharp diffraction peaks reveal that the prepared sample has a high crystalline quality.

Figure 2 shows the FT-IR spectrum of β-Ga_2O_3 nanoproduct in the range of 4000-400 400 – 4400 cm^{-1}.The minor bands recorded at 3476 and 2928 cm^{-1} are tentatively assigned to absorbed water and atmospheric CO_2 respectively. The strong bands organized at 687.79 and 458.35 cm^{-1} are due to $\nu_{Ga\text{-}O}$ band and crystal lattice vibration [11].

The morphology of as-synthesized material was studied by SEM and more accurate TEM techniques. Representative SEM image is shown in Figure 3, evidenced the 1D morphology of the as-synthesized β-Ga_2O_3 nanomaterial. The image display formation of irregular and randomly oriented nanorods with dense holes on their surface. The surface area of the β-Ga_2O_3 is determined to be 27.89 m^2 /g., and the pore size of the sample predominantly falls in the mesoporous range of 10- 50 nm.

Figure 4 shows the TEM image of β-Ga_2O_3 nanorods. From the figure, it can be seen that the β-Ga_2O_3 nanorods are single crystalline. The average length of nanorods is found to be about 100 nm with diameter 50 nm.

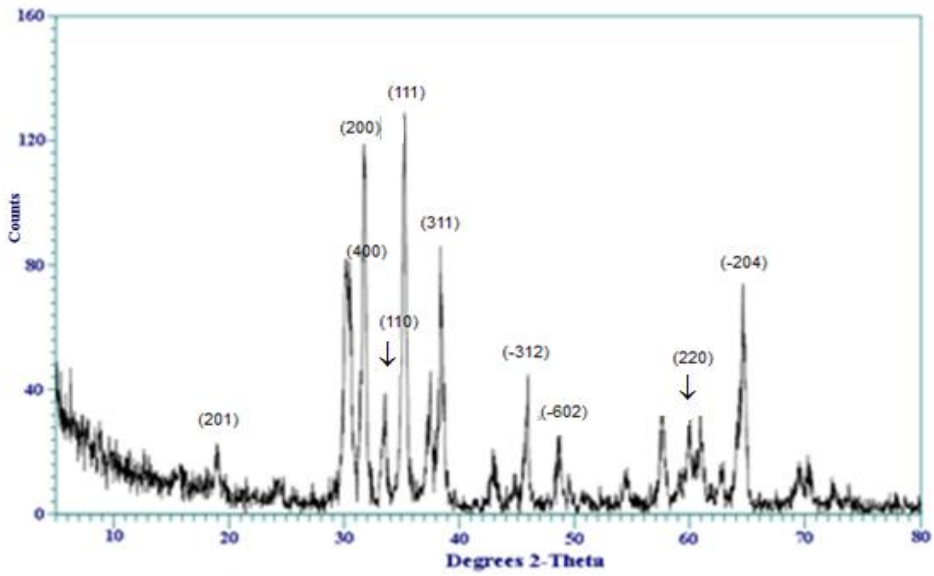

Fig. 1: XRD pattern of the as-synthesized Ga_2O_3 nanorods.

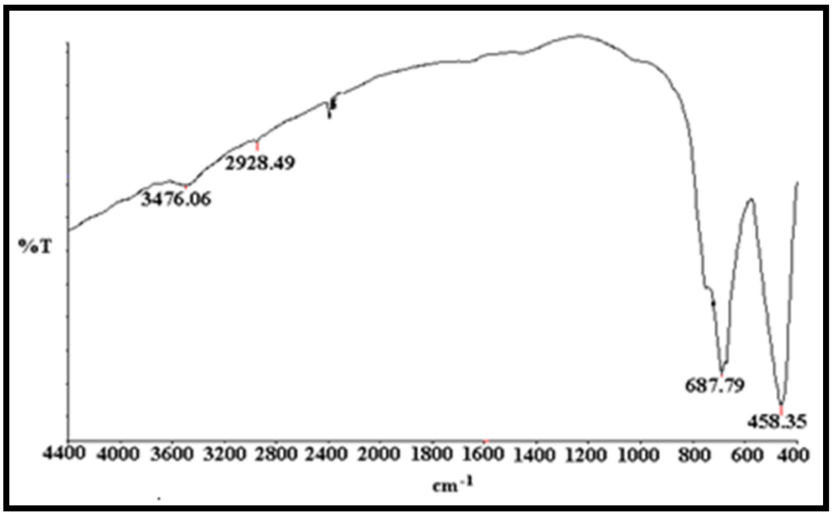

Fig.2: FT-IR spectrum of the as-synthesized Ga_2O_3 nanorods.

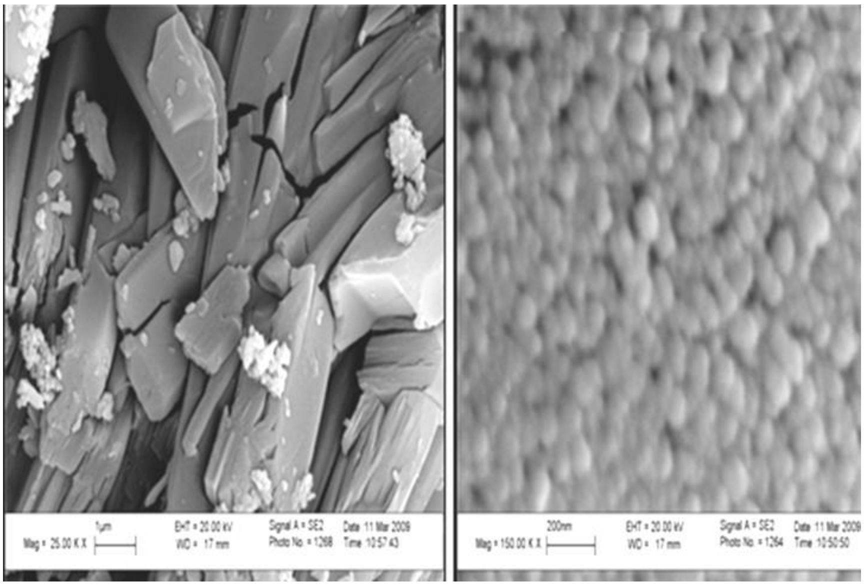

Fig.3: SEM image of the as-synthesized Ga_2O_3 nanorods

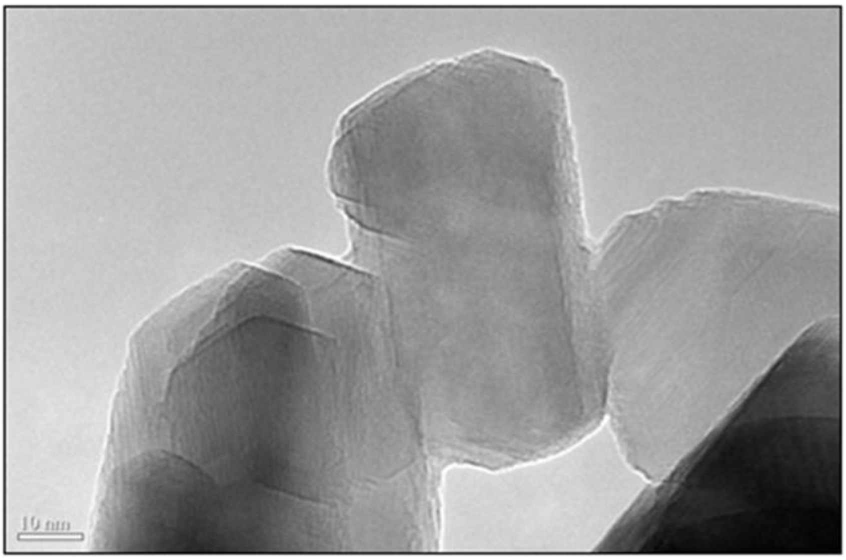

Fig.4: TEM image of the as-synthesized Ga_2O_3 nanorods.

3.2. Role of Irradiation

In the solid sample, the radiation effects are dominated by direct ionization of the material, whereas for aqueous solutions the reaction with radical species such as hydroxyl radical ($^{\bullet}OH$) or solvated electrons (e^{-}) is the dominated mechanism for damage to a solute.

Upon irradiation with Co-60 γ-ray source, Compton scattering is the main mode of interaction of the γ-ray with gallium and chlorine and multiple ionization occurs which subsequently leads to multi-step reductions (including intermediate vacancies) by trapped electrons in the host lattice of Ga crystal according to the following mechanism

$$Ga^{3+} + 3e \leftrightarrow \square\ Ga^{0}$$

Where □ refers to the atomic vacancy. These newly formed atoms act as new centres for nucleation and growth leading to *a)* shorten the calcination time for β-Ga_2O_3 formation compared with the time required by using of un-irradiated precursors reported in literatures , *b)* creation of deficient Ga atoms responsible for the formation of mesoporous nature of as-synthesized β-Ga_2O_3 nanoparticles.

4. Conclusion

In the present study, we succeeded to synthesize mesoporous structure of β-Ga_2O_3 nanorods using γ-irradiated $GaCl_3$ with 10^2 kGy total γ-ray absorbed dose by sol-gel method. The interaction of γ-ray with $GaCl_3$ host lattice led to the formation of point defect and lattice imperfection responsible for the formation of mesoporous structure.

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