International Journal of Engineering and Manufacturing Science.
ISSN 2249-3115 Volume 7, Number 2 (2017), pp. 273-279
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Influence of Trivalent Gadolinium (Gd^{3+}) on structural and optical properties of Titania

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Abstract

In this work, anatase phase pure and Gd^{3+} doped TiO_2 nanoparticles have been successfully synthesized via hydrothermal method. To evaluate the synthesized nanomaterials, several analytical techniques have been used, including X-ray diffractometry (XRD), Energy dispersive X-ray Analysis (EDAX), Fourier transform infrared spectroscopy (FTIR) and Diffuse Reflectance Spectroscopy (DRS). X-ray diffraction technique was employed to study the structure and crystalline nature of synthesized nanoparticles. The size of the pure and Gd^{3+} doped TiO_2 nanoparticles was calculated from XRD data is 7.71 nm and 7.92nm respectively. Diffuse Reflectance Spectroscopy studies revealed that optical band gap of is slightly varied due to the effect of size of the particle. The functional analysis was carried out by FT – IR.

Keywords: Gd^{3+}: TiO_2, Hydrothermal**,** Structural, Optical properties.

INTRODUCTION

Nanoparticles are being viewed as fundamental building blocks of nanotechnology. The most important and distinct properties is that they exhibit larger surface area to volume ratio. They exhibit completely new or improved properties based on specific characteristics such as size, distribution and morphology [1]. Titanium dioxide is widely known for its semiconductor photo catalysis activity. It uses the sunlight for the annihilation of pollutants and to convert the solar energy into hydrogen, which potentially meet the requirement of environmental pollution and energy crisis [2]. Titania can crystallize in three forms: anatase, rutile and brookite. It is generally accepted that for pure phases anatase exhibits a higher photocatalytic activity compared to rutile TiO_2 [3]. Various methods are available to prepare TiO_2 based nanoparticles, such as sol–gel, solvothermal, sonochemical, hydrothermal, chemical vapor deposition, electro-deposition, physical vapour deposition, combustion etc [4]. Hydrothermal synthesis refers to the preparation by chemical reactions of substances in a sealed heated solution above ambient temperature and pressure. Hydrothermal process can produce high temperature and high pressure, which has been proved to be efficient to promote some redox reactions [5].

EXPERIMENTAL SECTION

TiO_2 nanoparticles were synthesized by simple hydrothermal method from the source material of Titanium (IV) Isopropoxide. In a typical synthesis process stoichiometric amount of Titanium (IV) Isopropoxide was added to acetic acid. The above mixture was dissolved by distilled water under constant stirring. Then this solution was continuously stirred for 1 hour and the resultant solution was transferred to Teflon-lined stainless steel autoclave and maintained at 110 °C for 12 hours in muffle furnace. After the hydrothermal reaction the autoclave was naturally allowed to cool to room temperature. The product of white precipitate was collected and washed with Distilled water and ethanol to remove the residual and dried at 100 °C. The dried particles were annealed at 400 °C for 3 hours.

Similarly Gd^{3+} doped TiO_2 nanoparticles were prepared by hydrothermal method keeping the above experimental condition the same but the doping precursor of Gadolinium (III) oxide was added.

X-RAY DIFFRACTION

X-ray diffraction (XRD) is a popular analytical technique which has been used for the analysis of both molecular and crystal structures, qualitative identification of various compounds, quantitative resolution of chemical species, measuring the degree of crystallinity, isomorphous substitutions, particle sizes, etc.

The grain size and phase variety of synthesized nanoparticles was determined by X-ray diffraction spectroscopy (Philips PAN analytical). The synthesized titania nanoparticles were studied with CUKα radiation at voltage of 30 kV and current of 20 MA with scan rate of 0.030 /s.

Figure.1 shows the XRD pattern of Pure and Gd^{3+} doped TiO_2 nanoparticles. The diffraction peaks at $2\theta = 25.34^o, 37.90^o, 48.09^o, 54.10^o, 55.15^o, 62.85^o, 68.99^o, 70.49^o$, and 75.12^o, which can be respectively indexed to (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes of pure TiO_2 nanoparticles. This data compares favourably with the standard JCPDS file no 21-1721. This confirmed the presence of tetragonal anatase phase.

It can be noted that the peak at $2\theta = 25.41^{o}$ corresponding to (101) lattice plane was observed which signifies the addition of dopant.

The crystalline size was calculated from the half width of the diffraction peak of XRD pattern using the Debye-Scherrer equation:

$$D = 0.9\,\frac{\lambda}{\beta\cos\theta}$$

Where D is the average particle size, λ is the wavelength of source used (Cu Kα), β is the full width at half maximum, θ is the diffracting angle.

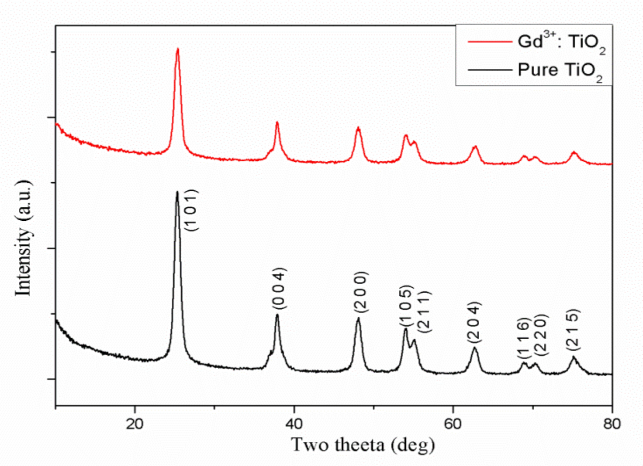

Figure 1: XRD pattern of Pure and Gd^{3+} doped TiO_2 nanoparticles

The calculated average crystallite size of the pure and Gd^{3+} doped TiO_2 nanoparticles were determined as 7.71nm and 7.92nm respectively.

Energy dispersive X-ray (EDX) analysis:

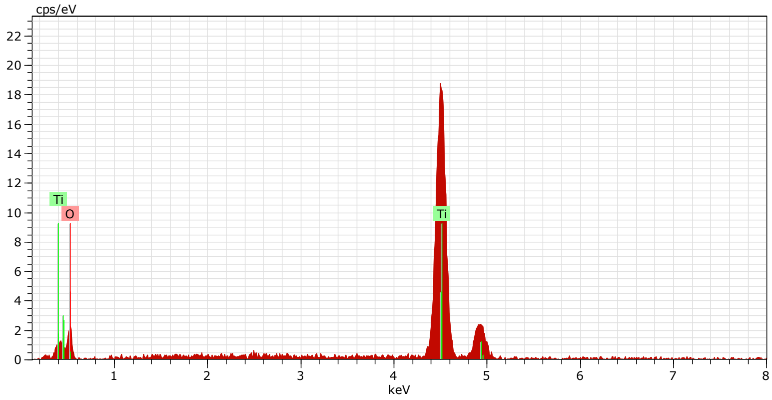

Figure 2a: EDAX spectrum of TiO_2 nanoparticles

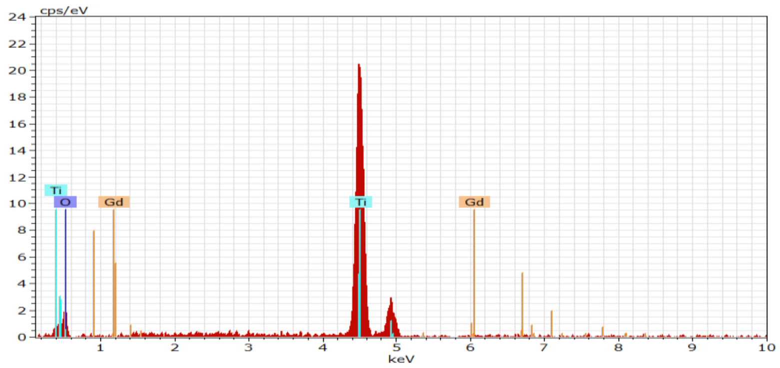

Figure 2b: EDAX spectrum of Gd^{3+} doped TiO_2 nanoparticles

To check the chemical compositions of the synthesized Pure and Gd^{3+} doped TiO_2 nanoparticles was measured by EDAX spectra and are shown in Figures 2a and 2b. In pure TiO_2 nanoparticles only Ti and O ions are detected, as shown in Figure 2a. From Figure 2b EDAX spectra indicated that the presence of Ti, O and Gd peaks.

FT- IR Analysis:

The chemical composition of the synthesized titania nanoparticles was studied by using FTIR spectrometer (Perkin-Elmer Luminescence spectrometer). Figure 3 shows the Fourier transform infrared spectroscopy (FT-IR) spectra of pure and Gd^{3+} doped TiO_2 samples were recorded in the range of 4000–400 cm^{-1} using KBr pellet method.

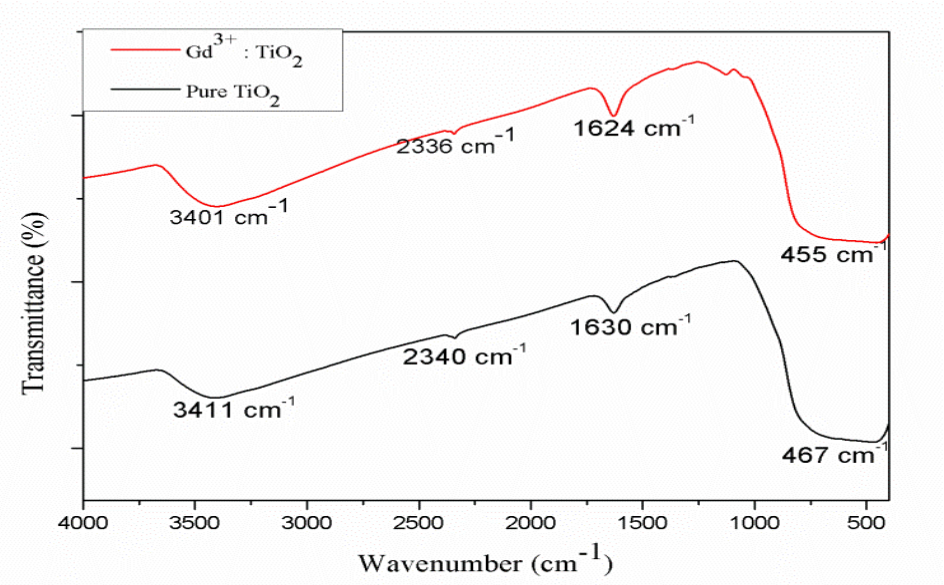

Figure. 3: FT-IR spectrum of pure and Gd^{3+} doped TiO_2 nanoparticles

FT-IR spectrum of pure TiO_2 nanoparticles shows absorption bands at 3,411 cm^{-1}, 2340 cm^{-1}, 1630 cm^{-1}, 467 cm^{-1} and FT-IR spectrum of Gd^{3+} doped TiO_2 nanoparticles exhibits absorption at 3401 cm^{-1}, 2336 cm^{-1}, 1624 cm^{-1}, 455 cm^{-1}. The bands appeared broad and strong peak at 3411 cm^{-1} is ascribed to O-H stretching vibration. A small peak appearing at 2340 cm^{-1} ascribed to C-H stretching vibration [6]. The bending vibration of Ti-OH is observed in the range 1630 cm^{-1} [7]. The 467 cm^{-1} spectrum is Ti-O bond of anatase phase [8].

Diffuse Reflectance Spectroscopy:

Diffuse Reflectance Spectrum (DRS) of the synthesized Titania nanoparticles were recorded in the wavelength range of 200-1000 nm. Figures 4 and 5 show the reflectance spectrum of TiO_2 and Gd^{3+} doped TiO_2 nanoparticles respectively. Kubelka-Munk function was used to determine the band gap of the materials. F(R) was derived from the relation

$$F(R) = \frac{(1-R)^2}{2R}$$

F(R) is the Kubelka – Munk function

$$(F(R)\, h\upsilon)^{n} = A\,(h\upsilon - E_g)$$

Where R is the reflection of the particles which is proportional to the extinction co-efficient (α).

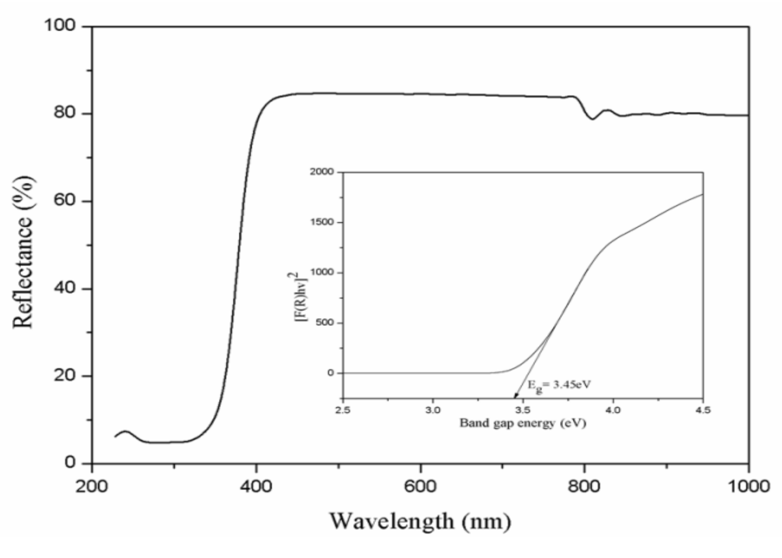

Figure 4: DRS spectrum of pure TiO_2 nanoparticles and the bandgap of pure TiO_2 (Inset figure)

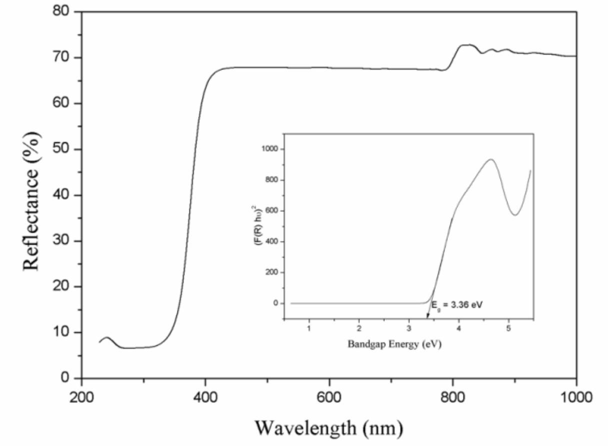

Figure 5: DRS spectrum of Gd^{3+} doped TiO_2 nanoparticles and the bandgap of Gd^{3+} doped TiO_2 nanoparticles (Inset Figure)

Plotting the value of $(F(R)h\nu)^2$ as a function of hν can find the direct band gap of nanoparticles. From the inset images, the optical bandgap of TiO_2 and Gd^{3+} doped TiO_2 nanoparticles was found to be 3.45 eV and 3.36 eV respectively. It is proved that the bandgap decrease with the particle size increases.

CONCLUSION

In summary, hydrothermal method has been developed to synthesize titania nanoparticles. Pure and Gd^{3+} doped TiO_2 nanoparticles were highly crystalline as revealed by XRD analysis. EDAX analysis was carried out for both samples. The bandgap of pure and doped TiO_2 nanoparticles was calculated from Kubelka – Munk Function. The bandgap of Gd^{3+} doped TiO_2 nanoparticle was decreased from bandgap of pure TiO_2 nanoparticles. The FT-IR spectra showed IR bands characteristic of titania nanoparticles.

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