Morphological, optical and structural properties of pure, zinc and magnesium doped TiO_2 nanoparticles for solar cell devices

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$Zn^{2+}$and Mg^{2+}ions doped Titanium dioxide had been synthesized using a hydrothermal method at 120°C with an annealing temperature at 450°C, including individual $Zn^{2+}$and Mg^{2+} ions. In addition, impact of these doping metal ions on the crystallization and phase transition of the Titanium dioxide nanoparticles were discussed by X-Ray Diffraction spectroscopy, Scanning Electron Microscopy, Fourier Transform Infra-Red spectroscopy, UV-Vis spectroscopy and Photo-Luminescence spectroscopy and also by photocatalytic measurements. The presence of anatase type structure in Titanium dioxide nanopowders with high crystallinity and high phase stability in spite of annealing at 450°C significantly specified that the dopants might prevent densification and crystallite growth in Titanium dioxide nanophase by on condition with different boundaries. Furthermore, with a suitable amount of Zn and Mg dopants, anatase grain size of Titanium dioxide powders was reduced. The band gap energy values of Zn^{2+} and Mg^{2+} ions doped nano-Titanium dioxide were lower than the pure nano-Titanium dioxide and they exhibited a red shift in the visible region.

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1. Introduction

Nanoparticles research is as of now an area of powerful efficient investigation, because of a broad range of potential cases in several fields such as electronic, optical and bio-medical [1]. The particle size is the major characteristics of nanoparticles for their performance in various fields. This is mainly due to two factors, *viz.*, increase in the ratio of surface-area to volume and the effect of outward atoms controlling the behavior of nanoparticles [2]. When in comparison with the bulk materials such as nano-powders, nano-plates and nano-sheets, there is a formation of greater surface area on nanoparticles on account of decrease in nano size. Specifically, the nanoparticle of titanium oxide has huge surface-region and indicates outstanding photocatalytic, optical and electric properties. Metallic nanoparticles, for example, Ag and Au included further consideration inferable from their high surface-region, stability and incredible conductivity and these are also widely utilized in the field of biotech and clinical [3]. This investigation features the production and properties of Zn and Mg NPs in photocatalytic measure. A few approaches such as solvothermal, sol-gel were accessible to synthesize titanium oxide nanoparticles [4]. A number of researchers have called attention to that the structural and optical execution of titanium oxide nanoparticles basically dependent on its crystallinity, morphology, crystal arrangement and surface-region[5,6]. To increase the crystallinity of titanium oxide, hydro-thermal synthesis was a broadly utilized procedure. Through the hydrothermal method, the nanosize of the samples was estimated by means of nucleation processes [7]. The optical properties of nanoparticles prepared

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were generally assessing by UV-Vis spectroscopy and Photo-Luminescence spectroscopy techniques to contemplate the electronic transitions in semi-conductors with band edge or close to band edge (NBE) transitions[8]. Restricted examinations dependent on absorption and energy-gap investigation of titanium oxide nanoparticles UV-Vis spectroscopy were introduced [9]. However, the optical effects of titanium oxide nanoparticles are not showed broadly. In this examination, the preparation of Pure titanium oxide, Zinc doped titanium oxide and Magnesium doped titanium oxide nanoparticles by hydrothermal method were reported. The structural as well as optical properties were examined by utilizing different techniques like X-Ray Diffraction spectroscopy, Scanning Electron Microscopy, Fourier Transform Infra-Red spectroscopy, UV-Vis spectroscopy and Photo-Luminescence spectroscopy.

2. Experimental details

2.1. Materials used and Preparation of Pure TiO_2, Zn/TiO_2 and Mg/TiO_2 Nanoparticles

Titanium isopropoxide $Ti\{OCH(CH_3)_2\}_4$ (≥99% purity), Zinc nitrate hexahydrate ($Zn(NO_3)_2$ $6H_2O$) and Magnesium nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$) (≥99% purity) were supplied by Sigma Aldrich and were used as precursors. All the chemical reagents, such as sodium hydroxide (NaOH) and ethanol were of analytic grade. All materials were used without further pretreatment. To 100 ml of distilled water, 25 ml of titanium isopropoxide [$Ti(OCH(CH_3)_2)_4$] was added under forceful stirring for about 10 minutes and homogeneous solution were attained by adding sodium hydroxide until the pH of 7. In order to increase the homogeneity, stirring was continued for about 10 minutes and the mixture was transferred to a 150 ml Teflon-lined stainless steel autoclave. It was set aside in an electric oven at 120°C for 24 hours. The mixture was cooled down to room temperature and washed with deionized water a number of times and then dried out at 100°C for about 10 minutes. Moreover, the samples of Zn & Mg doped titanium dioxide nanoparticles were prepared by hydrothermal technique. Initially titanium isopropoxide was dissolved in distilled water. A correct amount of zinc nitrate or magnesium nitrate was dissolved in deionized water. This solution was slowly mixed into the titanium isopropoxide solution, which was prepared by dissolving titanium isopropoxide in distilled water, by continuous stirring with sodium hydroxide solution till pH 8 for Zn^{+2} and Mg^{+2} correspondingly. The thoroughly mixed solution was then transferred to an autoclave at 120°C for about 24 hours. The obtained powdered samples were subjected to annealation 450°C in the presence of air for about 3 hours. The crystalline phases present in the different annealed samples were recognized by using X-ray diffraction (XRD) on a Brucker axis D8 diffractometer with crystallographic data software Topas 2 using Cu Ka (k = 1.5406 ÅA 0) radiation operating at 40 kV and 30 mA at a rate of 2/min. The diffraction data were recorded for about 2 hours values between 20 and 80. Transmission electron microscopy (TEM) and High Resolution Transmission Electron Microscopy (HRTEM) were performed with a JEOL-JEM-1230 microscope. The UV–vis absorption spectrum was deliberated by a UV–Vis scanning spectrophotometer (Jasco-V-570 Spectrophotometer, Japan) using a 1 cm path length quartz cell. Fourier Infrared absorption spectroscopy (FTIR) was measured by JASCO 3600 spectrophotometer (200–4000 cm^{-1}). The photo-luminescence of the colloidal solution was detected under the excitation of TiO_2 by UV light at 320 nm in air by means of an SHIMATDZU RF-5301PC Fluorescence spectrophotometer, Japan (150 W xenon lamp) at room temperature.

3. Results and discussion

3.1. X-ray Diffraction (XRD) Structural - Analysis

XRD diffraction patterns of pure and Zn & Mg doped Titanium dioxide nanoparticles prepared via the hydrothermal manner was shown in Fig.1. It was exposed that diffraction peaks of the pure sample matched well with those of a standard anatase titanium dioxide (JCPDS card number 04-0477) with high crystallinity [10]. The Zn & Mg doping did not lead to the vanishing of the indexed peaks, demonstrating that the crystallographic structure of the doped samples was

analogous to that of the pure Titanium dioxide sample. The impact of dopants of Zn and Mg lead to a slight shift of the peaks towards lesser diffraction angles. In view of the XRD data, the lattice constants a and c of the pure Titanium dioxide sample was observed to be 4.87 Å and 3.01 Å, correspondingly. For (Zn, Mg) doped samples, both parameters a and c were improved by 1%. As per Vegard's law, a statistical replacement of (Zn, Mg) dopants within the Titanium dioxide host lattice lead to expansion of lattice [11]. Their substitution for Ti^{4+} ion reduced the lattice parameters of the Zn & Mg doped samples. The crystallite size of Titanium dioxide nanoparticles was calculated from the most intense peak (1 01) using the Scherrer formula (1)[12]. The crystallite size determined for pure, Zn doped and Mg doped nanoparticles were 21 nm, 14 nm, and 16.8 nm respectively. It ought to be seen that other than the XRD peaks, these had emerged from the foremost phase of anatase Titanium dioxide.

$$D = 0.94\lambda/\beta\ cos\ (\theta) \tag{1}$$

where D - average crystallite size,

λ – Wavelength (1.5406 A^o),

β – FWHM (full width at half maximum) of individual peak at 2θ and

θ – Bragg angle.

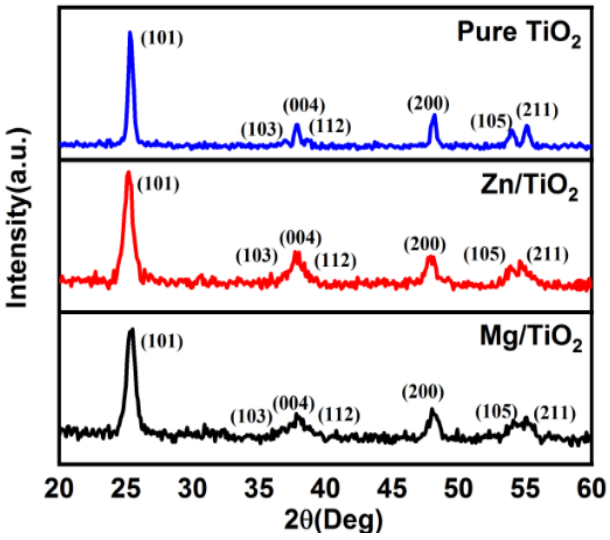

Fig. 1. XRD of synthesized Samples.

3.2. Fourier transform infrared spectroscopy (FTIR) – Analysis

From the FT-IR spectra, it is observed that the main bands were originated at 3400 and 1630 cm^{-1}. The bands observed at 3400 and 1630 cm^{-1} characterized the represented the broad stretching and bending vibrations of O–H hydroxyl groups. Furthermore, the few absorption bands located between 3450-3500 cm^{-1} were correlated to the small stretching band of OH hydroxyl group. The spectrum of (Zn, Mg)-doped TiO_2 showed the appearance of new peaks at 1370 cm^{-1} which signified the Zn–Ti and Mg–Ti bands, correspondingly. But these peaks were not detected in the pure TiO_2 nanoparticles. The peak observed at 1610 cm^{-1} was correlated to the bending vibration of coordinated H_2O along with Ti– OH, and this band could be normally condensed by annealing process at higher temperature, which demonstrated that a definite amount of O–H groups present in TiO_2 were removed during the annealing process. The absorption bands appeared in the range of 1100–1400 cm^{-1} were the vibration fingerprint lines of organic bond. The shoulder observed at 530 cm^{-1} was due to the presence of Ti–O–O bond[13,14]. The absorption peaks located between the regions of around 500cm^{-1} were attributed to the Ti–O–Ti bond.

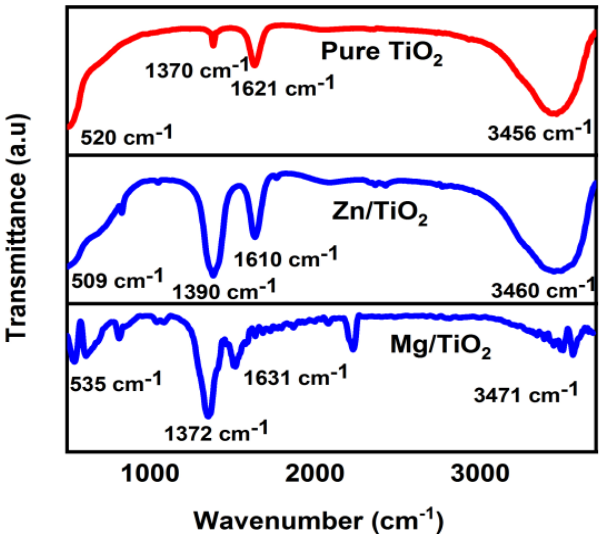

Fig. 2. FTIR Spectra of synthesized Samples.

3.3. Scanning Electron Microscope (SEM) - Analysis

The surface morphology of prepared samples of Pure titanium dioxide, Zn doped titanium dioxide and Mg doped titanium dioxide nanoparticles were revealed in the fig. from 3(a-c). The SEM images of pure titanium dioxide bring out a hexagonal like nanostructure which was shown in fig 3(a). Zn doped titanium dioxide and Mg doped titanium dioxide nanoparticles contained a sponge like materials which was demonstrated in fig 3(b) and 3(c) and 3(d). It was mainly due to more agglomeration of particles because of doping with Zn and Mg. These results obtained were in agreement with the XRD results that exposed the particles size of the anatase phase due to aggregation of nanoparticles doped with Zn and Mg.

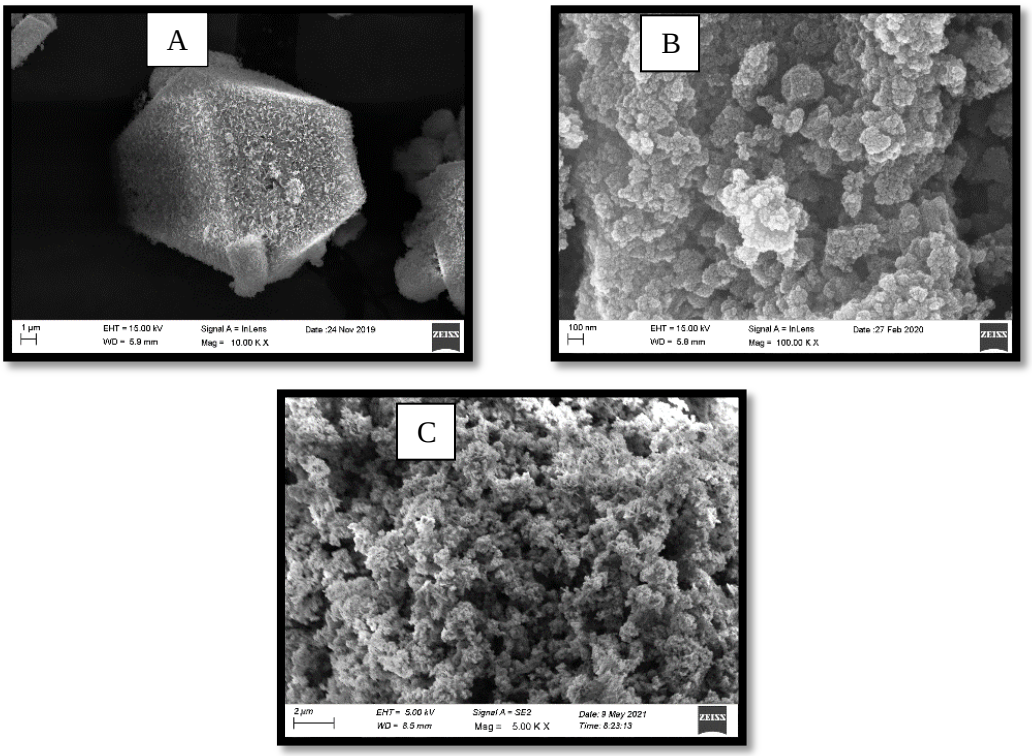

Fig. 3. SEM image of A) Pure TiO_2, B) Zn/TiO_2 and C) Mg/TiO_2 Nanoparticles.

3.4. Transmission Electron Microscopy(TEM) -Analysis

To study different morphological spectrums, the TEM microscopic technique was used, as shown in Fig-4(a-c). From the figure, it was known that their size was observed to be 52 nm, after the changes in their size and morphological behavior patterns. Fig 4(b) clearly demonstrated a Zinc doped titanium dioxide nano sheets, which was owing to the impact of dopant in the substrate. Fig-4(c) outlined Magnesium doped titanium dioxide nanocomposites in a rod-like arrangement that had been steadily clustered, with a size of about 37 nm. Due to its doping nature, thermodynamic aspects being used nanocomposites; the morphological characteristics of the nanoparticles should be modified.

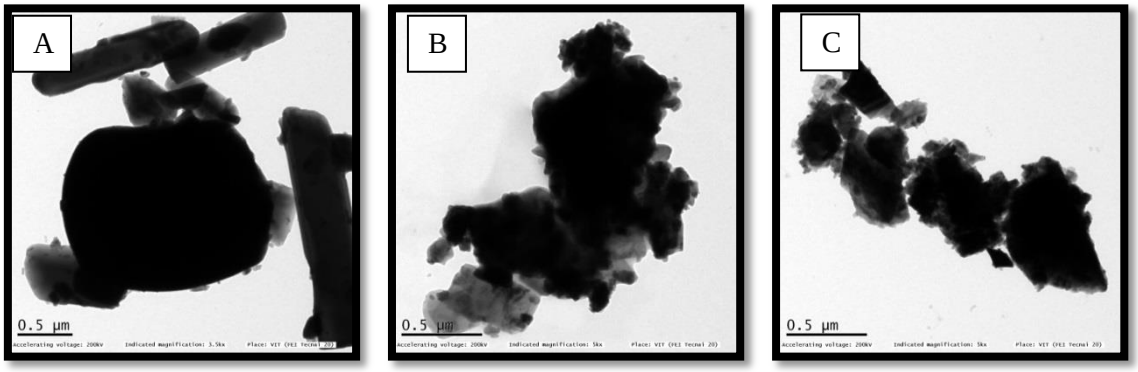

Fig. 4. TEM Analysis of A) Pure TiO_2 B) Zn/TiO_2 and C) Mg/TiO_2 Nanoparticles.

3.5. UV-Vis spectral Analysis

The optical spectra of the synthesized pure titanium dioxide, Zn doped titanium dioxide and Mg doped titanium dioxide nanoparticles were shown in Fig.5. Commonly, the position of absorbance rate was dependent upon the size, oxygen shortage, grain structure and energy band gap of the nanoparticles. The absorption bands appeared at 365 nm, 287nm and 354 nm were accounted for pure titanium dioxide, Zn doped titanium dioxide, and Mg doped titanium dioxide nanoparticles respectively. The excitonic peaks obviously showed the red shift for Zn and Mg doped samples. The absorption spectra of prepared nanoparticles showed that the absorption peak value was shifted to some extent towards the longer wavelength (red shift) when compared to that of pure titanium dioxide nanoparticles. This shift might be owing to the changes in particle size with Zn and Mg dopant**.**

$$\alpha h\nu = A(h\nu - Eg)^{1/2} \quad (5)$$

Equation (5) was referred to be Tauc Equation, where α is the absorption coefficient, hν is the photon energy, Eg is the optical band gap and A is a constant [15, 16]. The optical band gap value was determined using the equation (5) and shown in Table.3, as 3.19 eV, 3.07 eV and 3.09 eV for the synthesized pure titanium dioxide, Zn doped titanium dioxide and Mg doped titanium dioxide nanoparticles correspondingly.

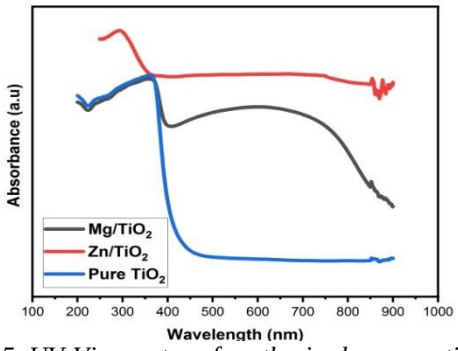

Fig. 5. UV-Vis spectra of synthesized nanoparticles.

Table 1. Band gap value of synthesized nanoparticles.

Samples	Wavelength (nm)	Band Gap (eV)
TiO_2	365 nm	3.19 eV
Zn/TiO_2	287 nm	3.07 eV
Mg/TiO_2	354 nm	3.09 V

3.6. Photolumineesnce (PL) – Analysis

The PL spectra of synthesized nanoparticles (Fig.6) showed the peaks at 461 nm, 463 nm, and 464 nm for Pure TiO_2, Zn doped TiO_2 and Mg doped TiO_2 nanoparticles correspondingly. The shape of the PL spectrum was expanded and separated into sharp peaks. The shifting of peaks towards longer wavelength might indicate the changes in nanosize. In the Figure, the sharp split of spectrum into two humps was owing to the various energy levels of mixed phase like anatase and rutile.

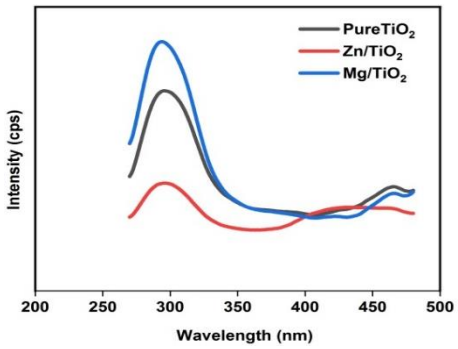

Fig. 6. PL spectra of synthesized nanoparticles.

4. Conclusions

Titanium dioxide nanoparticles doped with various Zn & Mg substances were synthesized via a modified hydrothermal technique. The Zn & Mg doped titanium dioxide advanced the crystallization process of the titanium dioxide particles when anneleation was carried out at 450°C. Additionally, the Zn & Mg dopants experienced a depression effect on the anatase grain growth. The crystallite size determined was 21 nm, 14 nm and 16.8 nm for pure nanoparticles, Zn doped and Mg doped nanoparticles respectively. TEM images demonstrated Zinc doped and magnesium doped titanium dioxide nano sheets, which was owing to the impact of dopant in the substrate. The absorption spectra of prepared nanoparticles showed that the absorption peak value was shifted to red shift when compared to that of pure titanium dioxide nanoparticles. The band gap energy of the powdered samples formed was estimated in the range of 3.09 to 3.19 eV. The powdered samples formed possessed the potential applications in catalysis and solar cell devices.

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