

RESEARCH PAPER

Synthesis and Structural Properties of $\text{Eu}^{3+}:\text{TiO}_2$ Nanoparticles

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ABSTRACT

Pure and doped TiO_2 with Eu^{3+} nanoparticles were prepared by a novel and simple preparation method due to their wide spectrum of applications such as solar cells, gas sensors photocatalyst, etcetera. The pure TiO_2 nanoparticles and the doping TiO_2 with the Eu^{3+} ions prepared at room temperature by the sol-gel method via the reaction of Titanium (IV) isopropoxide (TTIP) with an aqueous solution of hydrochloric acid in the presence of ethanol. The crystal structure of the prepared nanoparticles was investigated by X-Ray Diffraction (XRD) while the morphology of the samples was investigated by Field Emission Scanning Electron Microscopy (FESEM). All the prepared samples having excellent crystalline. As well, XRD proved that doping TiO_2 with Eu^{3+} reduced the crystallite size. The FESEM images showed that the doping of TiO_2 with Eu^{3+} results in larger particle sizes. In the present work, the effects of doping, particle size, and stabilization of the anatase phase were studied. As well as the deceleration of crystal growth by the rare-earth-doped into TiO_2 host was investigated.

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INTRODUCTION

Recently, several types of published research have been emphasized the preparation and usage of Titanium dioxide (TiO_2) nanoparticles in many applications such as hydrogen (H_2) generation, solar cells, photocatalyst, and gas sensors [1]. This is due to its low cost, high stability against photo-induced corrosion and chemicals [2]. It is non-toxic, has strong oxidizing power, a wide energy bandgap of 3.2 eV and maximum light scattering with virtually no absorption [3, 4]. The three different crystalline forms of TiO_2 are rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic) [5]. The formation of

each crystalline phase depends on the nature of starting material, sol composition, deposition method and calcination temperatures [6, 7]. TiO_2 bulk can be transformed from an amorphous phase into crystalline by calcination [8]. Several methods have been employed to synthesis TiO_2 , such as microwave [9-11], hydrothermal [12] polyol mediate solvothermal [13] and ultrasonic methods [14]. Among these methods, the sol-gel is widely used due to its simplicity, low cost, high flexibility, high yield and homogeneous product [15]. Sol-gel procedures consist of four steps: the main processes are hydrolysis condensation, growth and gel formation. In the initial steps,

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catalysts such as acid or base are used to speed up the reaction process [16]. Rare earth (RE) ions doped metal oxides (MO) had received great attention because they are applicable in several fields such as optical detectors and fibers, solid-state lasers, light-emitting diodes, and screens. Owing to the important properties of REs such they include several excited energy levels, promising optical properties such as long life-time and have absorption and emission spectra with sharp peaks shifted from ultraviolet to the infrared region [17].

Usually, TiO₂ nanoparticles are used as an electrode and an active layer in solar cells due to their transparency and conductivity. The photoactivity of TiO₂ depends on several factors, including crystal modification, particle size, preparative route, surface area, porosity, thermal history, foreign ions and so on. Doping TiO₂ with RE metals increases the photoactivity. Europium (Eu³⁺) ions represent the most promising and applicable ions compared to other RE. This is due to the fact that the Eu³⁺ ions have narrow fluorescence emission with long lifetimes [18].

Recently, doping TiO₂ nanoparticles with RE ions especially Eu³⁺ have been used in several prospective applications such as biomedical, sensors, photocatalytic, electrochemical, solar cells and so on [19]. Therefore, TiO₂ doped Eu³⁺ attracted a few researcher's considerations. Whereas, the preparation methods were complicated and required high temperature [20].

Our proposed preparation method solves this problem by developing a new method for preparation and doping TiO₂ with Eu³⁺ with various doping levels without the requirement of complicated instruments or high temperatures. To the best of our knowledge, this is the first report which addresses the doping of TiO₂ with Eu³⁺ at room temperature. The novelty of this work is to use a simple, green, inexpensive preparation method at room temperature which is considered an energy-saving method. The structural and morphological properties were investigated for the synthesized samples via XRD and SEM.

MATERIALS AND METHODS

The TiO₂ solution was synthesized using Titanium (IV) isopropoxide (TTIP) purity (97%), as a precursor material supplied by Aldrich Company. Ethanol (EtOH) purity (99.9%), as a solvent was purchased from GCC. Hydrochloric Acid (HCl) of purity (37 %) was provided by BDH as a catalyst.

The composition of the materials consisted of HCl:TTIP:H₂O:EtOH with a molar ratio of 0.1:1:1:10. HCl, H₂O and EtOH were added to the TTIP under continuous stirring. By using Europium (III) nitrate hydrate purity (99.9%) from Aldrich Company the doping with Europium Eu³⁺ is investigated. The doping rate of Eu³⁺ into TiO₂ were about 0.0, 0.7, 1.1, 1.9 and 2.3% molar ratio. The prepared solution was stirred vigorously for about 1-2 hours until a clear transparent solution was achieved. Following to hydrolysis and condensation process, the prepared solutions were aged for 24 hour. These preparation steps were totally done at room temperature to obtain a colorless powder. The samples were annealed in the furnace at 500°C for 2 hours. Finally, a yellowish powder was collected due to the doping of Eu inside TiO₂.

XRD patterns were obtained using (X'PERT PRO, PHILIPS) by CuK α radiation at 40 kV and 30 mA. The crystallite size of TiO₂ and TiO₂ doped Eu³⁺ powder were estimated by applying the Scherrer equation [21].

$$D_s = K \lambda / \beta \cos \theta \quad (1)$$

Where K is a constant (shape factor) and the value 0.94 was used for the calculation, λ is the X-ray wavelength which is 0.15405 nm, β is the full-width at half maximum of the diffraction line and θ is the half diffraction angle of the centroid of the peak in degree. To calculate the lattice parameters (a and c) and the unit cell volume (V) of the samples, the following relations (belongs to the tetragonal crystal system), were applied respectively [22, 23].

$$\frac{1}{d^2} = \frac{(h^2+k^2)}{a^2} + \frac{l^2}{c^2} \quad (2)$$

Where, d is the inter-planar spacing and (h,k,l) are Miller indices.

$$V = a^2 c \quad (3)$$

The surface morphology of the prepared samples was monitored by FESEM (MIRA3 TESCAN).

RESULTS AND DISCUSSION

X-Ray Diffraction analysis

Structural properties were investigated using the X-Ray diffractometer. The XRD patterns of the un-doped and Eu doped TiO₂ samples prepared

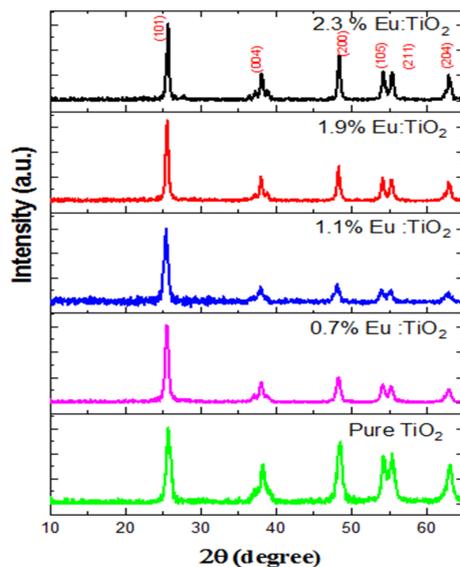


Fig. 1. XRD patterns of pure and Eu doped TiO₂.

Table 1. Crystal sizes, FWHM and, lattice constants (a and c) and volume cell for different Eu³⁺ Concentrations.

Eu% (wt.)	2θ°	d(hkl) EXP.(Å)	Crystal size(nm)	FWHM (Deg.)	a (Å)	c (Å)	V (Å ³)
0.0%	25.6	3.472	20.7	0.3936	3.751	9.415	132.54
0.7%	25.5226	3.4901	18.4	0.4428	3.773	9.477	134.94
1.1%	25.3839	3.5089	13.79	0.5904	3.785	9.464	136.18
1.9%	25.5275	3.4894	20.70	0.3936	3.770	9.459	134.46
2.3%	25.6158	3.4776	33.13	0.2460	3.769	9.461	134.45

by the sol-gel method after annealing at 500 °C are presented in Fig. 1. It is clear that all samples have anatase phase TiO₂, which corresponds to the standard diffraction data (ICSD 01-073-1764). This is due to the fact that the TiO₂ grows in three crystal structures: “anatase” and “brookite” at low temperature while “rutile” crystallizes above 600 °C [8]. The presence of a peak corresponding to Eu³⁺ ions is an indicator of TiO₂ doping with Eu³⁺ ions. The absence of peaks corresponds to other materials, is evidence of the high purity prepared structure. It can be observed from Fig. 1 that the diffraction peaks of the samples were slightly shifted to a lower angle due to the presence of Eu³⁺ ions into TiO₂. These results are matched well with previous work [24].

The peak intensity decreased dramatically due to the addition of Eu³⁺. The crystal size of Eu³⁺: TiO₂ = 0.0, 0.7, 1.1, 1.9 and 2.3% were estimated as 20.7, 18.4, 13.79, 20.70 and 33.13 nm, respectively. It can be seen that the crystal size decreases with

increasing the doping ratio of Eu³⁺ as shown in Fig. 2. The crystal size and full width at half maximum β at Miller indices (101) for the samples used in this study are explained in (Table 1). The reduction of anatase particle crystallite coherent sizes after doping with RE ions has been already reported in the literature [25,26] and can be attributed to the presence of RE-O-Ti bonds that inhibit the growth of crystals. The presence of ions in octahedral coordination with a larger ionic radius than the original (Eu³⁺ = 0.95 Å > Ti⁴⁺ = 0.68 Å) [25], induces the expansion of the unit cell volume and causes lattice disorder.

The selected miller indices (004) and (200) exhibited the following lattice parameters: a=3.7760 Å and c= 9.4860 Å, and α=β=γ=90°. It can be seen from (Table 1) that all the samples have good agreement with the TiO₂ stander data. As its listed in Table 1 the crystal size varied from 20 to 33 nm which is in agreement with previous work [27].

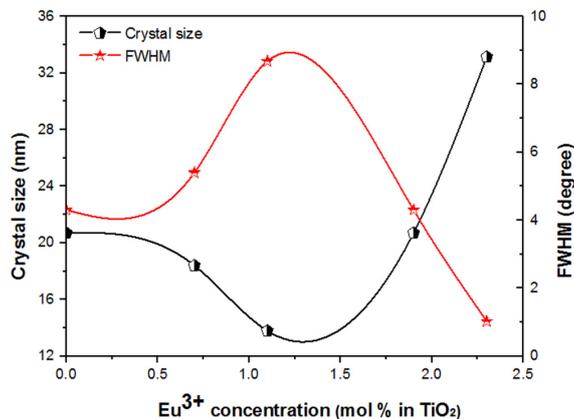


Fig. 2. The effect of the doping of Eu concentration on the crystal size and FWHM.

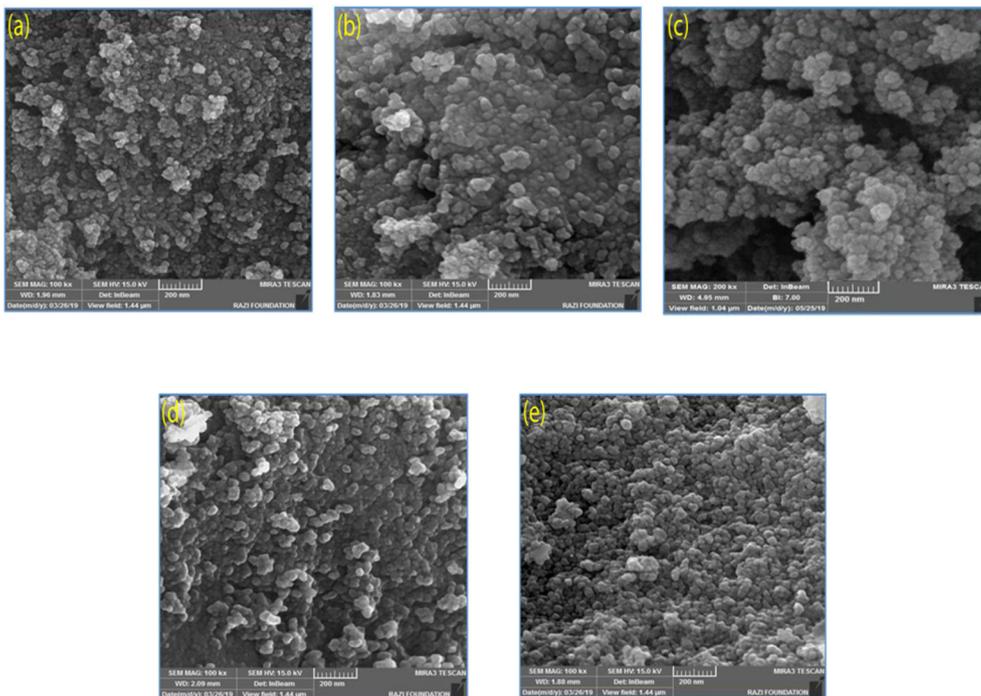


Fig. 3. FESEM of TiO_2 (a) 0.0% , (b) 0.7, (c) 1.1 (d) 1.9 and (e) 2.3% Eu.

Several studies reported that by doping TiO_2 nanoparticles with Eu, the crystal size decreased which is consistent with our study [3]. The effect of doping Eu^{3+} ions concentration on TiO_2 nanoparticles was also studied. It was found that the crystal size reduced with increasing Eu content [18, 26].

Moreover, we did not observe any peaks of the europium complex and no shifting of the anatase peaks was observed after grafting Eu^{3+} steroids.

That is revealing the Eu ions do not disperse in the amorphous Titania region instead of occupying Ti Locations within anatase nanocrystals.

FESEM results

Field Emission Scanning Electron Microscopy (FESEM) was used to probe the changes in the morphology and particle size of the TiO_2 powder. Fig. 3 (a, b, c, d and e) shows the FESEM images of TiO_2 powder doped with Eu = (0.0, 0.7, 1.1, 1.9

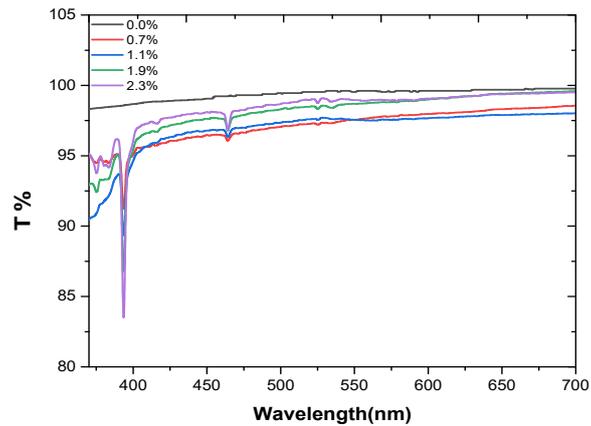


Fig. 4. Transmission spectra of TiO_2 doped with Eu

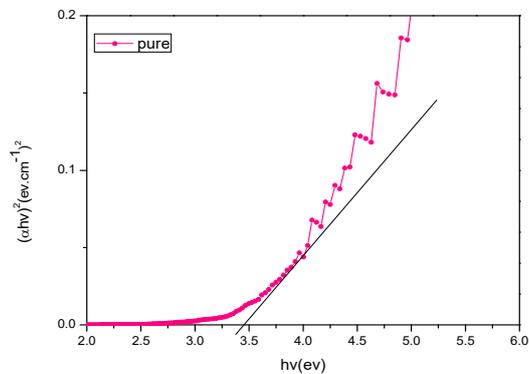


Fig. 5. $(\alpha hv)^2$ as a function of photon energy of TiO_2 pure

and 2.3 %), respectively. It was found that the average particle size of TiO_2 before Eu doping is $(30 \pm 5 \text{ nm})$. It can be observed that the average particle size increases by increasing the doping Eu content. Moreover, the amplified images of the samples illustrate the growth and agglomerations of the nanoparticles due to doping with Eu. It was reported that the incorporation of europium into titanium dioxide by the sol-gel technique strongly affects the structural properties of TiO_2 , where the particles are joined together to form irregular shapes with size in the range from 3 to $136 \mu\text{m}$ [26].

Optical characterization of $\text{TiO}_2:\text{Eu}^{3+}$

From the observation of the transmittance spectrum of titanium doped with Eu^{3+} Fig. 4, there is a behavior similar to that of pure titanium, and there is a clear concavity at the wavelength 394, as well as 464 nm.

When calculating the energy gap for pure titanium, the gap value was (3.48 eV), as shown in Fig. 5 which is the highest possible, and the reason is due to the discrepancy in the edge of the optical range due to localized deformation states of the Eu^{3+} , and this is consistent with the researcher's findings [27].

After that, the energy gap was calculated as shown in Fig. 6, and we note that there is a decrease in the value of the energy gap at some concentrations of Eu^{3+} , especially when concentration (1.9). Where the lowest value was (2.18 eV), and the highest value was 2.518 eV at concentration of (1.1). By comparing these results with previous work where the pure TiO_2 is around 3.1 that reduced to 2.7 eV by increasing doping level with Eu [28].

As mentioned before the preparation method plays an important rule to control the properties of the prepared materials. As example in this

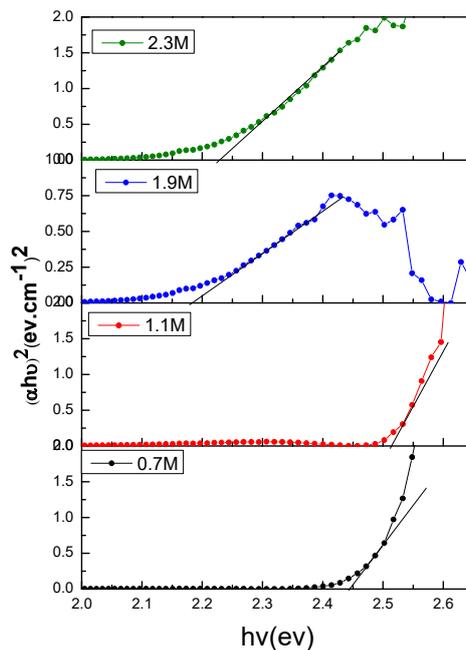


Fig. 6. $(\alpha hv)^2$ as a function of photon energy of TiO_2 doped with Eu^{3+}

manuscript the prepared materials exhibited promising properties which is differs from those obtained in previous work due to the preparation method which is totally different from that which have been used in the mentioned work [18].

CONCLUSION

High purity Eu^{3+} doped TiO_2 nanoparticles with doping rates of 0.0, 0.7, 1.1, 1.9 and 2.3% were successfully prepared by the sol-gel technique. The results showed that significant effects on the structural properties were achieved by doping Eu^{3+} into TiO_2 . XRD patterns revealed that the prepared samples had good crystallinity and shown that the prepared Eu^{3+} doped TiO_2 samples have a polycrystalline structure in the anatase phase. As well it proved the decrement in crystallite size by increasing the Eu^{3+} content. Consequently, the average particle size increase when the doping ratio increased as revealed by FESEM.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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