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A spectroscopic study of the effect of Er^{+3} ions concentration on the optical and structural properties of nanoTiO_2

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Abstract

Er^{3+}doped TiO_2 composites were synthesized by using the simple mixing process in order to study the effect of a rare earth metal ions (erbium) on the spectroscopic and structural properties of nano titanium dioxide. Three distinct erbium concentrations “10^{-2}, 10^{-3}, and 10^{-4} gm/cm3” were used for the spectroscopy study of TiO_2Er^{+3} compounds.. The corresponding fluorescence emission spectra were measured and compared using an excitation wavelength at 350 nm. The effect of Er^{+3} concentration on the composition and optical properties of nano-TiO_2 was studied. Structural and spectroscopic analysis confirm the presence of Er^{3+} in the composition and that it plays an important role in the upward shift of fluorescence. X-ray diffraction was used to examine the structural features of this material. In the XRD patterns, there were no extra peaks related to any polymorph of TiO_2 or contaminants, demonstrating that Er^{3+} was effectively integrated as a dopant. Through this work, the possibility of the existence of titanium nanoparticles doped with rare earths for optical applications becomes clear.

Keywords: Erbium, rare earths, optical attributes, TiO_2nanoparticle,Fluorescent materials, optical properties.

دراسة طيفية في تاثير تركيز الاريبيوم(Er) على الخصائص الطيفيةوالهيكلية لثاني اوكسيد التيتانيوم(TiO_2) النانوي

تم تصنيع مركبات TiO_2 النانوية المطعمة بـ$Er+^3$ باستخدام عملية الخلط البسيطة من أجل دراسة تأثير ايون الإربيوم على الخصائص الطيفية والهيكلية لثاني أكسيد التيتانيوم النانوي. استخدمنا ثلاثة تركيزات مميزة للإربيوم "١٠^-٢ ، ١٠^-٣ ، و١٠^-٤ جم / سم^٣" لدراسة التحليل الطيفي لمركبات TiO_2Er^{+3} . قمنا بقياس ومقارنة أطياف انبعاث الفلورة المقابلة باستخدام طول موجة إثارة عند ٣٥٠ نانومتر. تمت دراسة تأثير تركيز Er على التركيب والخصائص البصرية لثاني اوكسيد التيتانوم النانوي . يؤكد التحليل الهيكلي والطيفي وجود Er في التكوين وأنه يلعب دورًا مهمًا في التحول التصاعدي للفلورة. استخدمنا حيود الأشعة السينية لفحص الخصائص الهيكلية لهذه المادة. في أنماط XRD ، لم تكن هناك قمم إضافية مرتبطة بأي تعدد الأشكال من TiO2 أو الملوثات ، مما يدل على أن Er3 + تم دمجه بشكل فعال كمشوب. من خلال هذا العمل ،تتضح إمكانية وجود جسيمات التيتانيوم النانوية المطعمة بمعادن الارض النادرة للتطبيقات االبصرية.

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1.Introduction

New nanomaterials are constantly being synthesized to achieve properties suitable for various applications. These materials may contain oxides as host matrices, while the doped materials may be rare earth (RE) ions. One of the best oxides used as a host for RE emitters is titanium dioxide because of its good optical and thermal properties. This compound has been widely used in recent years [1-8]. In important applications such as communications, display devices, fiber amplifiers, and sensors, erbium (Er) is perhaps the most widely used of the rare earth elements due to its emissive properties [9–14].As well as photocatalytic applications, where titanium dioxide is considered the best among the semiconductors because it is high efficiency, readily available, less expensive, highly oxidizing, photo-generated holes, less toxic, extremely stable in a wide pH range and photostable [15,16]. There are three crystalline phases of titanium dioxide: anatase, rutile, and brookite. Anatase phase is the most stable and highly effective phase in photocatalysis due to its open structure, compared to rutile phase, the rutile also has photoreactivity but not efficiently, While brookite is an unstable phase and does not show any appreciable catalytic activity[17]. The application of TiO_2 is restricted to the UV region due to the wide bandgap (3.2 eV), the transition from the anata to the rutile phase also reduces the photocatalytic efficiency [18,19] . By minimizing electron-hole recombination these limitations can be overcome, and the absorption wavelength shifted to the visible region. These can be done by metal and non-metal doping [20], dye sensitization [21] and coupling [22]. Doping provides an effective and easy way to change the optical and electronic properties of titanium dioxide. Lanthanides have been studied as dopant TiO_2 for their significant role in changing the absorption edge of semiconductors, thus enhancing the absorption of low-energy photons. It has been shown that lanthanide metal ions form complexes with different Lewis bases such as alcohols, amines and aldehydes using their 4f orbital, which provides an ideal site for the adsorption of organic pollutants and improve their photocatalytic activity [16,23,24]. Also, these ions have the ability to alter the optical and catalytic properties of titanium dioxide [25-27]. The lanthanides are effectively deposited on the surface of TiO_2 due to their large ionic radius, which increases its surface area [23,28].

Xu et al.(2002) doped rare earth metal ions (Nd3+, Ce3+, Gd3+, La3+ , Sm3+ ,Pr3+) into TiO_2 nanoparticles using sol-gel method where they observed a decrease in the electron pair recombination rate, increase in interfacial electron transfer rates and red shift towards longer wavelength [24]. Fan et al.(2006) worked on the synthesis of nanostructures of cerium doped TiO2 and then verifying its photocatalytic activity, where the photocatalytic activity increased with increasing concentration of cerium [29] . The most common lanthanides are erbium, which is used as an dopant for

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titanium dioxide. It converts infrared or visible light into visible light and ultraviolet light, which is used in TiO_2 photocatalytic applications. [30].

In this paper A promising Er^{3+}-doped TiO_2 composite with sufficient Fluorescence emission characteristics in the visible ranges was synthesized and characterized. We have tried several concentrations of Er^{3+} (10^{-2}, 10^{-3}, 10-4, gm/cm3) to study the effect of Er ion concentration on the visible emission and fluorescence emission of nano-titanium dioxide (anatase).

High emission at 503 nm is observed in the visible region of the fluorescence emission spectra we studied. X-ray diffraction was also used to examine the structural features of our compound where we observed the clear influence of the erbium ion on the spectral properties of titanium dioxide.

2.Experimental details

2.1Chemical materials

The chemical materials used in this work were; rare earth metal (Erbium), Titanium Oxide (Anatase) Nanopowder 99.9% Pure,APS<5nm supplied from mknano, ethanol > (99 %) provided from Merck, India)

2.2 Samples preparation

TiO_2 " molecular weight is 79.866 gm/mol" The white powder of nano-titanium dioxide dissolved in ethanol using magnetic stirrer so that forms transparent solution**,** depending on their chemical formula- with concentration is ($1*10^{-3}$ gm/cm^3 names standard samples), by equation (1), also, Er " molecular weight is 167.259 gm/mol" dissolved in ethanol with concentration ($1*10^{-2}$) gm/cm^3 by equation (1) after that was diluted with ethanol to obtain the different concentrations depending on equation (2) (10^{-3}, 10^{-4}, gm/cm^3)

$$W=\frac{Mw\times c\times V}{1000} \quad \ldots\ldots\ldots(1)$$

W: weight in grams, Mw: Molecular Weight of materail, c: concentration and V: volume of water

$$C_1V_1= C_2V_2 \ldots\ldots\ldots\ldots\ldots (2)$$

Three samples were prepared , sample 1 by mixing a solution of TiO_2 at a concentration 10^{-3} gm/cm3 with an Er solution with a concentration of (10^{-2}, 10^{-3}, 10^{-4}, gm/cm3) respectively, All conditions were the same for the three samples and at

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room temperature , this samples was labeled as TiO_2 ,TiO_2Er2, TiO_2Er3 and TiO_2Er4 for 10^{-2}, $10^{-3}$and 10^{-4}, gm/cm3 concentration respectively.

3. Results and discussion:

3.1 Optical properties

(Fig.1) shows the absorption spectra for the samples TiO_2,TiO_2Er2, TiO_2Er3 and TiO_2Er4 dissolved in ethanol as a polar solvent within the range 280-780 nm. The lowest absorption value was recorded for nano-titanium dioxide solution alone at concentration(10^{-3} gm/cm3), at wavelength (320 nm) and the absorbance increased in the presence of erbium ion(Er^{+3}) with different concentrations, where the highest absorbance was obtained at concentration 10^{-4}, gm/cm^3 of Er (sample TiO_2Er4), at wave length 320 nm.

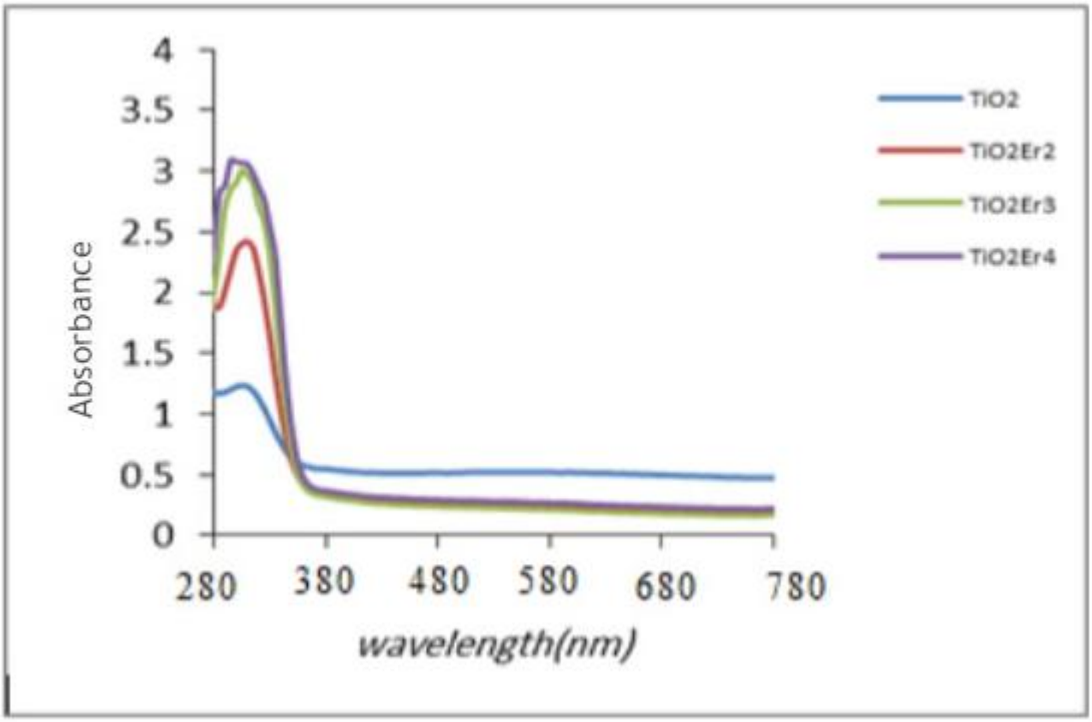

Figure1: Absorption spectra of Er and TiO_2 solutions with different concentrations

From the above, we note that the concentration of the erbium has a clear effect on the absorption spectrum of the titanium dioxide solution in terms of intensity and does not affect the shape of the absorption spectrum.

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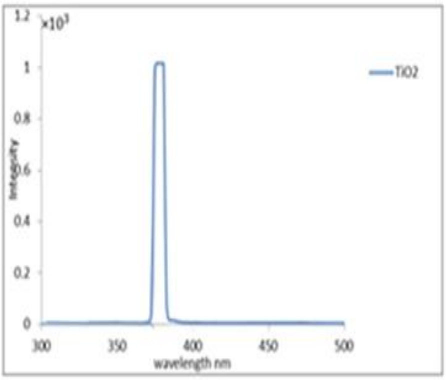
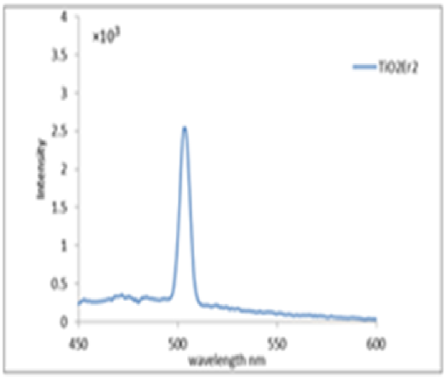
Fluorescence spectra were recorded for all pre-prepared samples, and it was noted that the concentration of Er^{+3} had a clear effect on the intensity of the emitted fluorescence spectrum of titanium dioxide without affecting the shape of the spectrum and without any shift in the location of the emission beam (Fig.2)demonstrate the Fluorescence spectra generated by employing a 350 nm excitation wavelength for materials in the 450-600 nm range.

We note from (Fig.2a), which represents the fluorescence spectrum of a titanium dioxide at a concentration of (10^{-3} gm/cm^3), the highest intensity was obtained at wavelength 380 nm , The other figures (2b,c,d) are the fluorescence spectra of the TiO_2Er^{+3} mixture of concentrations (10^{-2}, 10^{-3}, 10^{-4}, gm/cm3), respectively. As can be seen, the fluorescence intensity was increased by adding erbium ,and the strongest intensity occurred at 10^{-4}, gm/cm3 concentration of erbium ion in the mixture (sample TiO_2Er4) at wavelength 503.This peak in the green area that were linked to Er^{+3} transitions $^4S_{3/2} \rightarrow {}^4I_{15/2}$ [4,8]

I would like to point out here that no wavelength shift occurred in the fluorescence spectra for all concentrations of TiO_2Er^{+3}mixtures. The change was in intensity only, which indicates that the erbium ion(Er^{+3}) has a clear effect on the fluorescence properties of TiO_2 .





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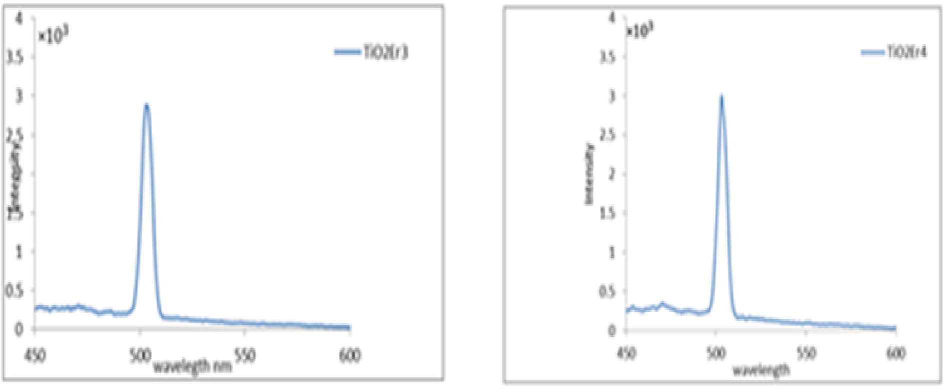

Figure 2: demonstrate the fluorescence spectra generated by employing a 350 nm excitation wavelength

3.2Crystal Structure

(Fig. 3) shows the XRD patterns of the prepared thin films by dip coating technique, which were thermally treated at sintering temperature 450°C for 1 hour , From the figure it is clear that . The effect of the erbium ion on the X-ray spectrum of TiO_2 is evident as the intensity of the titanium oxide peaks increases with the increase in the erbium ion concentration, Which indicates enhanced crystallinity of titanium ,this is in agreement with Y. Bader et al [4].

From XRD figure, we did not observe any additional peaks associated with any TiO_2 polymorphisms or contaminants, which indicated that Er^{3+} was effectively integrated as a dopant with TiO_2(anata) nanoparticles.

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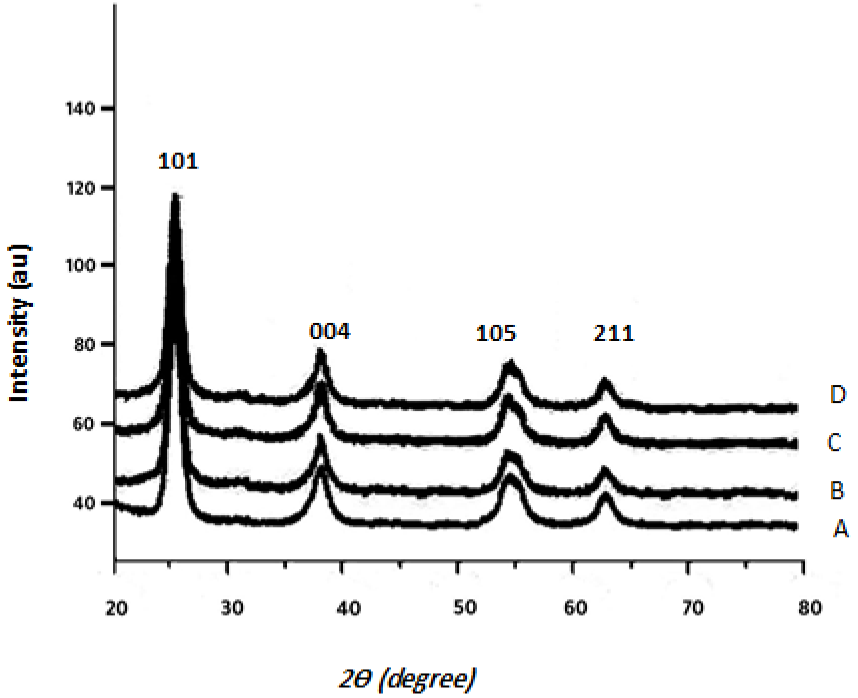

Figure 3: XRD spectra of nanoTiO_2 (anatase) and Er-doped TiO_2 samples at different concentrations (10^{-2},10^{-3},10^{-4} g/cm^3),which represented A,B,C,D respectively.

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4.Conclusion

Three distinct concentrations of erbium ion “10^{-2}, 10^{-3}, 10^{-4}gm/cm3” were synthesized for the Er^{+3}-doped TiO_2 compounds using a standard mixing procedure. Fluorescence emission spectra were obtained and compared using an excitation wavelength of 350 nm in order to study the effect of the erbium ion on the optical, structural and spectroscopic properties of the anatase phase titanium dioxide nanoparticles.

At various concentrations, we observed three distinct peaks in the green area that were linked to Er^{+3} transitions $^4S_{3/2} \rightarrow {}^4I_{15/2}$.[4,8].

Through the spectroscopic study of erbium ion-doped nano titanium dioxide compounds, it appears that the presence of erbium ion (Er^{+3})plays an important role in the upward shift of fluorescence .In the XRD patterns, there were no extra peaks related to any polymorph of TiO_2 or contaminants, demonstrating that Er^{3+} was effectively integrated as a dopant. This work demonstrates the possibility of rare earth doped titanium nanoparticles for photonic applications [6],also, Er^{3+} doped TiO_2 nanoparticles can be used in solar cells and bio imaging devices because of their structural, optical, and luminescent capabilities.

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