Visible Region Response of Cobalt Doped TiO_2 via Sol Gel Technique

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Abstract

TiO_2 nanoparticles were prepared via sol gel technique, and then doped with cobalt ions to form TiO_2 doped cobalt sol. Thin films were prepared from this sol using dip coating method and underwent calcination at a temperature of 550°C.The films were characterized by UV–Vis spectroscopy, X-ray diffraction (XRD), and atomic force microscopy (AFM). The UV–Vis. Absorption spectra show a red shift, which indicates that TiO_2 doped cobalt will responds to the visible region of spectrum rather than UV- region for pure TiO_2.

1-Introduction

Titanium dioxide (TiO_2) is one of the most interesting n-type semiconductor materials due to its wide applications such as self- cleaning surfaces, antifogging function, antibacterial function, and decomposition of pollutants [1,2].

TiO_2 has two main drawbacks it has a photocatalytic activity under UV-light irradiation only since its energy gap is wide (3.2 eV) for anatase phase, (λ= 387nm), and UV forms less than 5% of solar spectrum while the dominant spectral region of solar spectrum is visible.

Another drawback is the fast electron–hole recombination. To overcome these limitations, several efforts have been made by modifying the surface or bulk properties of TiO_2 through doping with metals and non-metals in order to reduce the band gap and delay electron–hole recombination[3] .

In this work, cobalt doped TiO_2 was studied since there are a few published papers on this transition metal.

Cobalt doped TiO_2 sol was achieved by sol gel technique, and thin films of this sol were prepared using dip coating method.

2-Experimental

Titanium tetra isopropoxide (TTIP), $Ti[OCH(CH_3)_2]_4$, (purity 97%) from (Sigma-Aldrich) was used as a precursor in the preparation of TiO_2 nanoparticles sol via sol gel technique. Different weights of cobalt nitrate (0.05, 0.1, 0.15, 0.2, 0.25)gm were dissolved in (5 ml) of Ethanol. Each of these weights was added to TiO_2 sol was gotten with stirring for 24 hours and adjusting the pH to (1.5) by adding drops of HNO_3. Hence, got cobalt doped TiO_2 sol. After that, a thin film of that sol was achieved by using dip coating method on glass substrates. The substrates with different weights of cobalt were calcined in a furnace at 550°C for three hours with rate temperature 10°C/ min.

1.3 UV-Visible Spectroscopy

Figure (1-a) shows the absorption spectra for pure and different weights of cobalt doped TiO_2. From this figure, it is clear that with the increase of the weight content of cobalt, the absorption edge shows a red shifted (i.e. shifting towards longer wavelengths), which indicates that the samples with cobalt doped TiO_2 will be responsd to visible region, and the optimum sample is (0.2gm of cobalt doped TiO_2).

Figure (1-b) shows the transmittance for pure and different weights of cobalt doped TiO_2, and it reduces with increase the weight content of cobalt. Cobalt ions (Co^{2+}) substitute (Ti^{4+}) site generates additional oxygen vacancies in the TiO_2 unit cell, which introduces extra energy levels, and hence, reduces the indirect energy band gap of TiO_2 nanoparticles [4]

The electrons of the six oxygen atoms in TiO_2 cell will repulse the electrons in the d-orbital of cobalt ion Co^{2+}, and hence split d-orbital of cobalt ion [5].

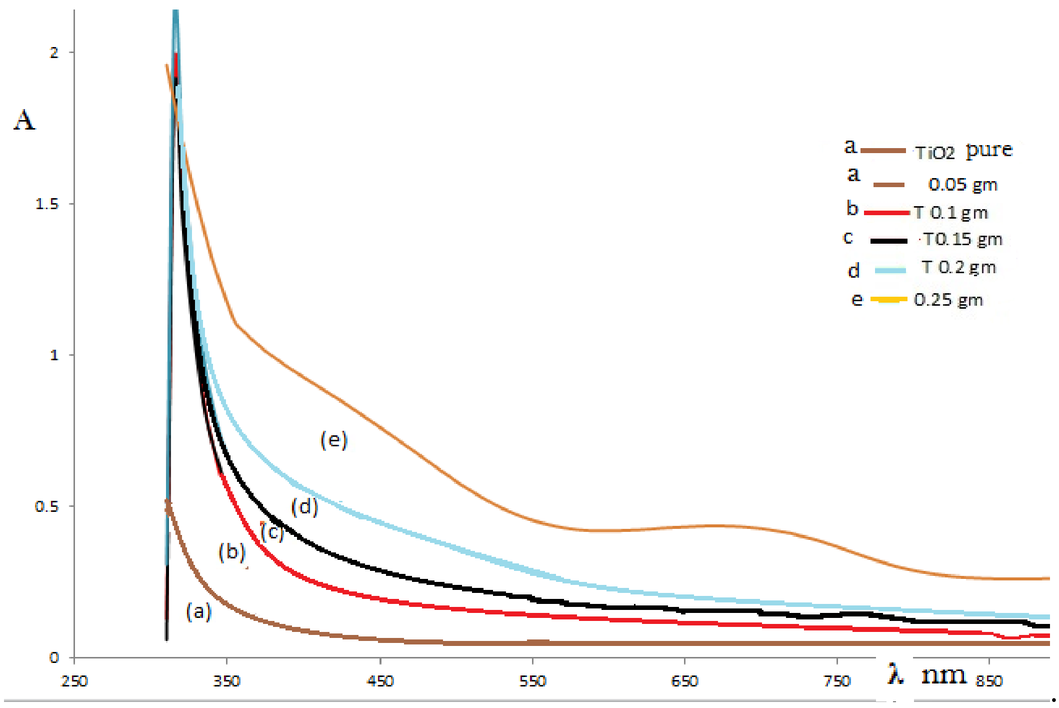


Figure (1- a): The Absorption Spectra for Pure and Different Weights of Cobalt Doped TiO_2.

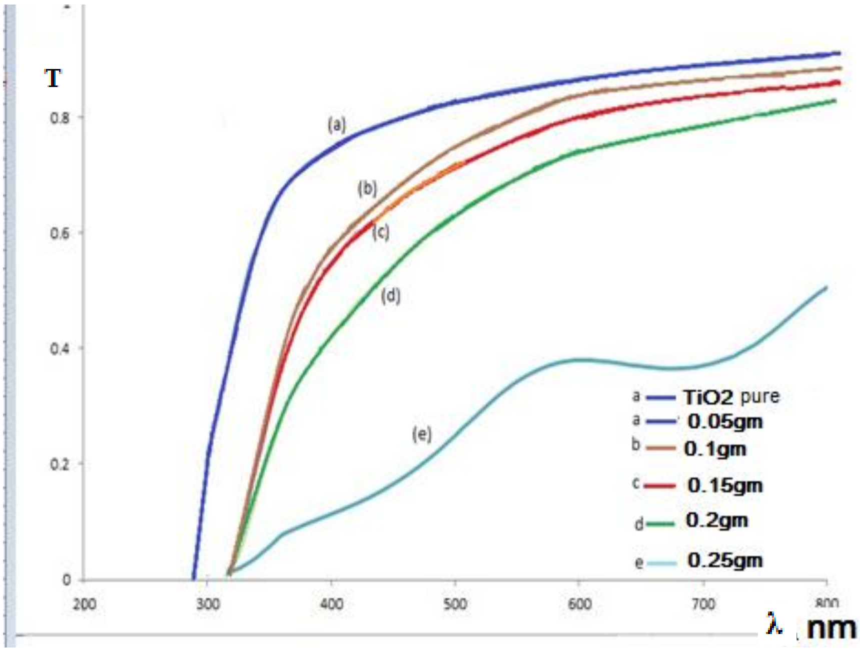


Figure (1- b): The Transmittance Spectra for Pure and Different Weights of Cobalt Doped TiO_2

2.3 XRD: Figure (2) shows the XRD patterns for pure and different weights of cobalt doped TiO_2 thin films. The patterns show a significant peak which represents the Anatase phase and small peaks indicating the formation of nano-crystalline TiO_2 films.

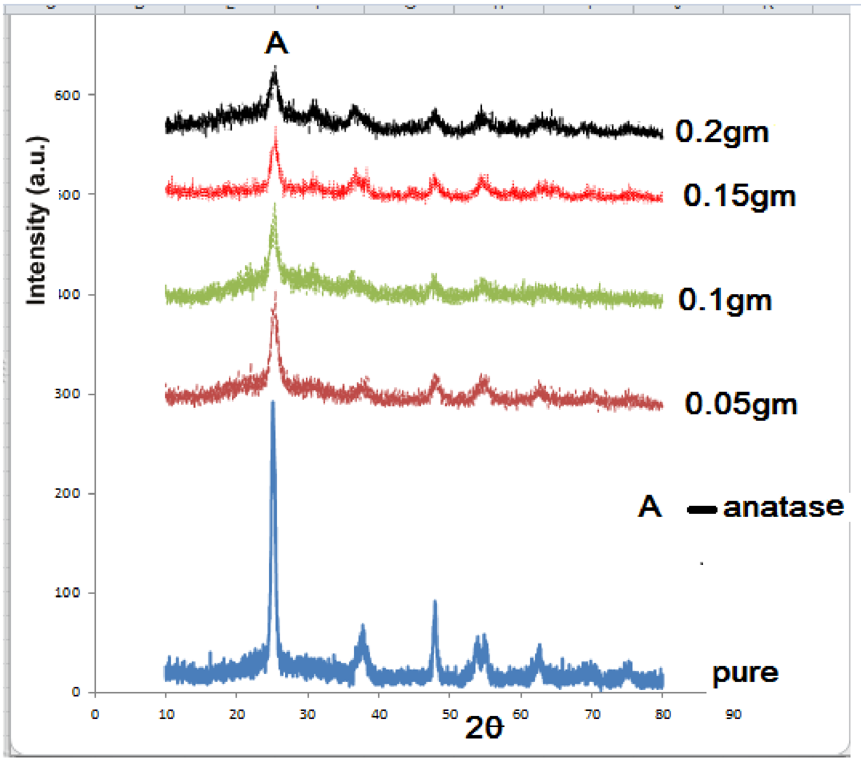
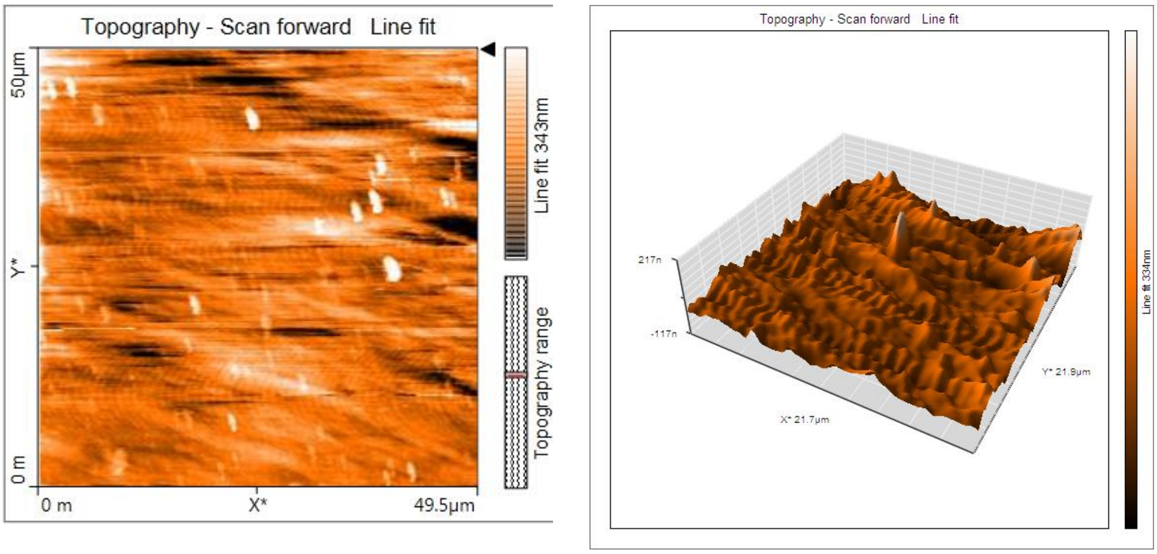


Figure (2): XRD Patterns for Pure TiO_2 and Different Weights of Cobalt Doped TiO_2 Thin Films

The X-ray diffraction patterns of cobalt doped TiO_2 thin films show no much change as compared with that of pure TiO_2 thin film, which confirms that there is no additional phase formation.

The measured crystal sizes using Debye formula were (10.9, 12.6, 13.1, 13.6, 13.9) nm for pure TiO_2, and (0.05, 0.1, 0.15, 0.2) gm cobalt doped TiO_2 respectively. According, we notice that the crystal size increases with the increasing the concentration of cobalt, and this due to that the radius of cobalt ion Co^{2+}, (0.74 A°), which is greater than that of Ti^{4+} ion (0.6 A°), so it will be on the surface of Ti^{4+} ion [6].

3.3 AFM: Figure (3) shows the AFM image of the optimum sample, (0.2 gm cobalt doped TiO_2)and thin film annealed at 550°C. As a result of the doping a clear particle structures with granular morphology were formed and this leds to the appearance of grains making the films to have higher surface roughness [7].



(a) **(b)**

Figure (3): AFM for the Sample (0.2 gm Cobalt Doped TiO_2) a- 2d Image, and b- 3d Image

4- Conclusion

Pure TiO_2 and cobalt with different weights doped TiO_2 thin films were synthesized via sol gel technique and calcined at 550℃. From XRD test, the samples become in anatase phase and with large crystal size after doping with cobalt since the radius of cobalt ion is greater than that of Ti ion. From UV-Vis spectroscopy, the sample doped with (0.2gm) of cobalt shows response to the visible region spectrum. AFM test shows higher levels of surface roughness.

5- References

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استجابة المنطقة المرئية لثاني اوكسيد التيتانيوم المطعم بالكوبالت باستخدام تقنية السول- جل

الخلاصة

تمتحضير جسيمات نانوية من ثاني اوكسيد التيتانيوم عن طريق تقنية السول– جل، ثم تم تطعيمها بايونات الكوبالت ليتكون سول من ثاني اوكسيد التيتانيوم المطعم بالكوبالت. كما تم تحضير اغشية رقيقة من هذا السول باستخدام طريقة الطلاء بالغطس وخضعت للتلدين تحت درجة حرارة ٥٥٠°م.

الاغشية ووصفت هذه الاغشية بمطياف UV–Vis، حيود الاشعة السينية(XRD)، ومجهر القوة الذرية (AFM).

وقد اظهر طيف الامتصاص ازاحة حمراء مما تشير الى ان ثاني اوكسيد التيتانيوم المطعم بالكوبالت سيتحسس للجزء المرئي من الطيف بدلا من منطقة الفوق بنفسجي لثاني اوكسيد التيتانيوم النقي.

الكلمات الدالة: ثاني اوكسيد التيتانيوم المطعم بالكوبالت، سول– جل، الطلاء بالغطس.