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# The Structural, morphological and optical properties of Ca doped $TiO_2$ thin films prepared by sol-gel method

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## Abstract

The pure and Ca doped $TiO_2$ thin films with 1 – 10% mol of Ca concentrations were prepared by sol-gel method and deposited on glass substrates with dip-coating. All samples were annealed at 500 °C for 1 h and characterized by field emission scanning electron microscope (FESEM), UV-Vis spectrometer, and fluorescence spectrometer. From the experimental results, all thin film samples exhibited the anatase phase of crystalline structure. The surface morphology and crystal size were sensitive to Ca doping concentration. All of film samples displayed clearly higher 80% of transmission in the visible range. In additional, the fluorescence intensity of the thin films samples decreased with increasing the Ca doping concentrations.

**Keywords**: $TiO_2$ thin films; Sol-gel; Dip-coating; Ca-doped



## 1. Introduction

Titanium dioxide, $TiO_2$ is one of metal oxide as important materials due to their unique physical, optical and electrical properties e.g. high reflective index, transparency, wide band gap, stability at high electric filed, dielectric constant and nontoxic material [1 – 3]. The preparation and developed properties of $TiO_2$ material have widely studied. In general, there are many methods to fabricated thin films of $TiO_2$ such as sputtering [4], evaporation [5] and sol-gel method [6], etc. Among of these methods, Sol-gel is an interesting method to prepared $TiO_2$ thin film because it's simple technique, and easier to control compositions. Furthermore, the doping of $TiO_2$ with transition metal or non-metal ion has been extensively investigated for the purpose of improves its on physical electrical and optical properties [6 – 8]. The type and oxidation numbers of doping metals influenced to the oxygen distribution in the $TiO_2$ matrix and the dopant behavior to act as donors or acceptors. The efficiency of a dopant also depends on concentrations. The aim of this research work consists on the preparation of the pure and Ca doped $TiO_2$ thin films with sol-gel technique and deposited them on glass substrates with dip-coating method. The effects of doping Ca concentrations on structural, morphological and optical properties were investigated.

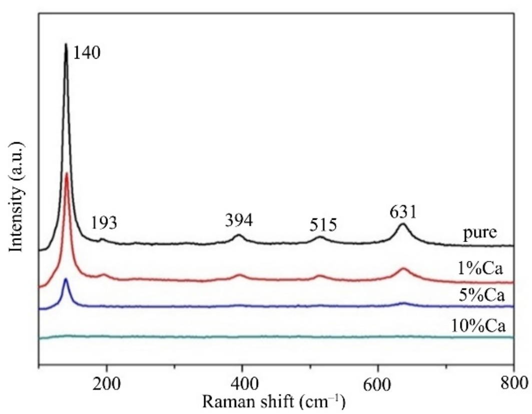
## 2. Materials and methods

The Ca-doped $TiO_2$ thin films were fabricated by sol-gel and dip coating method. In a typical procedure, 100 mL of 0.20 M titanium tetra-isopropoxide were prepared in isopropanol under continuous stirring. Calcium nitrate tetrahydrate was added to the above solution by varying the concentration of Ca from 1 to 10 mol % and then small amounts of deionized water was dropped into the previous precursor solution. The solution was stirred for 10 min before being added nitric acid to adjust a pH of solution until the pH of the solution was equal to 2. Each precursor solution was further stirred at room temperature for 1 h until the homogeneous solution was obtained. The precursor solution was coated on glass substrate using the dip coating method. The as-prepared films were dried at 90 °C in air for 10 min to remove an organic solvent in the films. Finally, the dried films were annealed at 500 °C for 1 h.

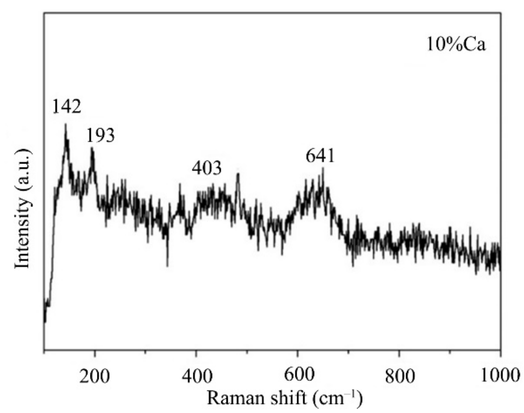
The surface morphology of the thin films was characterized by FESEM (Hitachi, S-4700). The phase analysis was carried out by Raman spectroscopy (NT-MDTNTEGRA spectra). The optical properties in the range of 300 – 900 nm of thin films were carried out by a UV–vis spectrophotometer (Shimadzu 2600). The fluorescence behavior was investigated by fluorescence spectrophotometer (Cary Eclipse) with an excitation wavelength of 310 nm.

## 3. Results and Discussion

The Raman spectrometer was widely used for structural and phase identifications of $TiO_2$ thin films. X. Chen and S.S. Mao reported [9], the Raman peak of the $TiO_2$- anatase phase has six Raman-active modes at 144, 197, 399, 513 and 639 $cm^{-1}$. The $TiO_2$-rutile phase has four peak of vibrational modes around 145 $cm^{-1}$, 445 $cm^{-1}$, 610 $cm^{-1}$, and 240 $cm^{-1}$ (second order) [10]. Fig. 1(a) shows the Raman signal of pure and Ca-doped $TiO_2$ thin film samples. The Raman spectrum of pure $TiO_2$ thin film shows five peaks around 140 $cm^{-1}$, 193 $cm^{-1}$, 394 $cm^{-1}$, 515 $cm^{-1}$ and 631 $cm^{-1}$ which confirm the presence of anatase phase without the rutile and brookite phases.




(a)




(b)

**Fig. 1** (a) The Raman signals of pure and Ca-doped $TiO_2$ thin film samples.
(b) The expanded Raman signals of 10% Ca doped $TiO_2$ film samples.

The Raman spectrum of 1% and 5% Ca-doped $TiO_2$ does not shift the peak position corresponding to anatase phase. However, the Ca concentrations affect the intensity and broadness of the Raman peaks. The Raman spectrum of the 10% Ca-doped $TiO_2$ thin film as shown in Fig. 1(b) displayed peak positions with appreciably estimated around 142 $cm^{-1}$, 193 $cm^{-1}$, 403 $cm^{-1}$, and 641 $cm^{-1}$. According to literature, the change in the width and shift of the Raman peaks is involved with the number of the impurity defects. The Ca doping in $TiO_2$ thin film less than 5% Ca does not affect the crystal size and structure of the films. It was slight change in the symmetry of the crystals due to the distortions of lattice which produced from defect with Ca ions substitutes [11].

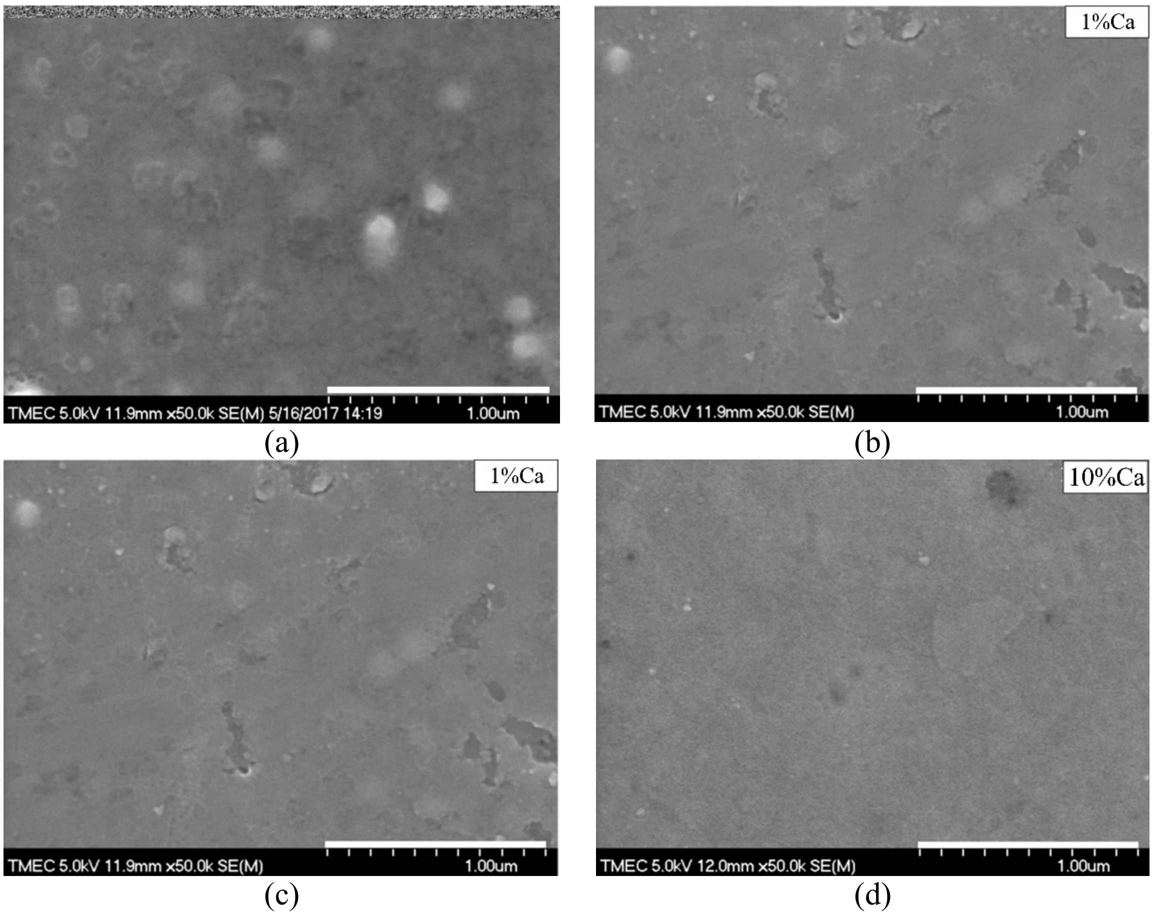



**Fig. 2** FESEM images of the prepared thin film samples (a) pure and (b) - (d) 1%, 5% and 10% Ca doped, respectively.

Fig. 2 shows the FESEM image of pure, 1%, 5% and 10% Ca-doped of $TiO_2$ thin film samples. The surface morphology of pure $TiO_2$ thin film (see Fig. 2(a)) has spherical particles with approximate sizes less than 100 nm. From Fig. 2(b), it can be seen that the surface morphology of Ca-doped $TiO_2$ film samples were slightly changed at 1% Ca-doping concentration. The microstructure and surface morphology of 5% and 10% Ca-doped were become smooth without cracks and pores.

The optical transmittance spectra at room temperature of pure and Ca-doped $TiO_2$ thin film samples were shown in Fig. 3. It can be observed that, the transmittance was almost similar for the pure and other Ca-doping concentrations. The average optical transmission in visible range of all of samples, pure and Ca-doped $TiO_2$ films was about 85%. It was probably due to the surface morphology has smooth and low roughness, which could result in less light scattering. The cut-off wavelength of transmission spectra of all samples was slightly shifted to short wavelength when the Ca concentration increases. These shifts can be attributed to some size effect and the thin film morphology. The optical transmission in 350 – 550 nm ranges of film samples show a slight increase and decrease in 550 – 900 nm when the Ca concentration increases might be related to the scattering and/or absorption.

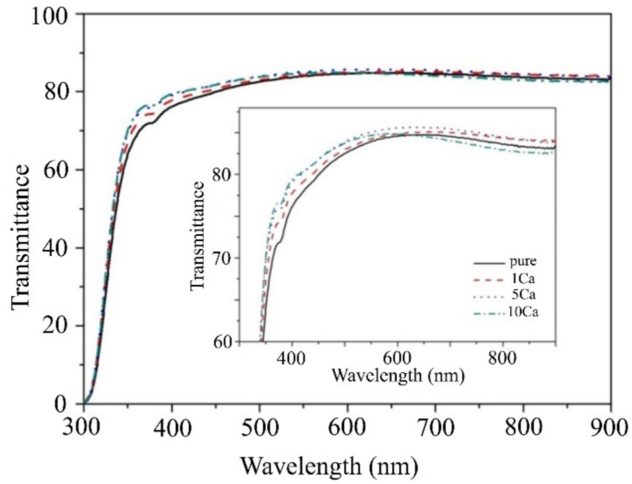



**Fig. 3** Optical transmittance spectra of pure and Ca-doped $TiO_2$ thin film samples.

Fig. 4 shows the fluorescence spectra of pure and Ca doped $TiO_2$ thin film samples measured by an excitation wavelength of 310 nm at room temperature. It can be seen that the board emission peaks were observed at 366, 423, 488 and 495 nm. The emission peak at 363 nm was attributed to the direct transition from the conduction band to the valence band [12]. The slightly emission peak at 423 nm that can be observed from pure and 1% Ca doping might be attributed to the mediated transition by defect levels in the band gap [13]. While, the emission peaks were located about 488 and 495 nm arise from the charge transfer of an oxygen vacancy trapped electron [14, 15]. However, the intensity of fluorescence spectra decreased with increasing Ca concentration. This result might be attributed to the reduction of defects and variation of crystalline size of Ca doped $TiO_2$.

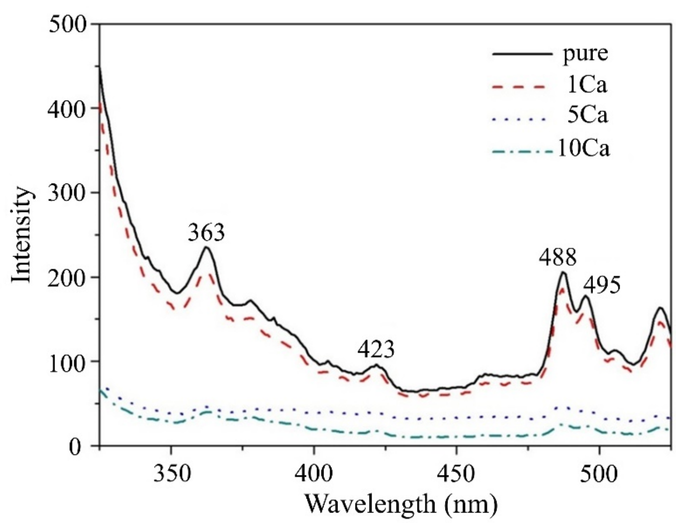



**Fig. 4** Fluorescence spectra of pure and Ca doped $TiO_2$ thin film samples.

## 4. Conclusion

In this work, Ca doped $TiO_2$ thin film samples were prepared glass substrate by sol-gel dip coating method. The Raman results showed pure anatase structures for Ca doped $TiO_2$ thin films without any impurity phased. Optical transmittance spectra of the samples indicated that all thin films were similarly transparent approximate 85% in the visible range. The surface morphology of Ca-doped $TiO_2$ thin films were smooth and low roughness and tended to form denser when increasing Ca concentration. The fluorescence measurements showed the fluorescence peaks in the visible region which can be ascribed to the presence of defect level and variation of the crystalline size when the Ca concentration increases.

## 5. Acknowledgement

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## 6. References

[1] K. Tonooka, N. Kikuchi, Super-hydrophilic and solar-heat-reflective coatings for smart windows, Thin Solid Films. 532 (2013) 147 – 150.
[2] M.F. Hossain, S. Biswas, T. Takahashi, Y. Kubota, A. Fujishima, Investigation of sputter-deposited $TiO_2$ thin film for the fabrication of dye-sensitized solar cells, Thin Solid Films. 516 (2008) 7149 – 7154.
[3] K. Eufinger , D. Poelman, H. Poelman, R. De Gryse, G.B. Marin, Photocatalytic activity of dc magnetron sputter deposited amorphous $TiO_2$ thin films, Appl. Surf. Sci. 254 (2007) 148 – 152.
[4] J.O. Carneiro, V. Teixeira, A.J. Martins, M. Mendes, M. Ribeiro, A. Vieira, Surface properties of doped and undoped $TiO_2$ thin films deposited by magnetron sputtering, Vacuum. 83 (2009) 1303 – 1306.
[5] D. Bhattacharyya, N.K. Sahoo, S. Thakur, N.C. Das, Spectroscopic ellipsometry of $TiO_2$ layers prepared by ion-assisted electron-beam evaporation, Thin Solid Films. 360 (2000) 96 – 101.
[6] J. H. Kim, G. Kwon, H. Lim, C. Zhu, H. You, Y. T. Kim, Effects of transition metal doping in Pt/M-$TiO_2$ (M = V, Cr, and Nb) on oxygen reduction reaction activity, J. Power Sources. 320 (2016) 188 – 195.
[7] T. Potlog, P. Dumitriu, M. Dobromir, A. Manole, D. Luca, Nb-doped $TiO_2$ thin films for photovoltaic applications, Mater. Des. 85 (2015) 558 – 563.
[8] F. Bensouici, M. Bououdina, A.A. Dakhel, T. Souier, R. Tala-Ighil, M. Toubane, A. Iratni, S. Liu, W. Cai, Al doping effect on the morphological, structural and photocatalytic properties of $TiO_2$ thin layers, Thin Solid Films. 616 (2016) 655 – 661.
[9] X. Chen, S.S. Mao, Titanium dioxide nanomaterials: synthesis, properties, modifications and applications, Chem. Rev. 107(7) (2007) 2891 – 2959.
[10] Y. Zhang, C.X. Harris, P. Wallenmeyer, J. Murowchick, X. Chen, Asymmetric lattice vibrational characteristics of Rutile $TiO_2$ as revealed by laser power dependent Raman spectroscopy, J. Phys. Chem. C. 117 (2013) 24015 – 24022.
[11] Y. Castro, A. Duran, Ca doping of mesoporous $TiO_2$ films for enhanced photocatalytic efficiency under solar irradiation, J. Sol-Gel Sci. Technol. 78 (2016) 482 – 491.
[12] F.B. Li, X.Z. Li, The enhancement of photodegradation efficiency using Pt–$TiO_2$ catalyst, Chemosphere. 48 (2002) 1103 – 1111.
[13] K. Vanheusden, W.L. Warren, C.H. Seager, D.R. Tallant, J.A. Voigt, B.E. Gnade, Mechanisms behind green photoluminescence in ZnO phosphor powders, J. Appl. Phys. 79 (1996) 7983 – 7992.
[14] D. Li, H. Haneda, S. Hishita, N. Ohashi, Visible-Light-Driven N−F−Codoped $TiO_2$ Photocatalysts. 2. Optical Characterization, Photocatalysis, and Potential Application to Air Purification, Chem. Mater. 17 (2005) 2596 – 2602.
[15] J. Zhang, Y. Hu, M. Matsuoka, H. Yamashita, M. Minagawa, H. Hidaka, M. Anpo, Relationship between the local structures of titanium oxide photocatalysts and their reactivities in the decomposition of NO, J. Phys. Chem. B. 105 (2001) 8395 – 8398.