CHARACTERISTICS AND OPTICAL PROPERTIES OF Fe^{3+} DOPED SiO_2/TiO_2 THIN FILMS PREPARED BY THE SOL-GEL DIP-COATING METHOD

Dang Mau Chien, Le Duy Dam, Nguyen Thi Thanh Tam and Dang Thi My Dung

Laboratory for Nanotechnology, Vietnam National University, Ho Chi Minh City

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ABSTRACT: *In this study, we have successfully synthesized Fe^{3+} doped SiO_2/TiO_2 thin films on glass substrates using the sol-gel dip-coating method. After synthesizing, the samples were annealed at 500^0C in the air for 1 hour. The characteristics and optical properties of Fe^{3+} doped SiO_2/TiO_2 films were then investigated by X-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-vis) and Fourier transform infrared spectroscopy (FT-IR). An antifogging ability of the glass substrates coated with the fabricated film is investigated and explained by a water contact angle under visible-light. The analyzed results also show that the crystalline phase of TiO_2 thin films comprised only the anatase TiO_2, but the crystalline size decreased from 8.8 to 5.9 nm. We also observed that the absorption edge of Fe^{3+}-doped SiO_2/TiO_2 thin films shifted towards longer wavelengths (i.e. red shifted) from 371.7nm to 409.2 nm when the Fe^{3+}-doped concentration increased from 0 to 1 % mol.*

1. INTRODUCTION

Titanium dioxide (TiO_2) is a nontoxic material and has been applied in environmental treatments such as water and air purification, water disinfection and sterilization because of

Its unique properties such as strong photocatalytic activity and chemical stability [1]. However, the major limitations of TiO_2 are the absorption region in the UV light (about 4% - 5% of solar energy) and fast recombination of hole–electron pairs within nanoseconds. To propose using TiO_2 to the coating on the ceramic tiles and glass to make intelligent materials was being able self-cleaning and antibacterial. In our previous papers [2, 3] we have reported the influence of doping SiO_2 was exhibited higher photocatalytic activity than pure TiO_2. This could be explained by the addition of SiO_2 into TiO_2 retarding or inhibiting the crystallization of anatase phase. A contact angle of SiO_2/TiO_2 thin films with 15 mol % SiO_2 concentrations is less than 2^0 and these films can maintain a super-hydrophilic property for a long time in dark conditions, thus exhibiting excellent antifogging capabilities [3]. In this paper we focused on improving the photocatalytic activity of SiO_2/TiO_2 films in the visible light region. Transition metal ions and noble metals have been employed to dope into TiO_2 in order to induce a red shift in the absorption band [4, 5]. Among these metals, iron has been considered to be an appropriate candidate owing to its radius of Fe^{3+} (0.64 Å) is similar to that of Ti^{4+} (0.68 Å), therefore, it can be inferred that Fe^{3+} ions might easily incorporate

into the crystal lattice of TiO_2. Furthermore, Fe^{3+} ions can play a role as e^-/h^+ pair traps because the energy level of Fe^{2+}/Fe^{3+} lies close to that of Ti^{3+}/Ti^{4+}, favoring the separation of the photo-generated e^-/h^+ pair, and consequently reducing e^-/h^+ pair recombination rate [6,10].

2. EXPERIMENTAL

The following chemicals were used: Tetra-isopropyl Ortho-titanate Ti $(OC_3H_7)_4$ (TIPOT-Merk), Tetra-ethoxyortho-silicate $Si(OC_2H_5)_4$ (TEOS-Merck), Ethanol C_2H_5-OH (Merck), HCl-Hydrochloric acid (China), Iron(III)Nitrate $Fe(NO_3)_3.9H_2O$ (Merck), DI water. The synthesis process of the Fe-doped SiO_2/TiO_2 solution is shown in Figure 1.

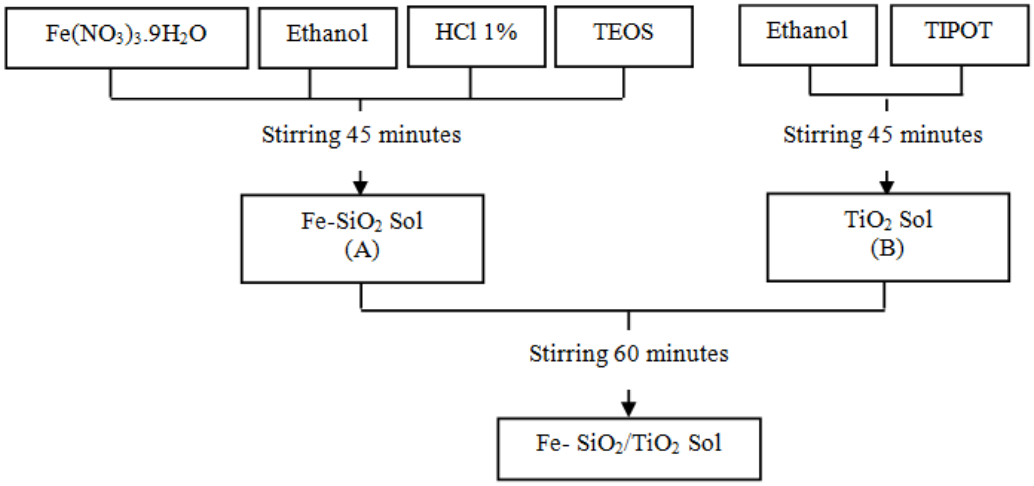


Figure 1. The synthesis process of the Fe^{3+}-doped SiO_2/TiO_2 solution prepared soil-gel method

The volume of H_2O containing 1 wt% HCl can be determined by the formula:

$$R = \frac{n_{H_2O}}{n_{TiO_2} + n_{SiO_2}} = \frac{8}{3} \quad (1)$$

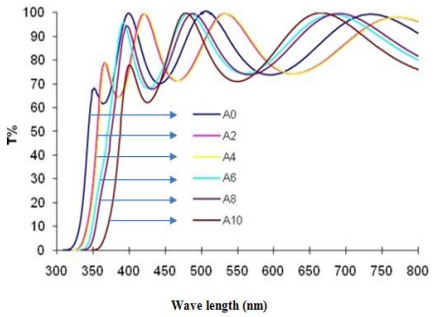
In this report, we synthesized the Fe^{3+}-doped SiO_2/TiO_2 coating solution with various $Fe/(SiO_2+TiO_2)$ molar ratios: from 0 to 1%. The Fe^{3+}-doped SiO_2/TiO_2 thin films were deposited on glass substrates by a dip coating process at room temperature. Glass slides with dimensions of (26x76) mm^2 were used as substrates. Before the deposition, the substrates were ultrasonically cleaned in dilute HCl, acetone and absolute ethanol for 30 min, respectively. Finally, they were thoroughly rinsed with DI water.

The substrates were immersed into as-prepared Fe-doped SiO_2/TiO_2 sol for 30 seconds. The substrates were then withdrawn from the sol with velocity 5 mm/s. If coating two times or more, each layer would be dried between two successive coatings at 230^0C for 5 min before the next coating was implemented. Afterward, the substrates were annealed at 500^0C for 1 h. X-ray diffraction (XRD) patterns of these powder samples were

measured with a diffractometer (D8 Advance). An atomic force microscope (AFM-Electronica S.L) was used to investigate the crystallization and surface structure. Synthesized samples were also studied using UV–VIS absorption spectra with UV-VIS equipment (Cary 100 Conc)-spectrophotometer in a wavelength range from 200 to 800 nm, and Fourier transform infrared spectroscopy (FTIR) TensorTM 37 (Bruker) in the range 400-4000 cm^{-1} by the KBr pellet technique.

3. RESULTS AND DISCUSSION

3.1. UV-vis results



Wavelength (NM)

Figure 2. The UV–vis spectra of SiO_2/TiO_2 thin films with different Fe-doped concentrations in the wavelength range of 300-800 nm.

The ultraviolet–visible (UV–Vis) spectra of SiO_2/TiO_2 thin films with different Fe^{3+}-doped concentrations in the wavelength range of 300–800 nm are illustrated in Figure 2. It reveals that the transmittance of SiO_2/TiO_2 thin film without Fe^{3+} doping has an abrupt decrease when wavelengths are below 350 nm. This indicates the absorption edge near 350 nm and reach almost near zero at about 300 nm. The transmittance quickly decreases when below 350 nm due to the absorption of light caused by the excitation of electrons from the valence band to the conduction band of TiO_2. The absorption edge shifted towards longer wavelengths (i.e. red shifted) from 350 to 410 nm with the Fe^{3+}-doped concentration increasing from 0 to 1% mol. Red shift associated with the presence of dopants can be attributed to a charge transfer transition between the iron d electrons and the TiO_2 conduction or valence band [7], [11]. With this result, this material system can be applied to manufacturing photo-catalyst Fe^{3+}-doped SiO_2/TiO_2 nano materials in the visible light range.

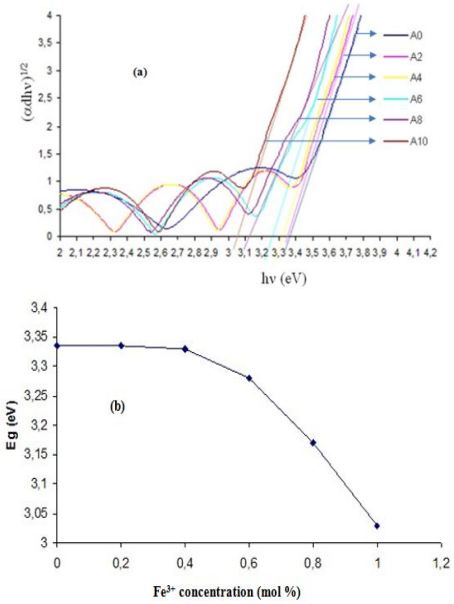


Figure 3. (a) The plot of $(\alpha dh\upsilon)^{1/2}$ vs. hυ, (b) The relationship between band-gap energyand Fe^{3+}-doped concentration.

Figure 3 (a) illustrates the plot of $(\alpha d h\upsilon)^{1/2}$ vs. $h\upsilon$ for the TiO_2 thin films with various Fe^{3+} contents. From the intersection of the extrapolation of each curve in Figure 3(a) and $h\upsilon$ axis gives the band-gap energy of TiO_2 thin films with different Fe^{3+} doping concentrations. The relationship between the band-gap energy and the Fe^{3+} content, for all SiO_2/TiO_2 thin films, are shown in Figure 3(b). It reveals that the band-gap energy decreases when the Fe^{3+} content increases. The band-gap energy of SiO_2/TiO_2 thin film without Fe^{3+} doping is 3.33 eV and the band-gap energy of SiO_2/TiO_2 thin film doping with 1 mol% Fe^{3+} has been identified to be 3.03 eV. Since localized 3d orbitals of Ti constitute the conduction band of TiO_2, doping Fe^{3+} to the TiO_2 lattice influence, the conduction band by admixing Fe^{3+} 3d orbitals [8]. Thus, the conduction band is shifted towards the lower energy and a systematic decrease in the valence band-conduction band occurs with an increasing concentration of Fe^{3+} in TiO_2 lattice or matrix.

Table 2. From the value of E_g (eV) and λ_{ht}

Samples	E_g (eV)	λ_{ht} (m)
A0	3.336	371.7
A2	3.335	371.8
A4	3.331	372.2
A6	3.28	378.0
A8	3.17	391.2
A10	3.03	409.2

3.2. X-ray diffraction Measurements

XRD patterns for undoped and various Fe^{3+}-doped SiO_2/TiO_2 powders calcined at 500^0C for 1h are shown in Figure 4. It is identified that all the diffraction peaks are ascribed to the anatase TiO_2 for undoped Fe^{3+} powders as illustrated in Figure 4 (A0). The XRD patterns of the SiO_2/TiO_2 powders with an Fe^{3+}-doping amount increasing from 0 to 1mol % are demonstrated in Figure 4(A2–A10), respectively. It has been registered that all the diffraction peaks in Figure 4(A2-A10) also belong to the anatase TiO_2, and no other phase can be detected. Moreover, the result of Figure 4 also reveals that the intensity of diffraction peaks decreases with an increasing Fe^{3+}-doped concentration. This phenomenon caused by the Fe^{3+}-doped can inhibit the crystallization of anatase TiO_2 [11].

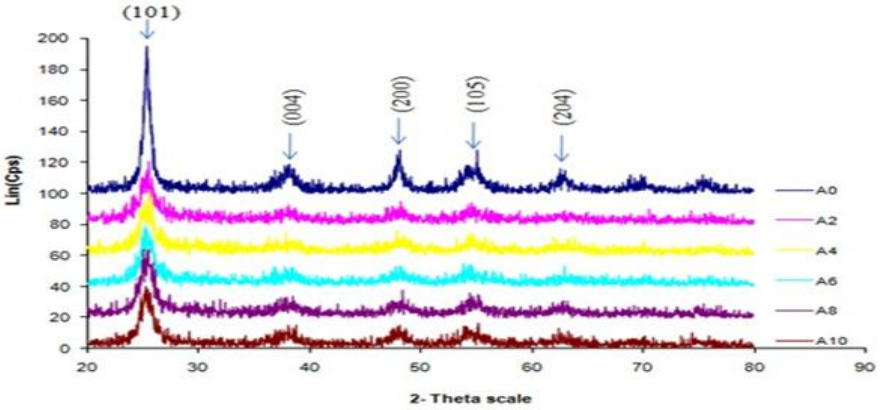


Figure 4. XRD patterns for undoped and various Fe^{3+}-doped TiO_2 thin films after calcining at 500^0C for 1h.

Moreover, in this study, although the Fe^{3+}-doped concentration attained 1 mol %, the iron oxides or Fe_xTiO_y are not identified in the XRD patterns. The average crystallite size of the TiO_2 powders with various Fe^{3+}-doped concentrations calcined at 500^0C for 1h are determined, by the Scherrer's equation, as follows:

$$D_{hkl} = \frac{0.89\lambda}{\beta cos\theta} \quad (2)$$

Where D_{hkl} denotes the average crystallite size of the TiO_2 powders with various Fe^{3+}-doped concentrations, λ= 0.15405 nm is the X-ray wavelength of Cu Kα, β is the full width of the peak measured at half maximum intensity and θ is the Bragg's angle of the peak. The effects of the Fe^{3+}-doped concentration on the crystallite size of TiO_2 powders calcined at 500^0C for 1h are demonstrated in Figure 5.

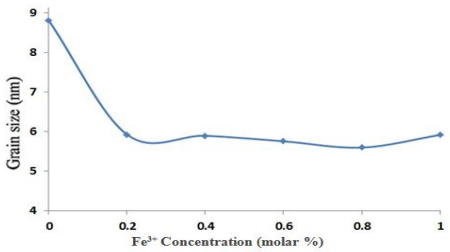


Figure 5. Effect of Fe^{3+} -doped concentrated on the crystalline size of TiO_2 thin films.

It reveals that the size of TiO_2 powder decreases from 8.8 to 5.59 nm when the Fe^{3+}-doped concentration increases from 0 to 0.8 mol%. The Fe^{3+}-doped has an effect on the crystallization of TiO_2 [9]. The larger the amount of Fe^{3+}-doping, the wider the width of the diffraction peaks, the worse the crystallization, and the smaller the grain size of TiO_2 powders.

3.3. Raman Measurement

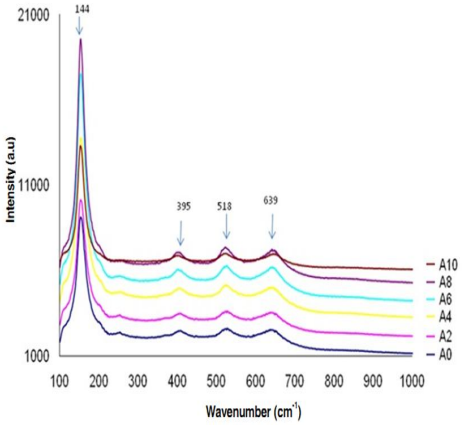


Figure 6. Raman spectrum of powder samples A0, A2, A4, A6, A8, A10.

Figure 6 shows the Raman spectra of different samples. Raman peak at about 144 cm^{-1} is observed for all the samples, which is attributed to the main E_g anatase vibration mode. Moreover, vibration peaks at 395 cm^{-1}, 518 cm^{-1} and 639 cm^{-1} are presented in the spectra for all samples, which indicate that anatase TiO_2 crystalline are the predominant species. Furthermore, there is no peak attributed to the iron oxide observed, which is consistent with the results of XRD patterns.

3.4. AFM result images

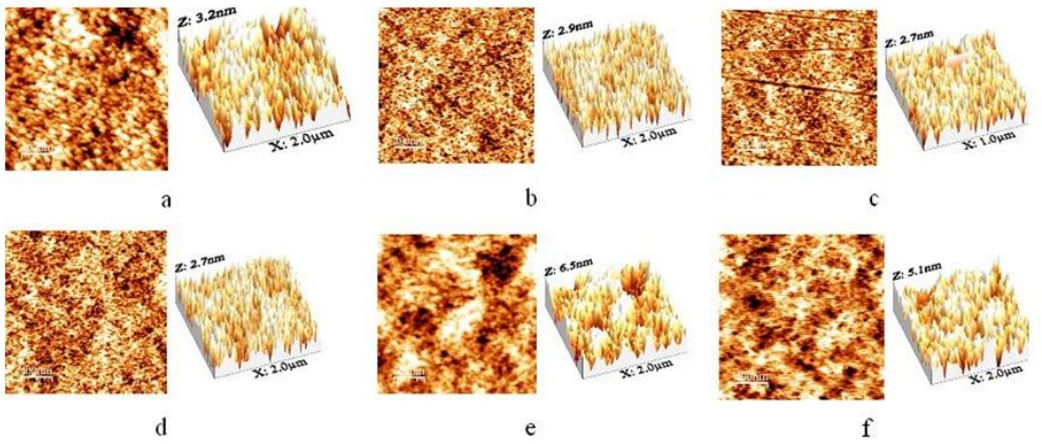


Figure 7. AFM images of film:a. A0 with RMS = 0.7565 nm; b. A2 with RMS = 0. 6772 nm; c. A4 with RMS= 0.5812nm; d. A6 with RMS=0.6526nm; e. A8 with RMS=1.5891nm; f. A10 with RMS = 1.2298nm.

The atomic force microscopy images were taken in order to study the morphology of the Fe^{3+}-doped SiO_2/TiO_2 thin films. The AFM images in Figure 7 indicate that the particle size and film roughness increased with the increase of Fe^{3+}. The surface roughness (RMS) increased from 0.7565 nm to 1.5891 nm with the addition of Fe^{3+} from 0 mol% to 0.8 mol% respectively. The surface roughness increases this mean that, it is favorable to a photocatalytic reaction by enhancing the contact surface area between Fe^{3+}-doped SiO_2/TiO_2 films and organic pollutants. The AFM images of samples showing RMS A8 is the largest, therefore the roughness of film A8 are the highest.

3.5. Visible photocatalytic activity

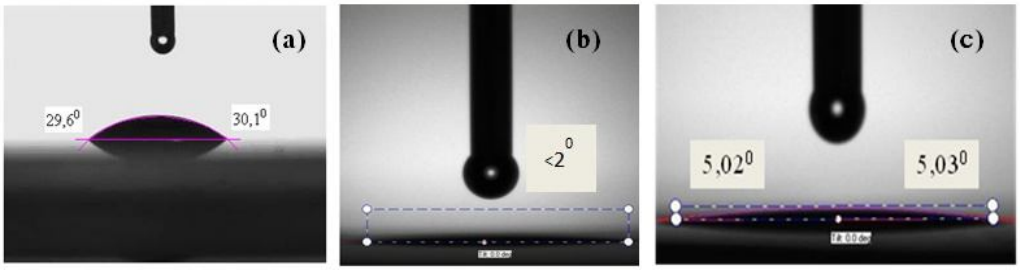


Figure 8. The contact angle of water on the normal glass substrate (a), on A8 film (b) and on A8 film stored 1 day in a dark environment (c).

Figure 8 shows that the dependence of photo-induced changesin the water contact angle of Fe^{3+}-doped SiO_2/TiO_2 thin film with Fe^{3+} 0.8 mol % coated on glass, which were irradiated under visible-light after 2 hours and then kept 1 day in a dark environment. The hydrophilic ability of the sample may be explained by the contact angle of water on the surface. The super-hydrophilic property of the surface allows water to spread completely across the surface rather than remaining as droplets. The observed result means that Fe^{3+}-doped SiO_2/TiO_2 film coated glass is a good material for antifogging and self-cleaning purposes.

Moreover, Figure 8(b) shows that, the contact angle of water on the Fe^{3+}-doped SiO_2/TiO_2 film coated sample was very low ($<2^0$), while higher values of water contact angle resulted when water was deposited on normal glass substrates. In addition, after storing 1 day in a dark environment, the contact angle of water on Fe^{3+}-doped SiO_2/TiO_2 film coated glass slowly increased to about 5^0 (Figure 8 (c)). This result means that the coated sample could maintain the super-hydrophilic capability for a long time in a dark environment.

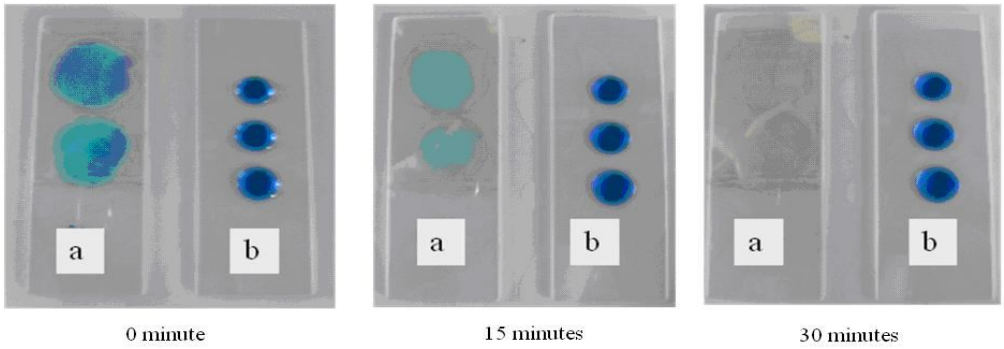


Figure 9. Photocatalysis decoloration of MB with A8 film/glass (a), and normalglass substrate (b)

Finally, we qualitatively analyze the photocatalysis property of Fe^{3+}-doped SiO_2/TiO_2 film on glass substrates by decoloration of MB. Figure 9 shows the photocatalysis decoloration of MB with A8-coated glass substrate. It can be seen that the concentration of MB on the experimental substrate decreased about 50% over a period of about 15 min and almost no MB was detected after a period of 30 min.

4. CONCLUSIONS

The SiO_2/TiO_2 films doped with different Fe^{3+} concentration have been prepared by a simple sol-gel method. The solutions have high stability and may be utilized for mass production. The absorption edge of thin films shifted towards longer wavelengths form 371.7 to 409.2 nm with increasing concentrations of Fe^{3+}. The result shows that, the optimum concentration of Fe^{3+} is 0.8 % mol at 500^0C temperature of substrates. It was found that doped Fe^{3+} increases the photosensitivity of nano TiO_2 with rather high retention time in characteristics. The as-prepared material can be used to manufacture TiO_2 operating in the region of visible light.

ĐẶC ĐIỂM VÀ TÍNH CHẤT QUANG CỦA MÀNG SiO_2/TiO_2 PHA TẠP Fe^{3+} CHẾ TẠO BẰNG PHƯƠNG PHÁP PHỦ NHÚNG SOL – GEL

Đặng Mậu Chiến, Lê Duy Đảm, Nguyễn Thị Thanh Tâm, Đặng Thị Mỹ Dung

Phòng thí nghiệm Công nghệ Nano, ĐHQG-HCM

TÓM TẮT: *Trong bài báo này, chúng tôi đã tổng hợp thành công màng SiO_2/TiO_2 pha tạp Fe^{3+} trên đế thủy tinh sử dụng phương pháp phủ nhúng Sol-Gel. Màng sau khi chế tạo được nung ở 500^0C trong không khí trong 1 giờ. Đặc điểm và tính chất quang của màng SiO_2/TiO_2 pha tạp Fe^{3+} đã được khảo sát bằng nhiễu xạ tia X, quang phổ UV-Vis và quang phổ hồng ngoại (FT-IR). Khả năng chống đọng sương mờ trên kính có phủ màng SiO_2/TiO_2 pha tạp Fe^{3+} đã được khảo sát và chứng minh bằng góc tiếp xúc của nước dưới ánh sáng khả kiến. Kết quả phân tích cũng chỉ ra rằng tinh thể TiO_2 tạo là pha anatase và kích thước tinh thể giảm dần từ 8.8 đến 5.9 nm. Kết quả thu được cũng cho thấy bờ hấp thụ của màng SiO_2/TiO_2 pha tạp Fe^{3+} dịch chuyển tới bước sóng dài hơn (dịch chuyển tới ánh sáng đỏ) từ 371nm tới 409.2 nm khi nồng độ tạp Fe^{3+} tăng lên từ 0 đến 1% mol.*

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