THE EFFECT OF IRON CONTENT ON THE PHASE TRANSFORMATION OF TIO₂ NANOCRYSTALLINE POWDERS PREPARED BY SOL GEL PROCESS

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Resumé

Les nanoparticules de TiO₂ pure et dopé par des ions +3 de fer (Fe³⁺) ont été préparées par la méthode Sol-gel, utilisant le TiCl₄ et le FeCl₃ comme des précurseurs, l'éthanol comme un solvant et l'hydroxyde d'ammonium comme un catalyseur. Les propriétés structurelles, morphologiques et optiques des poudres préparées ont été examinées par la diffraction des rayons X (DRX), la microscopie électronique à balayage (MEB) et la spectroscopie d’absorption UV-visible. La qualité des échantillons a été examinée par la spectroscopie Infrarouge (IR) et la photoluminescence à température ambiante (PL). Tous les échantillons cristallisent sous la phase anatase sauf l’échantillon dopé à 0.1 % mol, ou la phase rutile a été apparue. Les tailles de particules diminuent quand le pourcentage du fer augmente dans les échantillons. Les images du MEB montrent que la morphologie et la taille des particules sont affectées par la quantité du dopant. La limite d’absorption des échantillons (TiO₂ dopé Fe³⁺) se déplacée vers le spectre visible quand la concentration du fer augmente. Les spectres d’absorptions infrarouges, montrent que les échantillons dopés sont purs et possèdent des surfaces fortement hydratées.

Mots-clés: Dioxide de titane ; Sol-gel ; Iron ion doping ; Anatase ; rutile ; transformation de phase.

Abstract

Pure and Fe³⁺ - doped TiO₂ nanoparticles were prepared by sol–gel method, using TiCl₄ and FeCl₃ as starting materials, ethanol as a solvent and ammonium hydroxide as a catalyst. The structural, morphological and optical properties of as prepared powders were investigated by X-ray diffraction, scanning electron microscopy and UV-visible absorption spectroscopy. The quality of the samples was examined by Infra-red absorption spectroscopy and room temperature photoluminescence (PL). All samples shows anatase phase except the 0.1 mol % Fe³⁺ - doped TiO₂ sample, which rutile phase was appeared. The particle sizes decrease when the iron content increases. From SEM images, the morphology and size of particles were affected by amount of doped metal. The absorption edge of Fe³⁺ - doped TiO₂ shifted towards visible spectrum when the Fe³⁺ - doped concentration increased. from the infra-red absorption spectra, the materials showed a highly pure and strongly surface hydrated, the materials shows main PL emission peaks appears in UV, and visible regions.

Keywords: Titanium dioxide; Sol-gel; Iron ion doping; Anatase; rutile; phase transformation.
INTRODUCTION

Titanium dioxide (TiO₂) is one of the most famous semiconductor dioxides, due to its specific properties such as, high photocatalytic activities, transparency in visible region, low cost, non toxicity, easily deposited and easily doped [1 - 3]. However their physical and chemical properties and hence their potential applications depend strongly on their crystalline structure, morphology, particle size and phase composition [4, 5]. It has been well known that the titanium dioxide could be crystallize under three phases, the anatase, rutile and brookite. The anatase phase shows a better photocatalytic activity, the rutile is the thermodynamically most stable phase and the brookite is a high pressure phase. Thus only the anatase and the rutile play a part in the applications of TiO₂. The phase transformation can be affected by several factors like the presence of impurities and doping species, starting materials, synthesis processes, grains size and annealing temperature. Though, there are many contradictory reports concerning the crystallinity and phase transformation in titanium dioxide [6-9]. Recently, transition metals (Fe, Al, Ni, Co, Mn, Cr, Cu, Zn...) have been used to dope TiO₂ in the aim to improve its different properties, particularly crystalline and photocatalytic properties. It has been found, that the addition of small amounts of metal can induce the crystallization of amorphous materials at relatively low annealing temperature [10, 11]. Among transition metals dopants, iron has been considered to be an appropriate candidate because its oxidation state (+3) and its ionic radius (0.79Å) are comparable to those of the titanium (+4 and 0.75 Å). In addition, Fe-doped TiO₂ system is considered as a potential candidate for photocatalyst, and it has reported that the photocatalyst improved with optimal Fe content [12-14]. In the past decade, several techniques have been intensively used to synthesize TiO₂ powders, including sol-gel approach [15 - 17], ultrasonic method [18], hydrothermal technique [19], and solvothermal process [20]. Among these, the sol – gel process is considered an important approach because of its simplicity, less inexpensive and easy to control deposited parameters. Herein, we report the effect of low iron doping concentration on the phase transformation, structural and optical properties and the morphology of TiO₂ nanopowders prepared in one step by sol-gel method at fixed relatively low temperature (350°C), using titanium tetrachloride, iron (III) chloride, ethanol and ammonium hydroxide as a precursor, source dopant solvent and a stabilizer agent respectively. The effect of Fe doping on the crystallization, phase transition and morphology of TiO₂ nanoparticles are studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-visible and FT-IR spectroscopy and photoluminescence (PL) measurement.

2. Experimental
2.1. Preparation of the iron-ion-doped TiO₂

Fe³⁺ - doped TiO₂ nanoparticles were prepared by sol-gel method using titanium tetrachloride (TiCl₄) as the source of titanium and iron trichloride (FeCl₃) as the source of doping agent. In a typical reaction, 2.5ml of TiCl₄ were dissolved in ethanol with a volume ratio of 1:4 under vigorous stirring for 5min in ice water. In the preparation of 0.1 - 1.5 mol % Fe³⁺-doped TiO₂, the pre-determined amounts of the FeCl₃ were added to the previous solution. After the reagents were thoroughly mixed, 0.1M NH₄ – OH (pH=11) solution were added drop by drop under vigorous stirring for 30 min until final pH value of 9. After centrifugal filtration, the powders were dried at 100 C° for 24 h at room temperature, and then calcined under air at 350 C° for 3h.

2.2. Characterization

The phase, the crystallinity and the purity of as prepared Fe³⁺-doped TiO₂ nanoparticles were determined by X-ray powder diffraction (XRD) in the 20-70° range using Cu kα(λ=1.5406Å) radiation in a Bruker - AXS type D8 diffractometer. The morphology and the size of the nanoparticles were performed in 2 – theta angular range from 20 to 800 nm using an UV-visible spectrophotometer (Shimadzu UV – 2501PC).The composition quality and molecular structure of the synthesized material were characterized, by Fourier transform infrared (FTIR) spectrometer (8201PC, SHIMADZU) in the range (400 – 4000 cm-1) using the KBr pellet technique. The photoluminescence (PL) of Fe-doped TiO₂ powder was investigated at room temperature on Perkin Elmer LS 55 spectrophotometer using 325 nm Xenon laser as the excitation light source.

4. Discussion
4.1. X-ray diffraction

XRD is used to investigate the crystallinity and the phase structure of the samples. Fig. 1 shows the X-ray diffraction patterns of the pure and Fe³⁺ - doped TiO₂ nanoparticles were performed in 2 – theta angular range from 20 to 70 degrees. For undoped and 0.5 to 1.5 mol % Fe³⁺-doped TiO₂ samples all diffraction peaks obviously correspond to crystalline titanium oxide of anatase phase (JCPDS 78 – 2486). However, it is very surprising that for the sample of 0.1 mol % Fe³⁺ -doped TiO₂, practically all peaks assigned to the rutile phase (JCPDS 78 – 1508), except a very weak peak at 25.3°, which was attributed to the (101) anatase phase peak, indicating that the material mainly crystallize in rutile phase under these conditions. Transition iron oxide phases were not detected in the XRD pattern, suggesting, despite the small amount of dopants, that iron oxide could be existed as the amorphous phase, without incorporating to the TiO₂ lattice or goes to the substitutional sites in TiO₂ lattice, as we mentioned above.
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The average grain size is calculated from the broadening of the (1 0 1) XRD peak of anatase and (110) rutile phases using Scherrer’s equation: \[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]
and the distortion of the TiO₂ matrices was also estimated from the XRD spectra using the formula:

\[ \varepsilon = \frac{\beta}{4 tg \theta} \quad [21] \]

where \( \lambda \) is the x-ray wavelength (\( \lambda = 1.5406 \ \text{Å} \)), \( \theta \) is the Bragg angle and \( \beta \) is the half-height width of the diffraction peak of anatase and rutile phases. The different characteristics of the studied samples are summarized in Table 1. It can be concluded that doping iron-ion with proper content decreases the crystal size. For example the grain size decrease from 14 nm for the pure TiO₂ to 7.88 nm for 1.5mol % Fe³⁺-doped TiO₂. The top observation is the appearance of rutile phase at relatively low temperature in 0.1mol % Fe³⁺-doped TiO₂ sample. It is a surprise to find the appearance of the rutile phase for this amount of doping and at low temperature; it seems that there are other factors except the temperature that can influence the anatase-rutile phase transformation. As it has been reported [22 - 24] that the phase transformation of anatase to rutile is a surface phenomenon. So this means that the transformation is associated with nucleation on the surface of particles. It is believed that the difference between chemical potential of primary and final phases is the most likely factor which is responsible for activation energy of phase transformation. Nano-particles with small crystallite size have less thermal stability. Therefore, in anatase with smaller particle size it is easier to start the phase transformation at lower temperature than in the large particles under similar condition [25].

4.2. Morphology analysis

Figs. 2 show a typical SEM image of TiO₂ samples synthesized with and without Fe doping. SEM image (Fig. 2a) of the as-prepared TiO₂ shows an ultra-fine powder.

However, the particles in doped samples tend to aggregated together to form bigger particles with various size and shape, the surface of agglomerated particles is rough and compact (Fig. 2b).

4.3. FTIR spectroscopy

IR spectroscopy was used to examine the surface chemical states of the as-prepared sample. FTIR spectra of the TiO₂ and Fe³⁺-doped TiO₂ are shown in Fig.3. A broad absorption peak at 400–700 cm⁻¹ wavelength ranges is clearly visible. This is attributed to Ti–O stretching and Ti–O–Ti bridging stretching modes [26]. A several absorption bands correspond to the vibrational modes of organic species such as hydroxyl, carboxilate and alkenes groups are observed.
A broad band observed between 3700 and 3000 cm\(^{-1}\) and the broad peak at about 1630 cm\(^{-1}\) are related to the O-H stretching mode of hydroxyl groups. The peak at 1633 cm\(^{-1}\) in all spectra, is assigned to C-H stretching vibrations of alkenes groups. The weak peaks at about 2850 cm\(^{-1}\) and 2920 cm\(^{-1}\) are normally attributed to the symmetric and to the asymmetric stretching of -CH\(_2\)- groups and terminal CH\(_3\)- groups. Evidently, the composition of the start materials is the originated of these adsorbed species. These results suggest that the as-prepared TiO\(_2\) nanocrystals are highly pure and strongly surface hydrated, which is significantly different from the water-soluble TiO\(_2\) nanoparticles reported by Wang et al. [31]. In addition the transmittances generally, decrease as doping content increase.

### 4.4. UV–vis absorption spectra

The UV–vis absorption spectra of TiO\(_2\) and Fe\(^{3+}\)–doped TiO\(_2\) prepared by the sol–gel method are shown in Fig. 4. As we can see, the light absorption in the visible range increases with increasing the dopant amount of Fe. The red shift of absorption edge corresponds with a decrease in the band gap. It has been accepted that metal doping could introduce a dopant energy level into the band gap of TiO\(_2\). The red shift of absorption edge for the Fe\(^{3+}\)-doped TiO\(_2\) should come from the electronic transition from the dopant energy level to the conduction band of TiO\(_2\). It has been reported that the shift resulted from the incorporation of iron ions into the TiO\(_2\) nanoparticles prepared by sol–gel method [34, 35].

The UV–vis absorption of TiO\(_2\) and Fe\(^{3+}\)–doped TiO\(_2\) shows six main emission peaks at about 383, 410, 436, 448, 473 and 518 nm wavelengths respectively. The former is ascribed to the symmetric and to the asymmetric stretching of –CH\(_2\)– groups and terminal CH\(_3\)– groups.

The absorption spectra is extended to the visible range of 400 –500 nm, as a function of iron concentration doping, then show a highly value for 1.5 mol % Fe\(^{3+}\)-doped TiO\(_2\) sample. It has been shows a clear reduction in the band gap energy for TiO\(_2\) nanoparticles doped with Fe\(^{3+}\) (from 3.17 to 2.75 eV) in comparison with undoped TiO\(_2\) (3.23 eV). XRD and UV–visible studies in combination suggest that Fe\(^{3+}\) ions have been incorporated into the lattice of TiO\(_2\) nanoparticles, which is inconsistent with results reported by Wang et al [36]. The relationship of the absorption coefficient and the incident photon energy of semiconductor are given by the following equation [37, 38]:

\[
\alpha h \nu = (h \nu - E_g)^n
\]

Where \(\alpha\) is the absorption coefficient, \(h \nu\) is the energy of the incident photon, \(n\) is 0.5 and 2.0 for a direct transition semiconductor and indirect transition semiconductor respectively. The TiO\(_2\) is a direct gap semiconductor, which has a very small absorption coefficient. The band gaps of various iron ions doping concentration are summarized in Table 1.

### 4.5. Photoluminescence spectra

The room temperature photoluminescence (PL) spectra of the specimens are shown in Fig. 5. From the shape and position of the PL emission peaks, there is no evident difference, but their relative intensities exhibit remarkable differences between the undoped TiO\(_2\) and Fe\(^{3+}\)–doped TiO\(_2\). The PL intensity of the doped TiO\(_2\) is bigger than the undoped TiO\(_2\) in the visible region but generally is lower in UV band. It is well known that PL spectrum of nanostructure materials is related to its transfer behavior of photo-induced electrons and holes, reflecting the separation and recombination of charge carriers [39 – 41]. For the 1.5 mol % Fe\(^{3+}\)–doped TiO\(_2\) sample, its PL intensity is the weaker among the four doped samples. Thus, recombination rate of charge carriers is the lower. As we can see, at the Fig. 5, the room temperature PL spectra for TiO\(_2\) and Fe\(^{3+}\)–doped TiO\(_2\) shows six main emission peaks appear at about 3.23, 3.03, 2.84, 2.78, 2.62 and 2.39 eV, which correspond to the 383, 410, 436, 448, 473 and 518 nm wavelengths respectively. The former is ascribed to the emission of band to band recombination, while the latter is attributed to the electron transition mediated by defect levels such as oxygen vacancies in the band gap [42].
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![Fig. 5. PL spectra of pure and Fe$^{3+}$- doped Titania: (a) pureTiO$_2$, (b) 0.1 %, (c) 0.5%, (d) 1%, (e) 1.5% Fe$^{3+}$- doped TiO$_2$.](image)

Compared with the indirect band-gap energy of 3.23 eV obtained by UV–vis absorption measurement, the emission position of the radiative annihilation of excitons exhibited a slight red shift, which is suggested to be related to the light-induced relaxation of polar molecules [43, 44]. The latter is the emission signal originated from the charge-transfer transition from Ti$^{3+}$ to oxygen anionic a TiO$_6$$^{8-}$ complex [45, 46]. The difference of about 0.84 eV between the band gap energy (3.23 eV) and the emission peak energy (2.39 eV) is caused by the Stokes shift due to the Franck–Condon effect [39, 44].

**CONCLUSION**

It can be concluded that the weak amounts of iron ion doping can decrease the crystallite size and favor the Anatase–Rutile transformation at relatively low temperature (350 °C). In this study, the characterization of undoped and Fe$^{3+}$- doped TiO$_2$ prepared by a sol–gel method was performed. The particle size and morphology of the Fe$^{3+}$-doped TiO$_2$ were strongly dependent on the amount of Fe incorporated in TiO$_2$ matrix. It can be concluded from the Scherrer equation that doping iron-ion with proper content decreases the crystal size and the anatase to rutile transformation was appeared. The FT-IR analysis suggests that the as-prepared TiO$_2$ nanocrystals are highly pure and strongly surface hydrated. The undoped TiO$_2$ sample showed a lowest absorption towards visible light. When doping with iron ions, the absorption spectra are extended to the visible range of 400 –500 nm. UV spectra show a clear reduction in the band gap energy as a function of content doping. PL spectra for TiO$_2$ and Fe$^{3+}$ doped TiO$_2$ shows six main emission peaks. The UV band is ascribed to the emission of band to band recombination, while the visible bands are attributed to the electron transition mediated by defect levels such as oxygen vacancies in the band gap. The increase of PL intensity could be attributed to the introduction of new defect sites in the samples. The red shift in the visible range has a practical importance since an efficient utilization of visible light for photocatalytic reaction will be possible.

**REFERENCES**