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Characterization and Comparison of Visible Light Active Fe-Doped and N-doped TiO_2 Films Prepared by Sol-Gel Process

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ABSTRACT

In this study, Fe-doped and N-doped TiO_2 films were successfully prepared via sol-gel method through hydrolysis and polymerization of titanium tetraisopropoxide in 2-propanol. Dip-coating method was used to fabricate thin films. Various samples with different amount of iron and nitrogen dopant were prepared and characterized by X-ray diffraction, Fourier transform infrared spectroscopy and UV-Vis spectroscopy. XRD patterns show that all samples have pure anatase crystal structure and there is no significant change in XRD pattern after doping. The UV-Vis spectroscopy was used to characterize optical properties and its spectra show a small shift of absorption edge to the visible region by iron doping. The results show that the bang gap decreases by increasing of iron amount. But in the N-doped sample, the absorption edge does not increase by dopant amount changing.

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INTRODUCTION

The finding of the titanium dioxide photo catalytic effect in the late 1960`s has markedly widened the application range of $TiO_2$-coated materials (Fujishima, A., K. Honda, 1972). But, scientists` interest in heterogeneous photo catalysis by TiO_2 has increased greatly in recent decades. Titanium dioxide has a great interest in metal oxide semiconductors due to the wide bandgap, but the main disadvantages of the pure TiO_2 are low efficiency under irradiation in the visible light and undesirable recombination of the electrons and holes (Aman, N., 2010). Therefore, numerous dopants have been reported for the enhancement of the photo catalytic activity of TiO_2 (Aman, N., 2010; Mishra, T., 2007). One of the methods for visible light activation of TiO_2 is doping through chemical routes such as sol-gel process.

Several studies have been made on visible light response of TiO_2 by nitrogen doping (Asahi, R., T. Morikawa, 2007; Valentin, C.D., 2005; Valentin, C.D., 2007; Peng, F., 2008; Asahi, R., 2001; Shen, H., 2007; Peng, F., 2008; Irie, H., 2003; Sato, S., 2005; Chen, X., 2008; Zhang, J., 2008; Yuan, J., 2006; Guo, Y., 2007; Li, D., 2005; Huang, A.P., 2007; Zhao, L., 2008; Chen, X., 2008; Yin, S., 2006; Mi, L., 2008; Somekawa, S., 2008; Yamada, K., 2008; Zuyuan, W., 2006; Li, D., 2007). Asahi *et al.* (2007, 2001) proposed that substitutional nitrogen species generate states above the valence band to narrow the band gap of titania. TiO_2 absorbs visible light when doped with nitrogen. The other reason behind visible light response of N-doped TiO_2 might be intragap states (Asahi, R., T. Morikawa, 2007). It should be pointed out that visible light absorption does not ensure high visible light activity. More importantly, it is the location of the impurity states generated in the band gap of TiO_2 by nitrogen doping that determines the visible light activity of these samples. Visible light activity of nitrogen doped samples can be significantly reduced if these newly developed impurity states lay deep in the band gap of titania since they serve as recombination centers (Asahi, R., T. Morikawa, 2007).

And Fe-doping in TiO_2 generates impurity states within its bandgap and shifts the absorption edge to the visible light region (Li, D., 2007; Ambrus, Z., 2008; Hung, W.C., 2007; Bouras, P., 2007).

In this study, Fe-doped and N-doped TiO_2 films were successfully prepared via sol-gel method through hydrolysis and polymerization of titanium tetraisopropoxide in 2-propanol. Dip-coating method was used to

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fabricate thin films. Various samples with different amount of iron and nitrogen dopant were prepared and characterized by X-ray diffraction, Fourier transform infrared spectroscopy and UV-Vis spectroscopy.

Experimental:

Sol-gel method was used to prepare Fe-doped and N-doped titanium dioxide coatings on soda-lime glass slides (25 mm × 75 mm in size and 1-1.2 mm in thickness). The synthesis procedure of TiO_2 thin films outlined in Fig.1. To the preparation of TiO_2, titanium tetra isopropoxide (TTIP, Merck No. 821895) was dissolved in Isopropanol and hydrochloric acid with molar ratio IPA: TTIP: HCl equal to 20:1:0.2 . The different molar concentration (0.5%, 1.5% and 3%) of urea and iron nitrate as dopant were dissolved in the TiO_2 sol after the reagents were thoroughly mixed. The TiO_2 solutions were mixed and intensively stirred for four hours at room temperature. Then dip-coating method was used to film formation. The immersion rate and withdraw rate were initially optimized as 150 $mm.min^{-1}$ and then kept constant for all experiments. Finally, the prepared samples were dried at room temperature for 2h and then calcined at 450 °C for 2h (The heating rate of temperature: 4 °C /min). The prepared samples were shown in table1.

The XRD technique was used to identify the phases of the samples employing Rigaku diffractometer having CuK_α radiation. The Fourier transform infrared spectroscopy spectra was measured using Siemens. The UV-Vis spectra were investigated by T70 UV-Vis PG.

Table 1: Prepard sample and dopant concentrations.

Sample	Urea molar concentration	Iron nitrate molar concentration
P	0%	0%
F-0.5	0.5%	0%
F-1.5	1.5%	0%
F-3	3%	0%
N-0.5	0%	0.5%
N-1.5	0%	1.5%
N-3	0%	3%

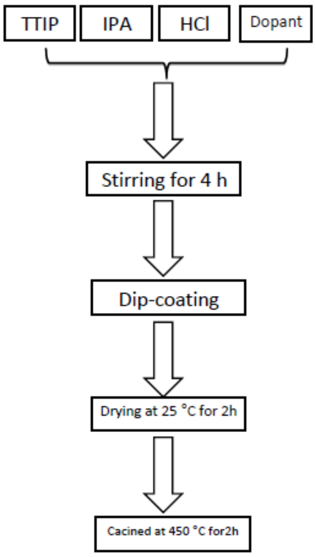

Fig. 1: Synthesis flowchart of doped TiO_2

Results:

The XRD patterns are shown in Fig. 1 which confirms the presence of the anatase crystal structure. The rutile peak is not seen at all samples and according to X`pert highscore files, anatase was observed in all samples that contained nitrogen doped and iron doped TiO_2. It seems that nitrogen and iron is distributed homogeneous on the anatase crystal lattice without forming any other phases. It can be concluded that the particle size decreasing by iron doping.

The FT-IR patterns of the TiO_2 sol and TiO_2 film were shown in Fig. 2 and Fig.3, respectively. The absorption band at 500-600 cm^{-1} in both figures is due to the vibration of the Ti-O band in TiO_2 lattice. The absorption band appearing at 950 and 1020 cm^{-1} are representing the stretching vibration of the O-C-C of the TTIP isopropyl group and large absorption peaks in the region 3000-3600 cm^{-1} are related to the OH stretching frequencies of 2-propanol. The bands appearing at 1100-1550 cm^{-1} are assumed to be due to the species containing CN bond coming from the decomposition of urea.

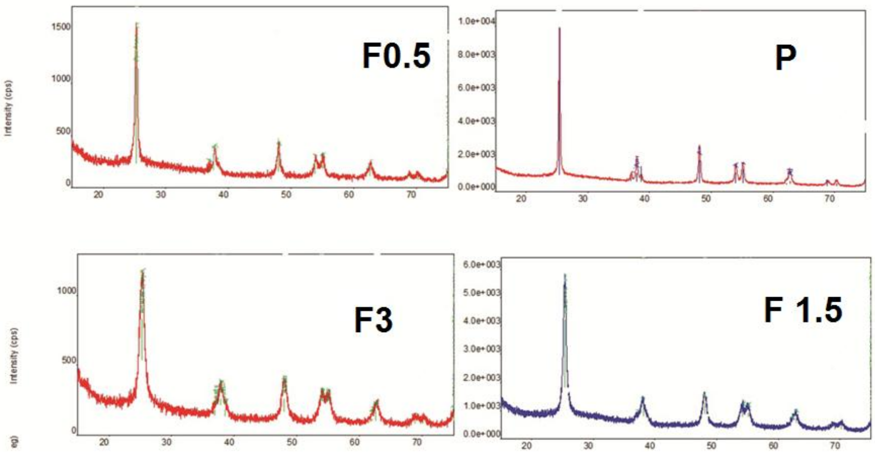

Fig. 1: XRD patterns of pure and iron doped TiO_2

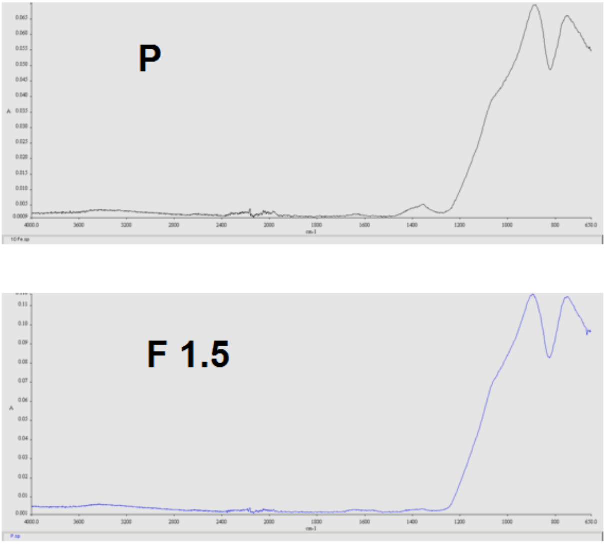

Fig. 2: FT-IR spectra of pure and Fe-doped TiO_2

Fig. 4 shows the transmission spectra of Fe-doped and N-doped TiO_2. The transmission spectra of Fe-doped TiO_2 show that the absorption edge increases by increasing of the dopant amount and shifts to the visible light region. Therefore, it can be proposed that the band gap of Fe-doped TiO_2 decreases by increasing of dopant amount. But in the N-doped sample, the absorption edge does not increase by dopant amount changing. The absorption edge of N-1.5 sample relies on visible light region only. It might be due to the newly developed impurity states lay deep in the band gap of titania since they serve as recombination centers (Asahi, R., T. Morikawa, 2007).

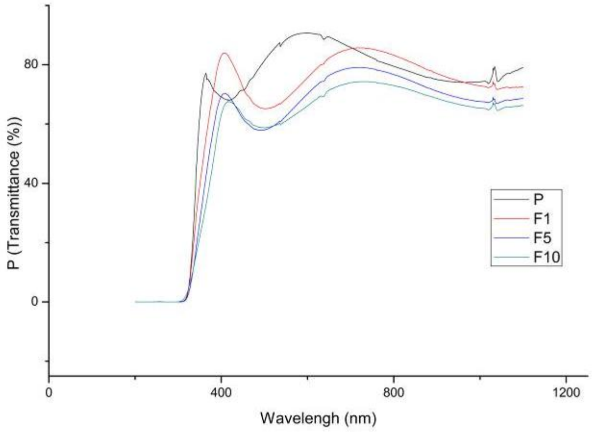

Fig. 3: UV-Vis transmission spectra of Fe-doped TiO_2

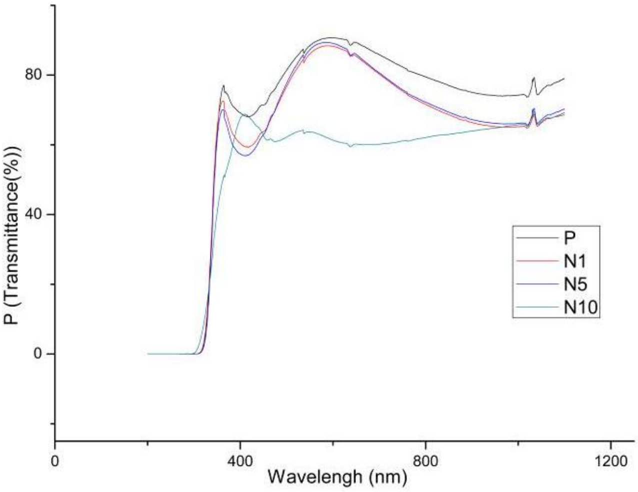

Fig. 4: UV-Vis transmission spectra of N-doped TiO_2.

Conclusion:

The Fe-doped and N- TiO_2 films were prepared via sol-gel method and the influence of dopant type and concentration on the structural and optical properties were investigated. The following knowledge was obtained:

1. All prepared samples have anatase crystal structure and nitrogen and iron is distributed homogeneous on the anatase crystal lattice without forming any other phase.
2. The FT-IR spectra of all prepared sample show that the composition of doped samples are similar to the pure anatase TiO_2.
3. The absorption edge increase and the band gap decreases with the increase of iron concentration.
4. The absorption edge does not increase with the increase of iron concentration.

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