

Study of Photocatalytic Behavior of Photochemical Doped TiO₂ Nanoparticles with In-V Synthesized by Sol-Gel and Hydrothermal Methods

M. Hamadani^{1,2}, A. Reisi-Vanani², P. Razi², S. Hoseinifard²

¹ Institute of Nano Science and Nano Technology, University of Kashan, Kashan, Iran

² Department of Physical Chemistry, Faculty of Chemistry, University of Kashan, Iran

(Received 20 June 2012; published online 24 August 2012)

Indium-vanadium doped with different molar percent (0.05-1%) was prepared by photochemical reduction method on pure TiO₂ nanoparticles synthesized by sol-gel and hydrothermal process. XRD, FT-IR, TEM, SEM and EDX analysis were done for characterized nanoparticles and methyl orange (MO) was used as an environmental pollutant to verify photocatalytic effect of synthesized particles under visible and UV lamps. Result of tests was showed that In-V doping restrain from crystal growth, that only hydrothermal TiO₂ particles with binary doped 0.2% molar of In-V can improve photocatalytic activity compared to sol-gel nanoparticles. Pure TiO₂ prepared by hydrothermal and sol-gel processes were calcined at 300,400,450,550 °C for 3h and 500° C for 2h, respectively.

Keywords: Co-doped TiO₂, Sol-Gel, Hydrothermal, Indium, Vanadium.

PACS number: 91.40.Ge

1. INTRODUCTION

Among photocatalytic nanoparticles, Titania is one of the best materials as photocatalyst for electrical and optical properties, low cost, high photocatalytic activity, chemical stability, non toxic and without chemical and corrosion abrasion against light [1-2]. These particles have rutile (B.G. = 3.0 eV), anatase (B.G. = 3.2 eV) and Brookite phases. Anatase crystals were used in solar cell, optical sensitive paints and optical catalyst [3]. Recombination of hole and electron is one of the important electronic properties in these nanoparticles]. The recombination could occur as thermally assisted detrapping or electron tunneling [4]. This process caused to decrease photo efficiency. A reducer (electron donor) or oxidant (electron acceptor) agents can prevention of their recombination to increase photocatalytic activity. Different methods are available for increasing area to volume ratio of TiO₂ particles to improve photocatalytic effect such as: noble metal doping [5], metal ion doping [6], anion doping [7] and dye sensitization [8]. Among them, doping method applied to improve the trapping efficiency of charge carriers [9]. Zhang et al [10] prepared V-Sc codoped TiO₂ by sol-gel method, S-N codoped TiO₂ was synthesized in many paper [11], Zhu et al [12] reported that P/N codoped caused to increase rutile to anatase transfer, Yang et al [13] prepared C/V-TiO₂ codoped by sol-gel method and Chen et al [14] prepared V-TiO₂ nanoparticles by sol-gel method.

In this paper, we used a photochemical reduction method for preparing In-V codoped TiO₂ nanoparticles to quantify photocatalyst activity and methyl orange was used as an organic compound for doing photodegradation tests.

2. EXPERIMENTAL

2.1 Material and methods

Different materials were used for preparing mentioned nanoparticles. TTIP [Ti [OCH(CH₃)₄] (Merck, >

98%), Glacial Acetic Acid (Merck, >99.8%), Ammonium metavanadate (NH₄VO₃, Merck), Indium chloride (InCl₃, Merck) and dionized water was produced by a Smart-2-Pure type made in TKA company of Germany.

Pure TiO₂ nanoparticles were prepared by sol-gel and hydrothermal methods according to [15] papers, respectively. Including the hydrothermal particles calcined in 300, 400, 450, and 550° C for checking intensity of Brookite phase and photocatalytic activity.

2.2 Preparation of In-V nanoparticles

For preparing In-V particles, first different molar percent (0.1, 0.2, 0.4, 0.6, 1.0%) of ammonium metavanadate as vanadium source with regard to molar percent of V to Ti, was added to certain amount of pure TiO₂ particles that synthesized by sol-gel and hydrothermal processes. Then 100 ml of solution was placed under condition N₂ atmosphere for 10 min and put it with aluminum paper. After this, it was placed against ultraviolet light with stirring for 15 h in photochemical box equipped with fan to prevent UV leakage, then indium chloride as indium source with the same molar percent (0.1, 0.2, 0.4, 0.6, 1.0%) was added to mentioned solution and repeat above stages. At the end, the mixture was centrifuged and dried in 100° C for 12 h.

2.3 Characterization

The X-ray diffraction (XRD) spectra in 0.006-5 nm wavelength of various titania samples were recorded on a Philip X Pert Pro MPD model using Cu K α radiation as the X-ray source. The pattern was used for checking nanoparticles size and phase analysis. Average particle size was showed by Debye-Scherrer equation. By scanning electron microscope (SEM) (Hitachi, S-4160) is obtained 3 dimension pictures from sample structure. FT-IR spectra were recorded on Nicolet Magna IR 550 spectrometer. It was used for checking surface structure of nanoparticles and get to information about surround organic layers of metal nanoparticles. Transmission electron microscope (TEM) (Philips, CN 10, HT

100 KeV) was applied for testing the particle morphology. Photodegradation of MO was tested by using UV-Vis spectrophotometer (Perkin Elmer Lambda 2S) against UV and visible light.

2.4 Photocatalytic effect

Mo solution was used as an environmental pollutant to evaluate photodegradation activity of synthesized nanoparticles. All of decolorization of dye solution tests were done in quart glass when samples were exposed to UV and Vis lamps as artificial sunlight. For tests, the mixture containing 100 mg catalyst nanoparticles and 100 ml MO solution [40, 41] was aerated for 30min to get on adsorption equilibrium and saturated solution with O₂. Then it was placed in photochemical box equipped with a fan with stirring in 40 and 25 cm distance from UV and Vis lamps, respectively. At certain times UV-Vis spectrometer was showed absorption changes [37, 42]. PH for MO solution was adjusted between 2-3 and maximum wavelength is 510 nm [43].

3. RESULT AND DISCUSSION

3.1 X-ray scattering analysis

Figure 1 is a plot of X-ray scattering (XRD) of pure hydrothermal TiO₂ particle in different calcinations temperatures. (101), (004), (200), (105), (211), (204), (116) diffraction peaks were proved anatase phase for pure TiO₂. A main peak for anatase phase around $2\theta = 25.2^\circ$ (101) has tetragonal form. Another peak around $2\theta = 30.8^\circ$ (121) exhibit brookite phase in this particles. When calcinations temperature was increased, we could decrease intensity and sharpness of the brookite peak in nanoparticles. Also any rutile diffraction peak wasn't in these spectra.

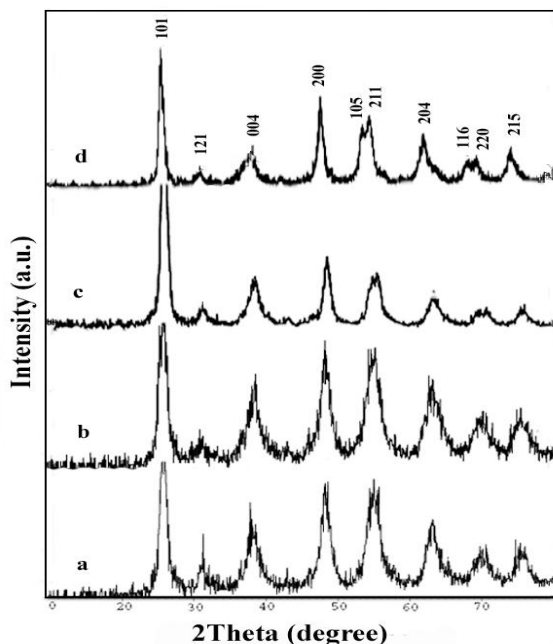


Fig. 1 – X-ray spectra (XRD) of pure hydrothermal TiO₂ particles in a)300, b)400, c)450 and d)550° C calcinations temperatures

Figure 2 shows the XRD plan of In-V photochemical doped hydrothermal TiO₂ samples. By using Debye-Scherrer equation on anatase ($2\theta = 25.2, 48.2, 55.2^\circ$) we have been calculated the average particle size for pure hydrothermal titania in 300, 400, 450 and 550° C, size of particles are about 8.26, 11.85, 18.75 and 25.2 nm, respectively. Size of 0.2% In-V photochemical codoped on hydrothermal titania is 14.3 nm.

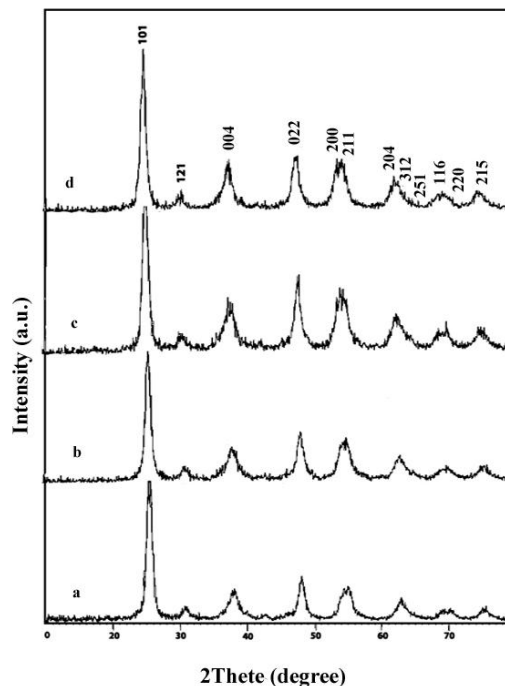


Fig. 2 – XRD plan of a) pure b) 0.1% c) 0.2% d)1% In-V photochemical codoped TiO₂ nanoparticles

3.2 SEM and TEM images

Figure 3 shows SEM and TEM images for 0.2% In-V photochemical doped on hydrothermal TiO₂ particles with different enlarge. These images exhibited spherical structure and adhesion of the particles. EDX measurement also was proved the presence of In and V in this sample. With this images particle size was estimated about 11-13 nm and Debye-Scherrer was calculated particle size about 12-15 nm, that TEM micrographs has proved this calculation synthesized nanoparticles have spherical morphology.

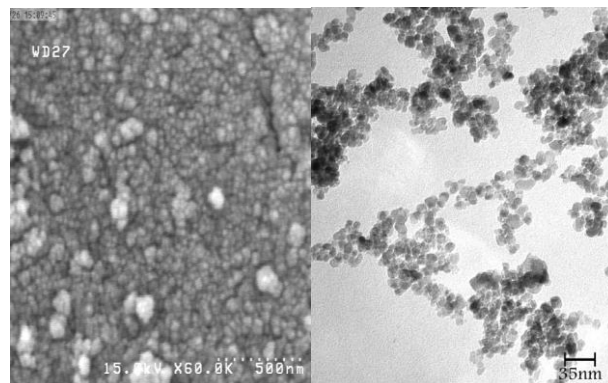


Fig. 3 – SEM and TEM images for 0.2% In-V photochemical doped on hydrothermal TiO₂ nanoparticles

3.3 Photodegradation effect

Result show In-V binary doped on hydrothermal TiO₂ compared to sol-gel TiO₂ had the best operation in competition between interfacial charge transfer ratios to rate of hole-electron recombination. Figure 4 exhibit in both UV and Vis region, 0.2% In-V codoped on hydrothermal TiO₂ could reduce the recombination rate

as electron trapper. Login Indium to V-TiO₂ structure prevent from particle growth and In³⁺ change to In²⁺ as electron trapper and form lower energy level from conduction band (CB). In absent the light source, again In²⁺ ions change to In³⁺ and atmospheric O₂ traps released electron as electron acceptor and produce O₂.

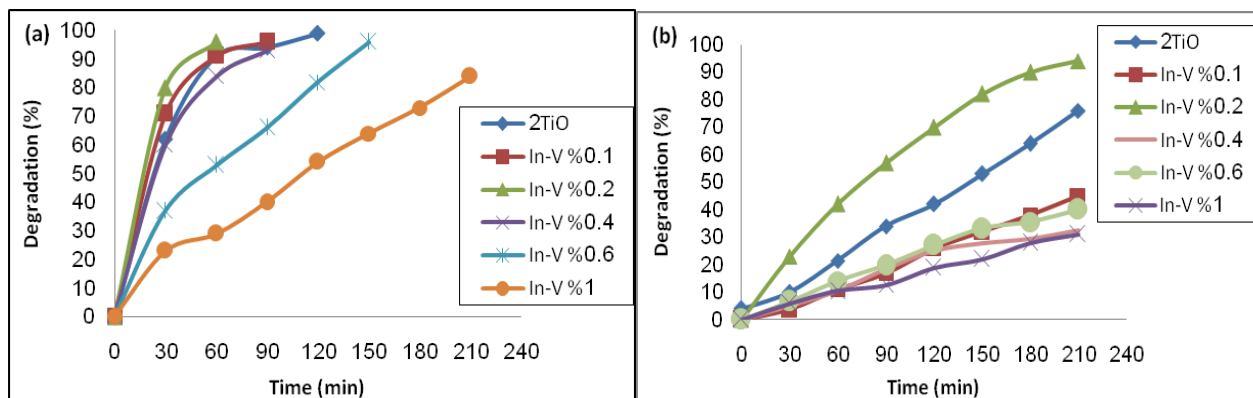


Fig. 4 – Photodegradation activity for In-V photochemical codoped on hydrothermal TiO₂ nanoparticles Under a) UV, b) visible lamps

4. CONCLUSION

The metal ion dopants influence the photo efficiency of TiO₂ by acting as electron or hole trap center within band gap of TiO₂ and alter the e⁻/h⁺ pair recombination rate through following process. In this paper, different molar percent of In-V codoped on hydrothermal and sol-gel pure TiO₂ by UV photochemical reduction process that In³⁺, V³⁺ deposited on TiO₂ surface as In₀,

VO and photodegradation activity of the MO can improve when 0.2% In-V codoped on hydrothermal TiO₂ and reduce recombination rate as electron trapper. In photochemical doped method, metal ions were into holes in TiO₂ structure with zero oxidation number, but in other doping methods, cation and anion were substituted at Ti⁴⁺ and O₂⁻ sites, respectively.

REFERENCES

1. A.N-Enyashin, G. Seifert, *phys. stat. sol.* **242**, 1361 (2005).
2. L. Armelao, D. Barreca, *Nanotech.* **18**, 375709 (2007).
3. X. Xiao, K. Ouyang, R. Liu, J. Liang, *Appl. Surf. Sci.* **255**, 3659 (2009).
4. W.S. Dillmore, M.N. Yousaf, M. Mrksich, *Langmuir.* **20**, 7223 (2004).
5. O. Rosseler, M. Shankar, K-L. DuM, L. Schmidlin, N. Keller, V. Keller, *J. Catal.* **269**, 179 (2010).
6. L.G. Devi, B.N. Murthy, S.G. Kumar, *Mater. Sci. Eng. B* **166**, 1 (2010).
7. D.M. Chen, D. Yang, Q. Wang, Z.Y. Jiang, *Ind. Eng. Chem. Res.* **45**, 4110 (2006).
8. H.S. Hilal, L.Z. Majjad, N. Zaatat, A. El-Hamouz, *Solid State. Sci.* **9**, 9 (2007).
9. A. Dawson, P.V. Kamat, *J. Phys. Chem.* **105**, 960 (2001).
10. D.R. Zhang, Y.H. Kim, Y.S. Kang, *Curr. Appl. Phys.* **6**, 801 (2006).
11. F. Wei, L. Ni, P. Cui, *J. Hazard. Mater.* **156**, 135 (2008).
12. C. Chang, C. Lin, C. Chan, C. Hsu, C. Chen, *Thin Solid Films* **494**, 274 (2006).
13. D. Chu, X. Yuan, G. Qin, M. Xu, P. Zheng, J. Lu, L. Zha, *J. Nanopart. Res.* **10**, 357 (2008).
14. K. Chen, J. Li, Y. Zhang, W. Wang, *Colloids and Surfaces A: Physicochem. Eng. Aspects.* **360**, 47 (2010).
15. M. Hamadianian, A. Reisi-Vanani, A. Majedi, *Mater. Chem. Phys.* **116**, 376 (2009).