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Photocatalytic and optical properties of vanadium doped zinc oxide nanoparticles

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Abstract

Vanadium-doped zinc oxide nanoparticles have been synthesized by sol-gel method using a supercritical drying in ethyl alcohol at 250°C.after heating under natural atmosphere at 500 °C for 2 hours, the obtained nanopowder was characterized by various techniques such as particle size analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and photoluminescence (PL). In the as-prepared state, the powder with an average particle size of 25 nm presents a strong luminescence band in the visible range. From photoluminescence excitation (PLE) the energy position of the obtained PL band depends on the wavelength excitation and this PL can be obtained by some visible excitations. This result is very promising for visible photocatalysis applications; which was confirmed by methylene blue photodegradation using visible lamp as light source. By comparison with undoped ZnO results, elaborated in the same conditions, we can conclude that the vanadium is responsible to this visible photocatalytic activation.

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1. Introduction

Recently titanium dioxide photocatalyst have been utilized successfully in various fields such as air-purification, deodorizing, sterilization and self-cleaning [1]. However, the major problem is that with TiO_2 photocatalyst we can use only the UV light witch presents only 2-3% of solar light [3]. For the improvement of photocatalytic degradation of pollutants at $\lambda > 400$ nm, several types of photocatalysts have been tried, for example, transition metal ion implanted TiO_2 [4-5], reduced TiO_2 [6], dye-sensitezed TiO_2 [7-8]. Athor semiconductors as photocatalysts have been studied by several research groups; zinc oxide is one of these photocatalysts. In the recent years, ZnO semiconductors, has received much attention due to his wide and direct band gap of 3.37 eV at room temperature, low cost and environmentally friendly feature [9-12]. However, the reactivity of ZnO with nanometer dimensions depends significantly on the optical and electronic properties; it is transparent in visible region. For this reason, ZnO semiconductor is widely used in photocatalytic degradation of organic and inorganic pollutants. Some problems still remain to be solved in its application, such us the fast recombination of photogenerated electron-hole pairs. Therefore improving photocatalytic activity by modification has become a hot topic among researches in recent years [13]. Transition metal doping and coupling semiconductors are the most way. Several methods have been used for the preparation of undoped and doped ZnO; such as sol-gel process witch is used in this work for the elaboration of pure and vanadium doped ZnO nanopowder. In order to clarify the photocatalytic properties of ZnO:V under visible irradiation. The relation between optical and photocatalytic properties was investigated

2. Experimental

2.1 Sample preparation

Vanadium doped ZnO nanoparticles were prepared by using 16 g of zinc acetate dehydrate in a 112 ml of methanol, with a 0,628 g of ammonium metavanadate. After 15 min of magnetic stirring the solution was placed in an autoclave and dried under supercritical

conditions of ethyl alcohol (EtOH). The obtained powder was then heated in a furnace for 2 h at 500 °C in air. For the preparation of pure ZnO we used the same protocol but without the doping element.

2.2 Characterization techniques

X-ray diffraction (XRD) patterns of vanadium doped zinc oxide nanopowder as prepared was carried out by a Bruker D5005 diffractometer, using CoK_{α} radiation (λ=1.78901 Å). The synthesized products were characterized using a JEM-200CX transmission electron microscopy (TEM). The specimens for TEM were prepared by putting the as-grown products in EtOH and immersing them in an ultrasonic bath for 15 min, then dropping a few drops of the resulting suspension containing the synthesized materials onto TEM grid. For PL measurements, the 450-W Xenon lamp was used as an excitation source. The emitted light from the sample collected by an optical fiber on the same side as the excitation was analyzed with a Jobin-Yvon Spectrometer HR460 and a multichannel CCD detector (2000 pixels). The PLE measurements were performed on a Jobin-Yvon Fluorolog 3-2 spectrometer. The photocatalytic activities of pure ZnO and vanadium doped ZnO catalysts were tested by using methylene blue degradation (MB). MB was chosen as a model pollutant in water. Experiments were performed in a photochemical reactor equipped with a Pyrex cell with a circulating water jacket and a 250 W (halogen lamp) with a maximum emission at 640 nm placed inside the Pyrex cell. All experimental conditions were kept constant as follows: initial MB concentration as C= 0.03 g/L; catalyst concentration 0.5 g/L and a magnetic stirring. Suspension was stirred in the dark for 1.5 h. During irradiation, the samples (2 ml) were taken out and then centrifuged to remove catalyst. The concentration of MB was determined by UV-VIS spectrophotometer (SHIMADZU) at 664.5 nm. For comparison, a commercially TiO_2 (Degussa P25) was tested in this study.

3. Result and discussion

Figure 1 shows typical XRD patterns of the nanopowder. Five pronounced diffraction peaks appear at 2Θ =37.071°, 40.201°, 42.401°, 55.821° and 66.811° which can be attributed to the (1 0 0), (0 0 2), (1 0 1), (1 0 2) and (1 1 0) planes of ZnO, respectively [14]. The lattice constants calculated from the XRD pattern are a = 3.249 Å, c =5.205 Å, which are very close to wurtzite ZnO ones, i.e., a = 3.250 Å, c = 5.207 Å [15]. Two secondary additional phases were detected corresponding to $Zn_3 (VO_4)_2$ and $Zn_2V_2O_7$.

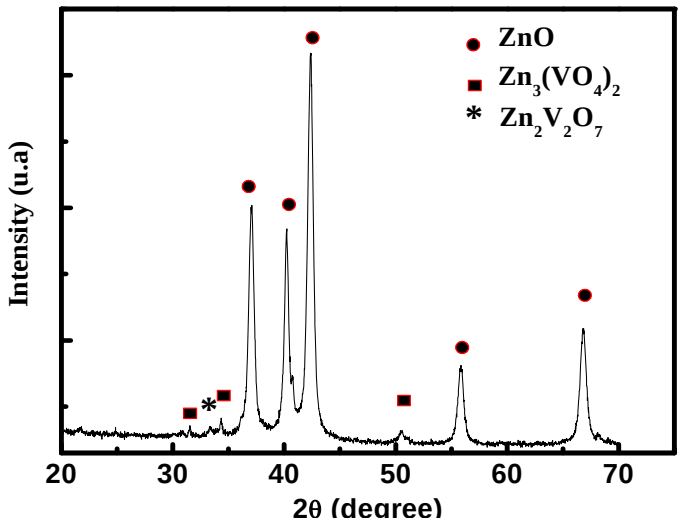

Fig.1: X-ray diffraction of nanoparticles powder of ZnO:V.

The average grain size can be calculated using the Debye–Sherrer equation [16]:

$$G = \frac{0.9\lambda}{B\cos\theta_B} \qquad (1)$$

where λ is the X-ray wavelength (1.78901 Å), θ_B is the maximum of the Bragg diffraction peak (in radians) and B is the linewidth at half maximum. After a correction for the instrumental broadening, an average value of the basal diameter of the cylinder-shape crystallites was found to be 14–20 nm, whereas the height of the crystallites was 22–28 nm.

SEM and TEM images in Figures 2 and 3 have shown that very small ZnO crystallites present very similar prismatic shapes with a narrow particle size distribution assembled in aggregates; the sizes vary between 15 and 30 nm in good agreement with the results of crystallite size obtained by Debye–Sherrer formula.

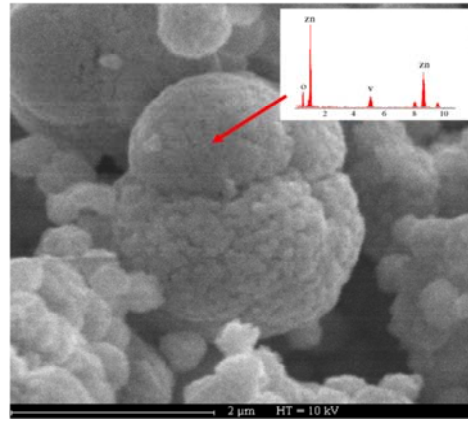

Fig. 2: SEM image of vanadium-doped zinc oxide powder and EDX analysis

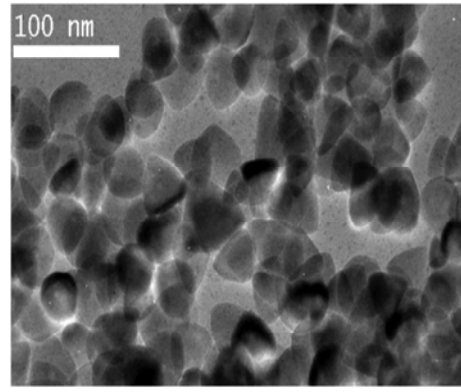

Fig. 3: TEM picture of vanadium-doped zinc oxide nanopowder.

The PL spectra of the ZnO:V nanopowder consist of very wide strong emission band located in the visible range where the position depends on the excitation wavelength (Figure 4).

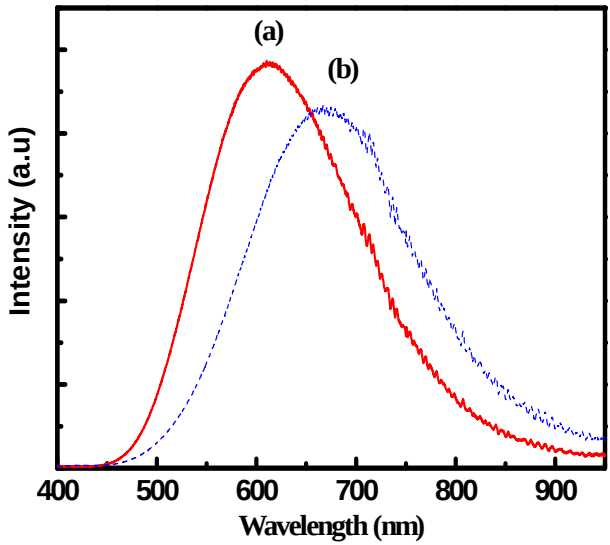

Fig.4: Wavelength-dependent PL of ZnO:V nanoparticles;
(a) λ_{exc} = 325 nm, (b) λ_{exc} =371 nm.

From PLE study in Figure 5, it is clear that luminescence band can be obtained using visible range excitation source it means that the visible PL band correspond to deep level in zinc oxide that can be excited by visible light source. This particular behavior is very promising for the photocatalysis process.

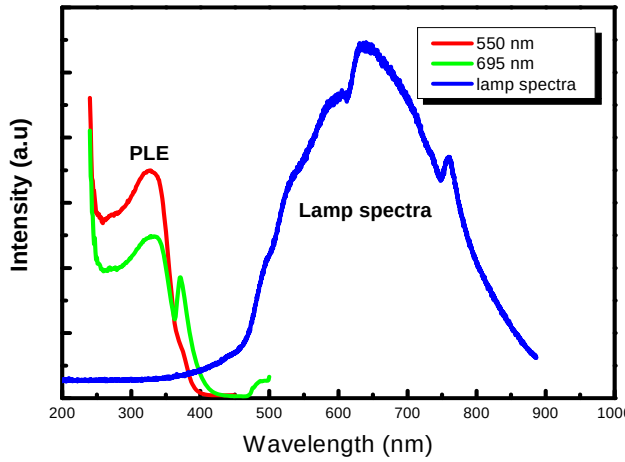

Fig. 5: Intersection between lamp spectra and PLE spectra.

Also, Figure 5 shows that the intersection between lamp and PLE spectra at different wave length analysis, this intersection shows that there is an answer at 400 and even to 500 nm which explain the choice of the visible lamps for the excitation. In fact it's well known that the photocatalytic activity of nanoparticles mainly depends on many properties of photocatalyst, like electronic and optical properties. According to the PL spectra it can be seen that on the both excitation wavelengths, the ZnO:V shows a pick in the visible range. However it is known from the mechanism of photodegradation that in order to increase the photocatalytic activity of semiconductors nanoparticles we should enhanced their absorption in the visible light range.

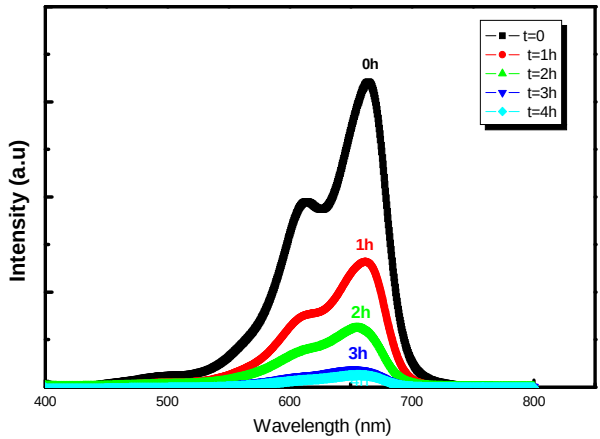

Fig.6: Absorbance spectra of methylene blue.

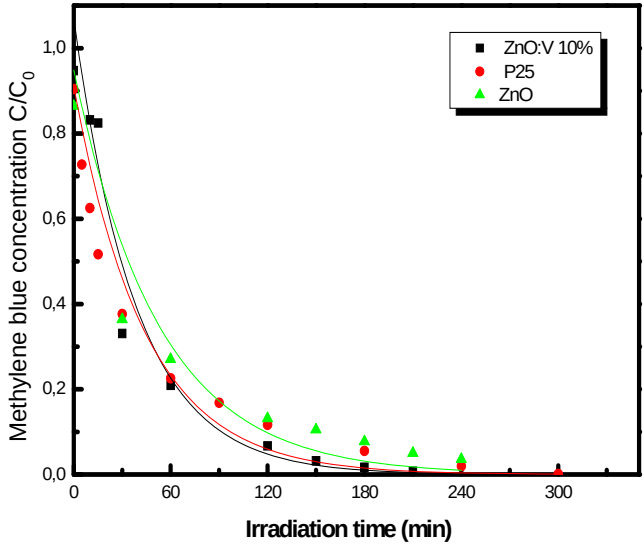

Fig.7: Methylene blue degradation under visible light

Figures 6 and 7 have shown that doping ZnO with vanadium has an influence on the photodegradation of methylene blue. In fact, it can

be seen that the photodegradation increases remarkably with the doping of ZnO by vanadium under visible light excitation. Compared to pure ZnO and commercially TiO_2 (Degussa P25) generally used as reference for photocatalysis, ZnO:V with vanadium concentration of about 10 at% presents the most interesting visible photoactivity.

4. Conclusion

Pure and vanadium doped zinc oxide nanoparticles aerogel were synthesized by sol-gel method from zinc acetate dihydrate used as a precursor. These particles were obtained by slow hydrolysis of the precursors using an esterification reaction, followed by a supercritical drying in EtOH. The X-ray diffraction and TEM show a crystalline phase with a particle size ranging between 15 and 30 nm.Upon heat treatment at 500 °C for 2 h in air atmosphere, room temperature PL spectra of the obtained ZnO:V nanoparticles showed a strong yellow luminescence where the position depend on wabelenght excitation. From the analysis of the PL and PLE spectra, it can be concluded that the luminescence band can be attributed to deep level in bandgap of the zinc oxide. This defect produced by the incorporation of vanadium in zinc oxide inpruve the photocatalitic activity of this semiconductor under visible irradiation. To improve the efficiency of this doping element, many sol-gel synthesis parameters as vanadium concentration can be adjusted.

References

[1] Yoichi Ishibai, Junya Sato, Takashi Nishikawa, Shigeyoshi Miyagishi. Appl. catalysis B: environmental **79** (2008) 117
[2] K. Hashimoto, H. Irie, A. Fujishima, Jpn. J. Appl. phys. **44** (2005) 8269
[3] Chen Shifu, Zhao Wei, Liu Wei, Zhang Sujua. Appl. Sur. Science **255** (2008) 2478
[4] Choi, A. Termin, M. R. Hoffmann. J. Phys. Chem. **98** (1994) 13669
[5] M. Anpo, catal. Suv. Jpn. **1** (1997) 169
[6] I. Nakamura, N. Negishi, S. kutsuna, T. ihara, S. Sugihara, K. Takeuchi, J. Mol. Catal. **161** (2000) 205

[7] J. Hodak, C. Quinteros, M. I. Litter, E. San roman, J. chem. Soc. Faraday Trans. **92** (1996) 5081
[8] E. Bae, W. Choi, J. Park, H. S. Shin, S. B. Kim, J. S. Lee, J. Phys. Chem. B **108** (2004) 14093
[9] L. El Mir, J. El Ghoul, S. Alaya, M. Ben Salem, C. Barthou, H.J. von Bardeleben, Physica B **403** (2008) 1770
[10] L. El Mir, Z. Ben Ayadi, M. Saadoun, H. J. von Bardeleben, K. Djessas, A. Zeinert, Phys. Stat. Sol. (a) **204** (2007) 3266
[11] L. El Mir, Z. Ben Ayadi, M. Saadoun, K. Djessas, H.J. von Bardeleben, S. Alaya, Appl. Surf. Sci. **254** (2007) 570
[12] L. Grigorjeva, D. Millers, K. Smits, C. Monty, J. Kouam, L. El Mir; Solid State Phenomena **106** (2007) 135
[13] S. Chen, W. Zho, W. Liu , S. Zhang, App. Surf. Scien. **255** (2008) 2478
[14] L. El Mir, A. Amlouk, C. Barthou, S. Alaya, Physica B **388** (2007) 412
[15] S. H. Jeong, B. S. Kim, B. T. Lee, Appl. Phys. Lett. **82** (2003) 2625
[16] B. D. Cullity, *Elements of X-ray Diffractions*, Addison-Wesley, Reading, MA, (1978) 102