



## A Comparative Photocatalytic Activity of ZnO/SiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> by Investigating the Degradation of Rhodamine B

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### Abstract

ZnO/SiO<sub>2</sub> was prepared using sol-gel method, and vanadium particles were loaded on this nano-photocatalyst by wet incipient method. They characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive (EDX) analysis and Fourier transform infrared spectroscopy (FT-IR). The XRD patterns showed that the zinc oxide samples have a wurtzite structure and vanadium doped is in V<sub>2</sub>O<sub>5</sub> crystalline structure. The particle sizes were around 32 nm calculated using Scherrer's equation. For photocatalytic test, decomposition of Rhodamine B (RB), as an organic pollutant, was carried out. The photocatalyst V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> was found to be more efficient as compared with ZnO/SiO<sub>2</sub>.

**Keywords:** Photocatalyst, Rhodamine B, UV-vis, ZnO, V<sub>2</sub>O<sub>5</sub>.

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### Introduction

Elimination of persistent organic pollutants that remain for a long time in the environment is one of the most difficult processes of the effluent treatment. Many methods are employed to remove or destroy the pollutants of effluents and contaminating gases. Some destructive methods use strong oxidants which are harmful. On the other hand, currently used non-destructive methods bring also serious

losses. For example, air stripping (a method for the removal of volatile organic compounds from surface water or groundwater in which air is blown into water and the contaminants are evaporated into air) converts water contamination to the air pollution. Carbon adsorption (eliminating volatile and non-volatile chemicals) produces a harmful solid which should be destroyed. One of the weaknesses of these old processes is that the

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pollutants are not destroyed, but displaced from one phase to another. Therefore, methods for destruction of organic pollutants should be replaced with methods exerting less or negligible harms on the environment [1-6].

ZnO is an n-type semiconductor with a wide direct band gap of 3.37 eV. Recently, much effort has been devoted to study ZnO as a promising photocatalyst for photocatalytic degradation of water pollutants, owing to its high activity, low cost, and environmentally friendly feature [7-8]. ZnO present as nano-scale particles has a high surface area to volume ratio and provides more active sites on the surface and therefore increases the rate of reaction on its surface such as for photocatalytic degradation [9]. However, a major drawback of ZnO is the large band gap of 3.37 eV, so wavelengths below 400nm are necessary for excitation. Another disadvantage of ZnO is that charge carrier recombination of photo-generated electron/hole pairs occurs within nanoseconds and the photocatalytic activity is low [9-10]. Therefore, it is necessary to improve its visible-light activities by extending its absorption threshold from the UV light region to the visible light region and also to reduce the recombination of photo-generated electron/hole. Different attempts were made recently to improve the activity of ZnO catalyst.

Synthesis of nano-size particles is a method to increase the surface area of a photocatalyst to

enable the reactive sites on its surface to be increased. To increase the active centers of a catalyst, it can be covered on a stabilizer such as silica [11-13]. The use of ultraviolet light for destroying pollutants by photocatalysts is a limitation for industry which can be overcome by reducing the band gap, because photocatalysts are semiconductor. A method for reducing the band gap is to dope metals such as platinum, vanadium and silver into the structure of photocatalysts [14-16].

In this work, the preparation results of two nano-photocatalysts: ZnO/SiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> have been reported [17]. Also, the photocatalytic decomposition of Rhodamine Bas an organic dye pollutant using two photocatalysts under UV-Vis light irradiation has been investigated.

## Experimental

All materials used in this work were purchased from Merck and used without modification.

### *Preparation of ZnO nanoparticles*

In a typical synthesis, a solution of 5 mmol zinc acetate dihydrate in 30 mL absolute ethanol was added to a solution of surfactant CTAB (Zn(Ac)<sub>2</sub>.2H<sub>2</sub>O to CTAB molar ratio was equal to 1) in 30 mL of absolute ethanol under stirring. Then, 20 mL of NaOH (0.3M) solution was added to the above solution under continuous stirring in order to get the pH value of solution about 10. The new solution was

kept in a water bath at 70 °C for 2 h. It was observed that the solution started precipitating after one hour in water bath. After cooling the system to room temperature, the product was separated by centrifugation, washed with absolute ethanol and deionized water for several times, and then dried under vacuum at 70 °C for 10 h. Finally, the nanoparticles were calcined at 750 °C for 3 h.

#### *Preparation of nano-photocatalyst ZnO/SiO<sub>2</sub>*

pH of 20 ml of a suspension containing 0.01 mole ZnO was adjusted on 9-10 through dropping NaOH 0.3 M. This mixture refluxed after severe stirring for 10 h at 70 °C until stable zinc hydroxide sols were formed. After the reflux was finished, some tetraethyl orthosilicate was dropped on the sol at the same temperature to achieve a mole ratio of zinc to silicon of 30 to 70. The formed sol was held in the vacuum at room temperature for two days. Then it was calcined at 400 °C for 3 h.

#### *Doping of vanadium into ZnO/SiO<sub>2</sub>*

First, 50 ml of deionized water was added to 3 g of ZnO/SiO<sub>2</sub> and stirred for one hour to obtain a uniform suspension. Then, the amount of ammonium metavanadate (V/Zn = 0.1) was added to this suspension under vigorously stirring at 70 °C until the yellow paste obtained. The dough was placed in a 70 °C vacuum oven overnight. The resulting yellow solid catalyst was calcined at 400 °C for 2 h.

#### *Degradation of Rhodamine B dye using the synthesized catalysts*

Suspensions containing 150 ml of 10 ppm Rhodamine B dye together with ZnO/SiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> catalysts with a concentration of 0.2, 0.3, and 0.4 g/L (pH of the suspensions was stabilized at 3, 4, 5, and 6), a magnetic stirrer, and an air flow which was blown into a reactor through a tube to uniform the environment were used in each experiment. The reactor consisted of two tungsten lamps; those with wavelength of 220-230nm was used for irradiation at UV range and those with wavelength of 500-700nm for irradiation at visible range.

It should be noted that in the experiments to optimize the amount of catalyst and the environment pH, the irradiation time was 120 min.

Before irradiation, all solutions were stirred for 30 min in the dark to balance absorption and desorption of pollutants on the catalyst surface. A UV-Vis spectrophotometer was used to study the degradation of pollutants. Thus the absorption spectra of the samples were measured at certain intervals and the amount of the pollutant removal or its conversion to another substance was evaluated by the decrease in intensity of the relevant absorption peak.

#### *Characterization*

The crystal phase and particle size of the synthesized products were characterized

by X-ray diffraction (XRD) using FK60-04 with Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ), and with instrumental setting of 35 kV and 20 mA. The morphology of the nanostructures was observed by emission scanning electron microscopy (SEM, PHILIPS-XL $\phi$ 30). Fourier transform infrared (FT-IR) spectra were recorded on a SHIMADZU-840S spectrophotometer using KBr pellet. BET analysis was carried out with QUANTASORB. UV-Vis Diffuse Reflectance Spectra (DRS) were obtained for the dry-pressed disk samples using a UV-Vis Spectrophotometer (SHIMADZU-2550). The amount of degradation of the Rhodamine B was investigated measuring the adsorption intensity of the Rhodamine B remained in the solution by means of UV-Vis spectroscopy (SHIMADZU-2550).

## Results and Discussion

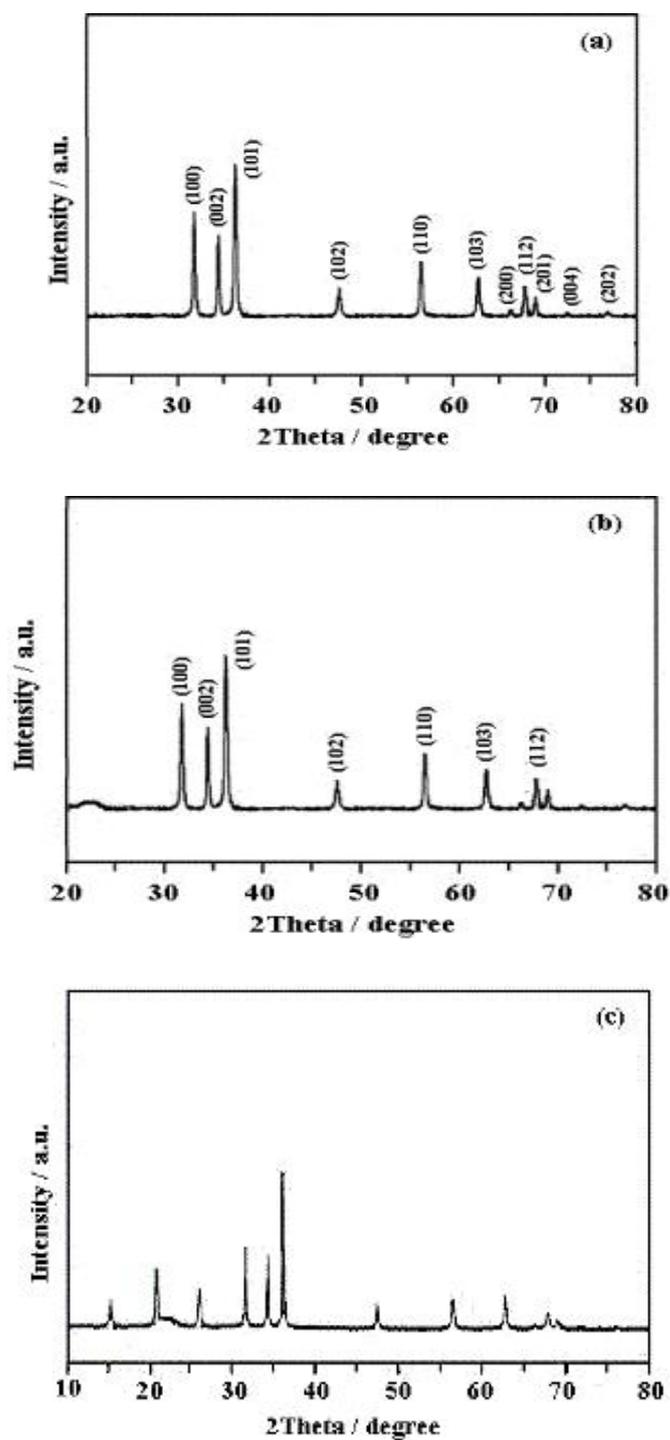
### *Structural analysis of the catalysts*

The XRD patterns of bare ZnO nanoparticles (a), ZnO/SiO<sub>2</sub> (b) and V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> nanophotocatalysts (c) are shown in figs. 1(a-c). All peaks can be well indexed to wurtzite

structure (hexagonal phase) with lattice constants of  $a = 0.32495 \text{ nm}$  and  $c = 0.52069 \text{ nm}$  (JCPDS, No.36-1451). No other crystalline phase was found in the XRD patterns, indicating the high purity of the products. The particles sizes can be calculated using Scherrer's equation:  $D = 0.9 \lambda / (\beta \cos\theta)$  where  $\lambda$  is the X-ray wavelength ( $1.54 \text{ \AA}$ ),  $\beta$  is the full-width at half-maximum intensity of the diffraction line and  $\theta$  is the diffraction angle. The crystallites sizes are estimated to be around 32 nm. Also the surface area of 358 m<sup>2</sup>/g was obtained for ZnO catalyst calcined at 750°C temperature.

In fig.1b a broad new peak is appeared at diffraction degree about 22°, which presents the SiO<sub>2</sub> amorphous state in the product.

Figure 1c shows the XRD pattern of vanadium doped ZnO/SiO<sub>2</sub> sample. In figure 1c three new peaks are appeared at diffraction degrees 15.37°, 20.29° and 26.20°, which can be well indexed to V<sub>2</sub>O<sub>5</sub> crystalline structure (JCPDS, No. 41-1426). Therefore it can be concluded that the V<sub>2</sub>O<sub>5</sub>-loaded ZnO/SiO<sub>2</sub> is carried out successfully.

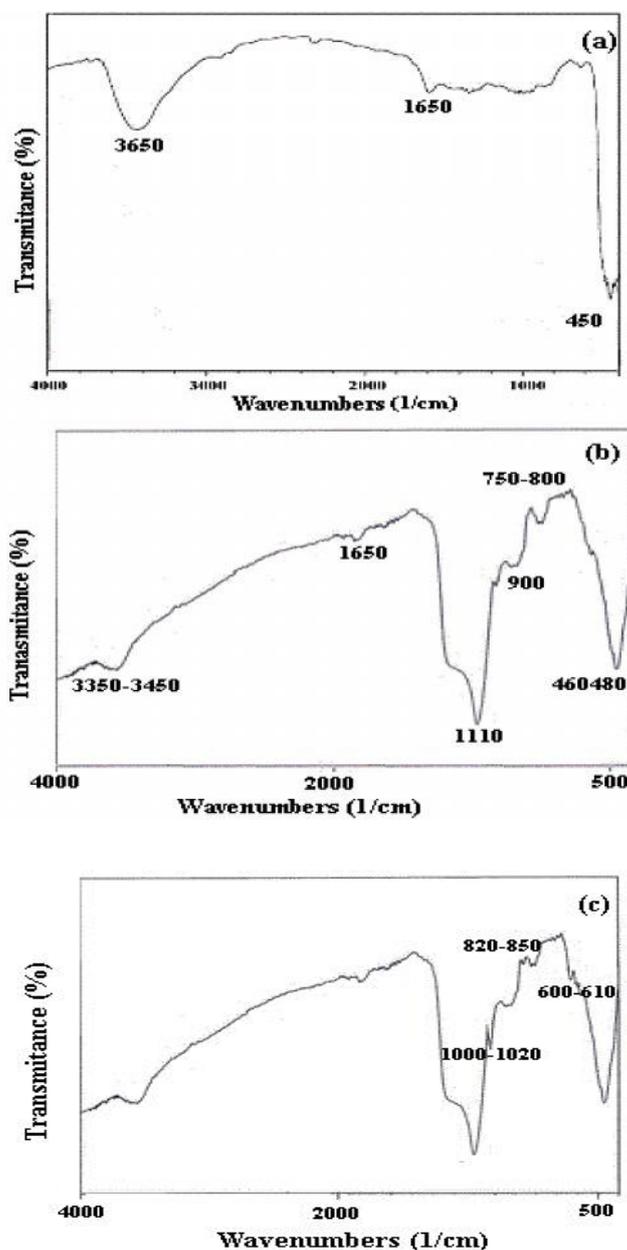


**Figure1.** XRD patterns of (a) ZnO, (b) ZnO/SiO<sub>2</sub>, and (c) V<sub>2</sub>O<sub>5</sub> - ZnO/SiO<sub>2</sub> samples.

The FT-IR spectra of ZnO, ZnO/SiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-doped ZnO/SiO<sub>2</sub> nanoparticles are shown in figure 2(a-c). The vibrational peaks in the range of 3600-3650 cm<sup>-1</sup> and 1600-1650 cm<sup>-1</sup> can be attributed to the stretching and bending vibrations of structural hydroxyl groups of the

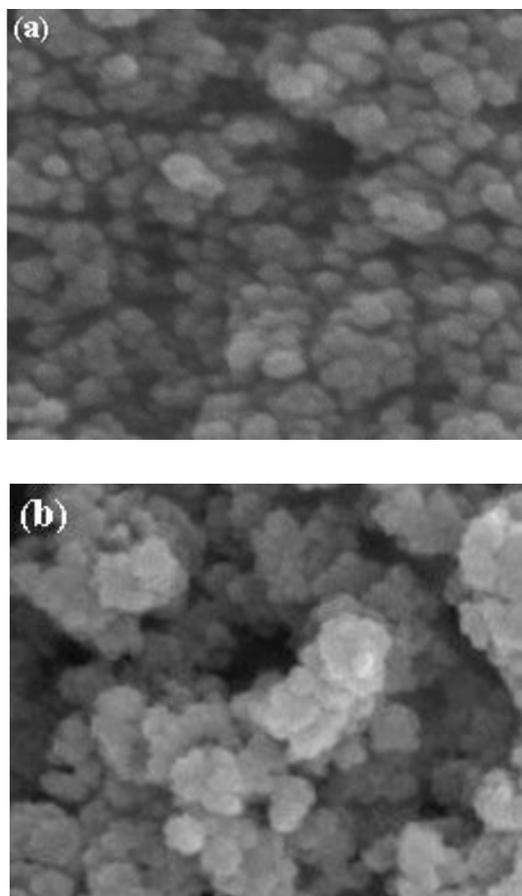
adsorbed water. The peak in the range of 420-450  $\text{cm}^{-1}$  can be associated to the stretching vibration mode of the Zn-O [18-20]. The peaks in the ranges of 1050-1110  $\text{cm}^{-1}$  and 750-800  $\text{cm}^{-1}$  in figure 2(b, c) are corresponded to the asymmetric and symmetric stretching vibration modes of the Si-O-Si, respectively, and are absent in Figure 2a. The peak which is appeared at 440-480  $\text{cm}^{-1}$  is due to the bending vibration

mode of Si-O-Si [21, 22]. Also, the peaks which are appeared at 610, 815 and 1023  $\text{cm}^{-1}$  are due to the stretching vibration mode of V-O, the bending vibration mode of V-O-V and the stretching vibration mode of V=O, respectively, and are absent in figs. 2(a, b) [23-25]. These results clearly show that  $\text{V}_2\text{O}_5$  is successfully dope the ZnO nanoparticles. This is in agreement with the results of XRD patterns.



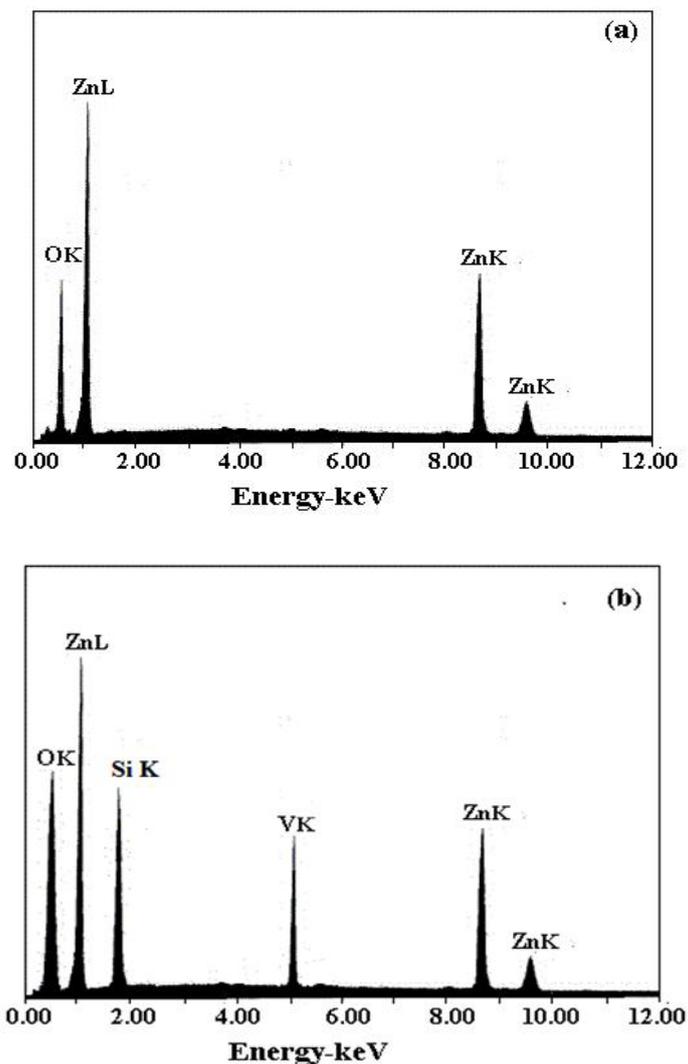
**Figure 2.** FT-IR spectra of (a) ZnO, (b) ZnO/SiO<sub>2</sub>, and (c) V<sub>2</sub>O<sub>5</sub> - ZnO/SiO<sub>2</sub> samples.

The morphology of the products was observed and  $V_2O_5$ -doped  $ZnO/SiO_2$  nanoparticles are by SEM images. The SEM images of  $ZnO$ , shown in figure 3(a-b), respectively.



**Figure 3.** SEM images of (a) bare  $ZnO$ , and (b)  $V_2O_5$ -  $ZnO/SiO_2$  nanoparticles.

The energy dispersive X-ray (EDX) analyses of prepared samples are shown in figure 4(a-b). The EDX analysis of  $ZnO$  sample confirms that the product consists of Zn and O (figure 4a). Also, The EDX analysis of  $V_2O_5$ -doped  $ZnO/SiO_2$  sample confirms the presence of V and Si in the product (figure 4b). These results are consistent with the XRD and FI-IR data.



**Figure 4.** EDX spectra of (a) bare ZnO, and (b) V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> nanoparticles.

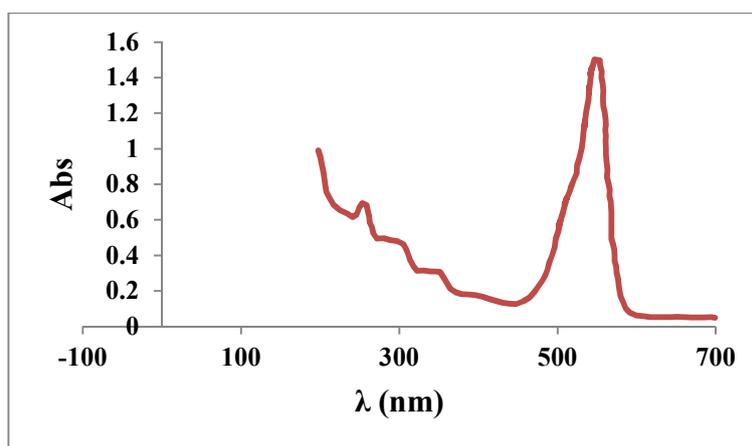
### *Photocatalytic activity*

#### *Degradation of Rhodamine B dye using ZnO/SiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> photocatalysts under UV irradiation*

Rhodamine B dye has three absorption bands at wavelengths of 522, 352, and 224 nm which are related to the transfers of  $\pi \rightarrow \pi^*$  of the aromatic ring induced by N-ethyl groups attached to them, and  $n \rightarrow \sigma^*$  and  $\sigma \rightarrow \sigma^*$  of the aromatic ring, respectively (fig.5). The

mechanism of Rhodamine B dye degradation proceeds through either conjugated structure degradation or diethyl removal. If decrease in the absorption intensity during the reaction is associated with a shift of the absorption peak (522nm) toward shorter wavelengths, the reaction proceeds through diethyl removal. The reason for this shift is the removal of N,N-diethyl chromophore which is an electron donor and its gradual elimination during

degradation results in the absorption range of aromatic system to shift toward shorter wavelengths. If the maximum peak intensity gradually decreases without any shift in the absorption wavelength, the reaction proceeds through the conjugated structure degradation [26].



**Figure 5.** UV-Vis spectrum of Rhodamine B (10ppm).

Figures 6-9 show the degradation of Rhodamine B dye at pH range of 3-6 on ZnO/SiO<sub>2</sub> (0.3 g/L). As seen in the general pattern of the spectra, the absorption amount of Rhodamine B dye on this catalyst is directly related to the pH increment. To justify this increase, it can be noted that the pHzcp of the catalyst is 8.7 and at pH below pHzcp the catalyst surface is positively charged, thus it has more potential to attract negatively charged ions. By increasing pH and its approximation to pHzcp, negative charges are gradually increased on the catalyst surface, and therefore, Rhodamine B dye with an unstable positive charge is better absorbed by the catalyst.

Along with the degradation progress,

decreasing of the maximum peak absorption intensity without any shift in the absorption wavelength can be seen in all UV-Vis absorption spectra shown in the Figs. 6-9. As mentioned earlier, if the maximum peak intensity gradually decreases without any shift in the absorption wavelength, the reaction proceeds through the conjugated structure degradation.

At pH = 5, the peaks are completely removed over two hours. According to the degradation reactions of Rhodamine B in the presence of ZnO/SiO<sub>2</sub> (0.3 g/L) at pH = 3-6, the highest photocatalytic activity of ZnO/SiO<sub>2</sub> was realized at pH = 5.

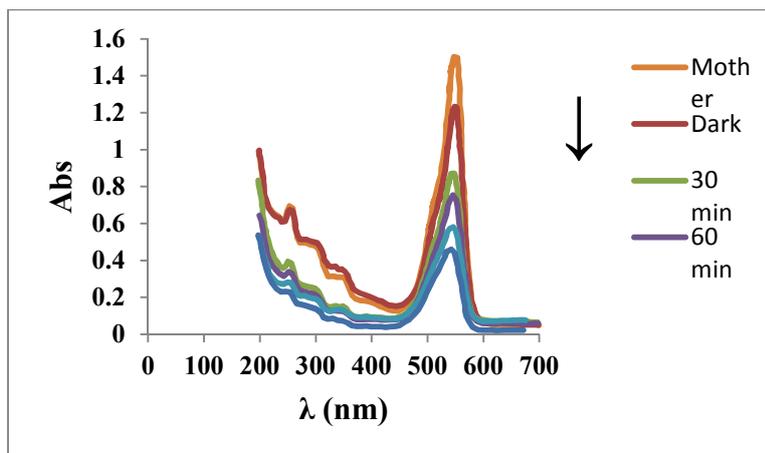


Figure 6. Photodegradation of RB on bare ZnO/SiO<sub>2</sub> photocatalyst at pH=3.

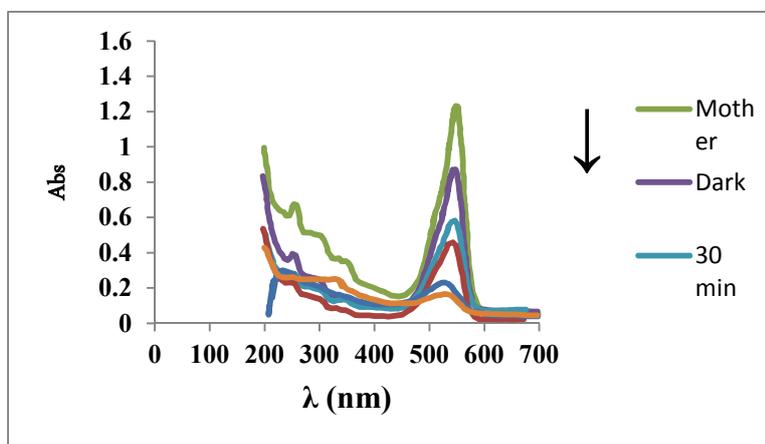


Figure 7. Photodegradation of RB on bare ZnO/SiO<sub>2</sub> photocatalyst at pH=4.

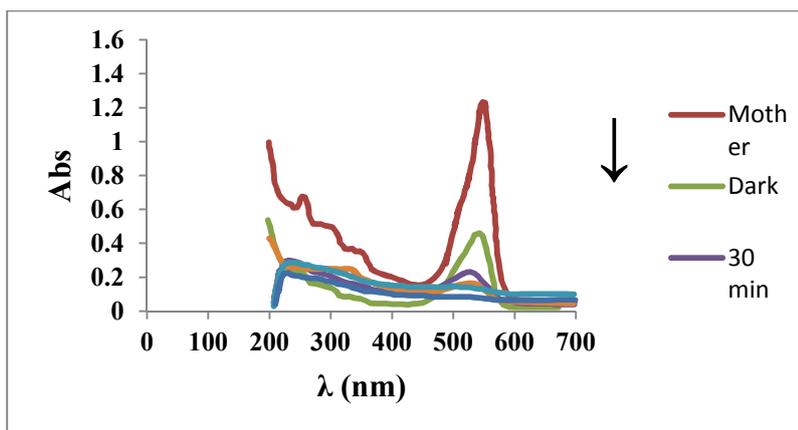
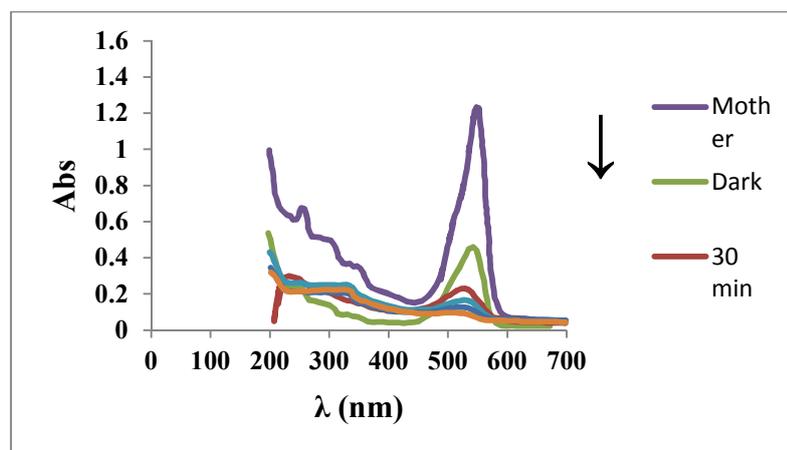


Figure 8. Photodegradation of RB on bare ZnO/SiO<sub>2</sub> photocatalyst at pH=5.



**Figure 9.** Photodegradation of RB on bare ZnO/SiO<sub>2</sub> photocatalyst at pH=6.

The optimum amount of ZnO/SiO<sub>2</sub> and concentration of 10 ppm were obtained 0.3 appropriate pH of the solution for degradation g/L and 5, respectively, (Tables 1 and 2). of 150 ml Rhodamine B dye with a

**Table 1.** The results of photodegradation of RB (%) on ZnO/SiO<sub>2</sub> photocatalyst (0.2, 0.3 and 0.4g/L) at pH=5.

The amount of ZnO/SiO <sub>2</sub> (g/L), pH=5	The degradation of RB (%)
0.2	72.5
0.3	100
0.4	74.3

**Table 2.** The results of photodegradation of RB (%) on ZnO/SiO<sub>2</sub> photocatalyst (0.3 g/L) at pH=3, 4, 5, and 6..

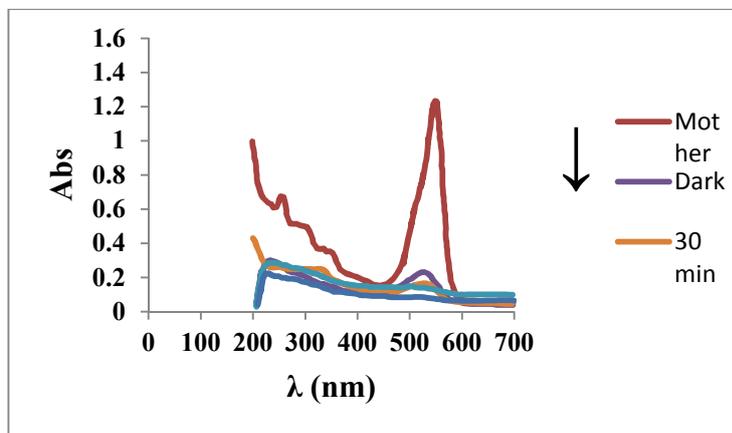
pH (The amount of ZnO/SiO <sub>2</sub> = 0.3 g/L)	The degradation of RB (%)
3	22.4
4	63.3
5	100
6	70.2

Figure 10 shows the variation of Rhodamine B spectrum treated through heterogeneous photocatalysis with 0.3 g/L V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> at pH= 5 (optimal conditions) for 90 minutes. The decreasing of the maximum peak absorption intensity and the variation of dye concentration are quite obvious from the spectra. As seen, the absorption initial amount

of the dye is more in this catalyst than ZnO/SiO<sub>2</sub>, while UV-Vis spectra pattern of both pure and doped catalysts are like each other. Higher dye adsorption of V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> is due to low pHzcp of this catalyst (4.6). In addition, alteration of the dye concentration from spectra shows that the destructive reaction of Rhodamine Bon V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> occurs faster

than ZnO/SiO<sub>2</sub> under UV irradiation. This is due to the presence of vanadium. As we know, doped metal ions affect optical activity through

trapping electrons or holes and altering the reproduction rate of e<sup>-</sup>/h<sup>+</sup> [27].



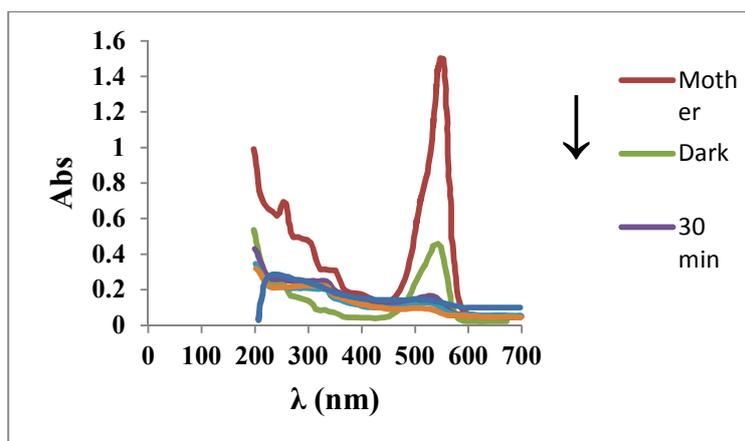
**Figure 10.** Photodegradation of RB on V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> photocatalyst at pH=5.

*Degradation of Rhodamine B dye with ZnO/SiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> photocatalysts under visible light*

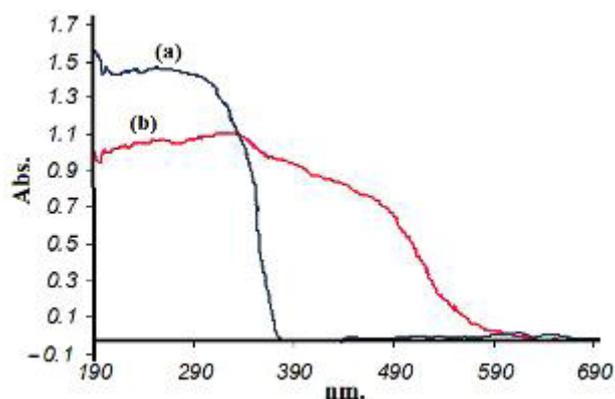
ZnO/SiO<sub>2</sub> has a large band gap and hence is not able to perform photocatalysis reaction in the visible light.

Figure 11 shows changes in the absorption spectra of Rhodamine B by V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> under visible light. As seen in this figure, changes in the absorption spectra of Rhodamine B catalyst by V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> under visible light are similar to the degradation mechanism under UV radiation.

The reaction is continued for about 120 min and Rhodamine Bis completely degraded by V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> under visible light. Given the band gap distance of zinc oxide (3.37 eV), the activity of ZnO/SiO<sub>2</sub> in the visible light is minimal, while doping of V<sub>2</sub>O<sub>5</sub> in ZnO network displaced the band gap toward longer wavelengths (visible light) and increased the photocatalysis activity in the range of visible light. UV-Vis diffuse reflectance spectra of catalysts (fig. 12) confirm the decreasing of V<sub>2</sub>O<sub>5</sub>-ZnO/SiO<sub>2</sub> band gap compared to ZnO/SiO<sub>2</sub>.



**Figure 11.** Photodegradation of RB on  $V_2O_5$ -ZnO/SiO<sub>2</sub> photocatalyst at pH=5 (under visible light).



**Figure 12.** UV-Vis Diffuse Reflectance Spectra of (a) ZnO/SiO<sub>2</sub>, and (b)  $V_2O_5$ -ZnO/SiO<sub>2</sub> nanoparticles.

## Conclusion

ZnO/SiO<sub>2</sub> nanocomposite was prepared using sol-gel method, and vanadium particles were successfully loaded on this nano-photocatalyst by wet incipient method. The results were found that the amount of adsorbed Rhodamine B dye on this catalyst is directly related to the pH increment. The optimum amount of ZnO/SiO<sub>2</sub> and appropriate pH of the solution for degradation of 150 ml Rhodamine B dye with a concentration of 10 ppm were obtained 0.3 g/L and 5, respectively. In optimal conditions,

alteration of the dye concentration from spectra shows that the destructive reaction of Rhodamine B on  $V_2O_5$ -ZnO/SiO<sub>2</sub> occurs faster than ZnO/SiO<sub>2</sub> under UV irradiation. Also, the activity of ZnO/SiO<sub>2</sub> in the visible light is minimal, while doping of  $V_2O_5$  in ZnO network displaced the band gap toward longer wavelengths (visible light) and increased the photocatalysis activity in the range of visible light. The results of the photocatalytic test reveal that  $V_2O_5$ -ZnO/SiO<sub>2</sub> may be an extremely viable adsorbent for application in the treatment of water and

industrial wastewater contaminated with dyes.

### Acknowledgments

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