

Research Article

Photocatalytic Activity of TiO_2 - WO_3 Composites

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TiO_2 - WO_3 photocatalysts were prepared in a vacuum evaporator by impregnation of TiO_2 with WO_3 dissolved in an H_2O_2 solution (30%) and followed by calcination at 400 and 600°C. XRD analyses showed that at 400°C monoclinic phase of WO_3 was dominated whereas at 600°C both monoclinic and regular phases of WO_3 were present. Modification of TiO_2 by WO_3 caused increasing in the absorption of light to the visible range. TiO_2 and photocatalysts modified with low amount of WO_3 (1–5 wt.%) showed high adsorption of Acid Red (AR) on their surface and enhanced photocatalytic activity under UV irradiation. Under visible light irradiation, TiO_2 - WO_3 photocatalysts prepared at 400°C were more active for AR decomposition than those prepared at 600°C suggesting that monoclinic phase of WO_3 is more active under visible light than regular WO_3 . Although TiO_2 - WO_3 photocatalysts appeared to be active under visible light for decomposition of AR, the UV irradiation was more efficient.

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1. Introduction

The photocatalytic process using TiO_2 photocatalyst is very promising for application in the water purification, because many organic compounds can be decomposed and mineralized by the proceeding oxidation and reduction processes on TiO_2 surface. The most commonly tested compounds for decomposition through the photocatalysis are phenols, chlorophenols, pesticides, herbicides, benzenes, alcohols, dyes, pharmaceuticals, humic acids, organic acids, and others [1–3].

TiO_2 is the most commonly used photocatalyst, because it is nontoxic, chemically stable, cheap, and very efficient. However it has some disadvantages, from which one of the most important is a relatively high value of the band gap, around 3.2 eV, which limits its using to the UV light. Therefore nowadays a lot of research work is focused on the preparation of visible light active photocatalysts in order to utilize the solar light more efficiently and stop using UV lamps as a driving force of photocatalytic process, because it consumes a lot of energy.

A lot of works have been done in preparation of anion-doped TiO_2 photocatalysts, such as nitrogen, carbon, and sulphur-doped TiO_2 , which showed the photocatalytic

activity under visible light [4–6]. The other solution is coupling of TiO_2 with semiconductor, which has sensitivity to the visible light. Such semiconductor can be WO_3 , which has a band gap of 2.8 eV and can absorb the light in the visible range. However it also shows high speed of recombination process between generated free carriers. It was reported that by coupling of these two semiconductors, TiO_2 and WO_3 , an efficient charge separation can be achieved which results in enhanced photocatalytic activity of TiO_2 photocatalyst [7–9].

Different methods of preparation of TiO_2/WO_3 photocatalysts were applied, such as sol-gel, ball milling, hydrothermal, sol-precipitation, and impregnation [9–14].

In presented results the preparation of TiO_2 - WO_3 photocatalysts was performed by dissolving of WO_3 in hydrogen peroxide, wet impregnation on the anatase particles, and calcination at 400 and 600°C. The impregnation method was selected for preparation to get well dispersion of tungsten oxide particles on the used TiO_2 material, which as original exhibits high BET surface area, around 300 m²/g. Addition of tungsten oxide before calcination can also retard the phase transformation of anatase to less active rutile. The influence of doping WO_3 to TiO_2 on its photocatalytic activity under UV and visible light irradiations was tested.

2. Preparation of WO₃-TiO₂ Photocatalysts

As a source of TiO₂, a raw material of white TiO₂ was used, which was supported by the Police S.A. Company in Poland. This TiO₂ has BET surface area of 300 m²/g and contains poorly crystalized anatase phase and some nuclei of rutile. WO₃-TiO₂ composites were prepared by mixing of TiO₂ with WO₃ dissolved in an H₂O₂ solution (30%) in a vacuum evaporator at 70 °C for 1 hour. Then the solution was heated up to 100 °C to evaporate the water. The obtained powder was dried in a dryer overnight and then was subjected to calcination at 400 and 600 °C. The amount of WO₃ in the prepared WO₃-TiO₂ samples ranged from 1 to 90 wt.%.

3. Analytical Methods

The phase composition of TiO₂ and WO₃-TiO₂ composites was measured by XRD in X'Pert PRO diffractometer of Philips Company, with CuK α lamp (35 kW, 30 mA). The obtained XRD patterns were compared with (JCPDSs Joint Committee on Powder Diffraction Standards) cards. The morphology of the photocatalysts surface and content of WO₃ in WO₃-TiO₂ composites were evaluated by SEM measurements with EDS analysis. The particle size was measured in Zetasizer Nano ZS of Malvern Company by (DLS Dynamic Light Scattering) method. For measurements photocatalyst samples were suspended in ultra pure water solution with dispersant and were treated with ultrasonic vibrations.

UV-Vis spectra of TiO₂ and WO₃-TiO₂ powders were taken in UV-Vis spectrometer Jasco V-540. These spectra were transformed to Kubelka-Munk equation for indirect semiconductor, and the band gap was calculated.

Hydroxyl radicals were detected by using fluorescence technique. Coumarine can easily react with hydroxyl radicals to form highly fluorescence compound, 7-hydroxycoumarin, which is determined in the Fluorescence Spectrometer Hitachi F-2500. For these measurements the photocatalyst samples were irradiated under UV in the coumarin solution (10⁻³ M), and then the solution after separation from a photocatalyst was taken to analysis. The fluorescence measurements were performed at the excitation wavelength of 332 nm and the emission of 335–600 nm with maximum peak at 460 nm. The detailed procedure has been described elsewhere [15].

For photocatalytic test, azo dye, Acid Red (AR) was decomposed, 30 mg/L AR in 500 mL solution and catalyst loading 0.2 g/L under UV irradiation with UV intensity 154 W/m² and Vis 100 W/m². Experiments of AR decomposition were also performed under fluorescence light irradiation with intensity of Vis = 715 W/m², for that photocatalytic test lower concentration of AR solution was used, 10 mg/L. Fading of AR solution was monitored by UV-Vis spectroscopy.

4. Photocatalytic Activity Test

The photoactivities of prepared samples were tested for decomposition of azo dye Acid Red under irradiation of two different sources: UV and fluorescence lamps. UV was

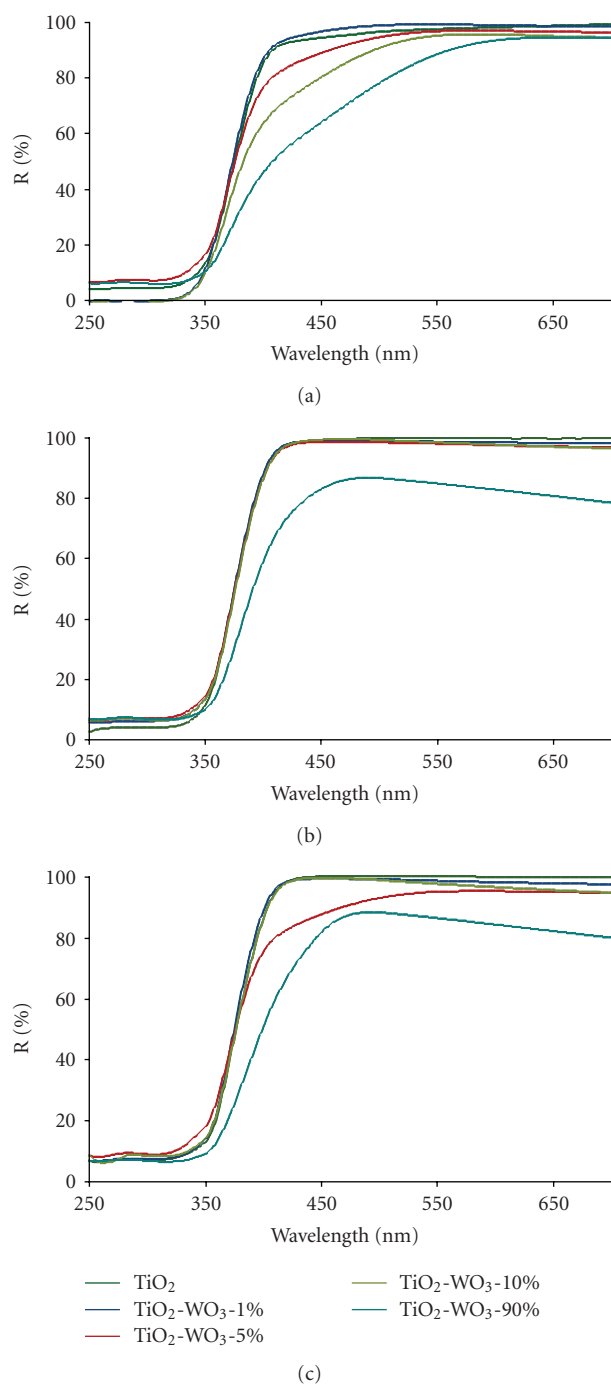


FIGURE 1: Diffuse reflectance spectra of TiO₂ and WO₃-TiO₂ photocatalysts, (a) as received, (b) calcined at 400 °C, and (c) calcined at 600 °C.

emitted from UV six lamps of Philips Company with power of 20 W each. These lamps emit the radiation at UV range of 154 W/m² and at the visible region of about 100 W/m² in the range of 312–553 nm with a maximum at around 350 nm. The fluorescence lamps used as a source of visible light (4 × 18 W) emit light in the visible region with intensity of 715 W/m² and insignificant amount of UV with intensity of 0.22 W/m².

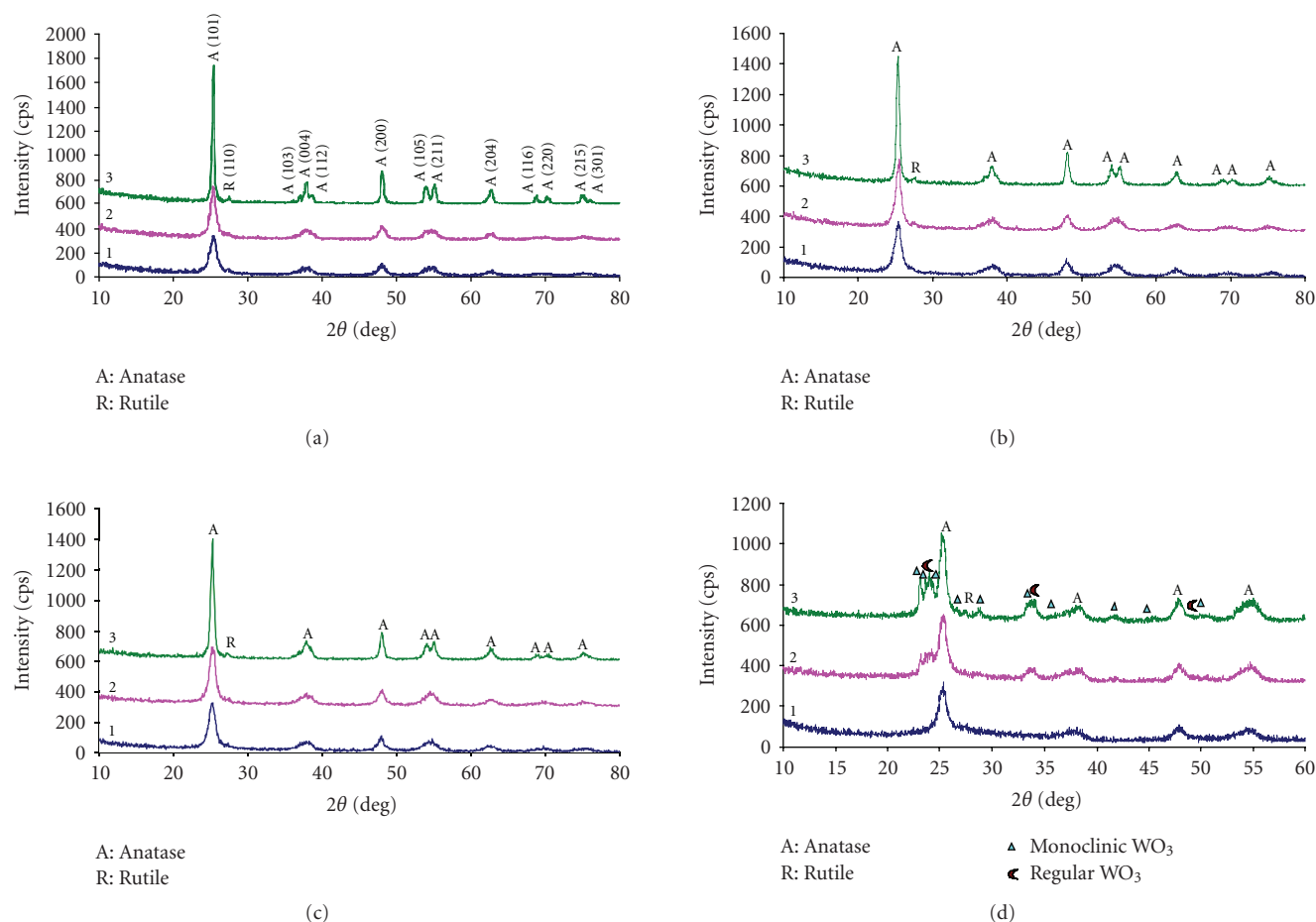


FIGURE 2: XRD patterns of (a) TiO₂, (b) TiO₂-WO₃-3%, (c) TiO₂-WO₃-10%, and (d) TiO₂-WO₃-90% photocatalysts: (1) as received, (2) 400 °C-treated, (3) 600 °C-treated.

Each time, for the photocatalytic test, the beaker with 500 mL of a dye solution of concentrations around 0.03 g/L under UV, and 0.01 g/L under visible light and 0.1 g of photocatalyst was used. The solutions were first magnetically stirred in a dark for 30 minutes in order to estimate the adsorption of dye on the photocatalyst surface and then were irradiated under UV or visible lights from the top of the beaker. The concentration of a dye solution was analyzed in UV-Vis spectrophotometer,

5. Results and Discussion

UV-Vis spectra of measured TiO₂ and WO₃-TiO₂ photocatalysts are shown in Figures 1(a)–1(c).

In general modification of TiO₂ by WO₃ caused increasing the absorption of light to the visible range; however heat treatment caused almost complete reduction of absorption in the range of 400–700 nm, and only a few percentage of light absorption in the range of 500–700 nm could be noticed for modified samples; the exception is WO₃-TiO₂ with doped amount of 5 and 90 wt.%, which exhibited higher absorption of visible light even after heat treatment.

XRD measurements of TiO₂ and WO₃-TiO₂ photocatalysts were performed. Phase WO₃ was difficult to observe in the prepared samples with doping WO₃ less than 50%. In Figure 2 XRD patterns of TiO₂ and TiO₂ with different amounts of doped WO₃ photocatalysts as received and calcined at different temperatures are presented.

Original TiO₂ consists of poorly crystallized anatase phase with insignificant amount of rutile. Heating of anatase-TiO₂ caused narrowing of the diffraction peaks of anatase phase due to the growing of its crystals. The additional reflexes from anatase phase such as 103, 112, 116, 220, 215, and 301 were clearly observed for well crystallized anatase. In case of TiO₂-WO₃-90% photocatalyst monoclinic phase of WO₃ appeared at 400 °C whereas at 600 °C additionally regular WO₃ phase was present.

Doping WO₃ to TiO₂ caused inhibition of growing anatase crystals during heat treatment, and narrowing of the anatase reflex (101) was insignificant, mostly for the samples with doped WO₃ amount up to 3%. Above 3% of doped WO₃ the anatase reflexes 103 and 112 were not observed, and some reflexes as 105 and 211 were not distinguished due to the presence of broad peaks, even after heated at 600 °C.

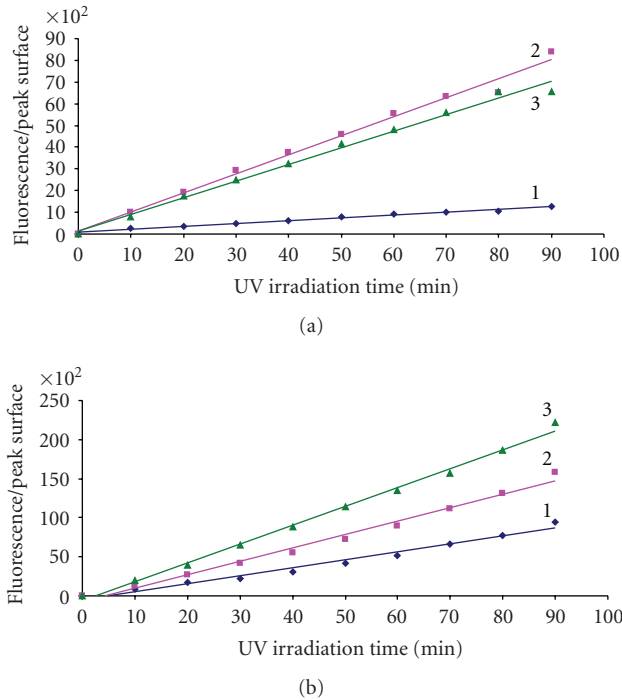


FIGURE 3: OH radicals formation on the photocatalyst surface by the fluorescence measurements of 7-hydroxycoumarine for (a) TiO_2 and (b) $\text{TiO}_2\text{-WO}_3\text{-3\%}$; (1) as received, (2) 400°C -treated, and (3) 600°C -treated.

The exception is TiO_2 with doped amount of WO_3 10%, in which narrowing of anatase 101 reflex was significant, and reflexes 105 and 211 were clearly identified. In this sample probably distribution of WO_3 particles on TiO_2 was not homogeneous.

Photoactivity of TiO_2 and prepared photocatalysts in direction of OH radicals formation was tested by the fluorescence technique. In Figure 3 there are presented results from OH radicals measurements on TiO_2 and $\text{TiO}_2\text{-WO}_3$ photocatalysts during UV irradiation.

The linear correlation of OH radicals formation from the irradiation time can be noticed. Doping WO_3 to TiO_2 and higher calcination temperature caused increasing in the amount of OH radicals formation. This tendency was observed for modified samples with doping WO_3 up to 3%; for higher amount of doped WO_3 the photocatalysts heat treated at 400°C showed higher amount of OH radicals formation than those as received and calcined at 600°C . The highest photoactivity toward OH radicals formation was noted for $\text{TiO}_2\text{-WO}_3\text{-3\%}$ heat treated at 600°C . In Figure 4 OH radicals formation on the photocatalysts under visible light are presented.

OH radicals formation under visible light was much lower than under UV, when we compare Figures 3 and 4, but again TiO_2 doped with WO_3 showed higher amount of OH radicals formation than TiO_2 . From Figure 4 it can be seen that $\text{TiO}_2\text{-WO}_3\text{-10\%}$ heat treated at 400°C was much more photoactive than heat treated at 600°C and no calcinated one. The same tendency was kept for the other photocatalysts

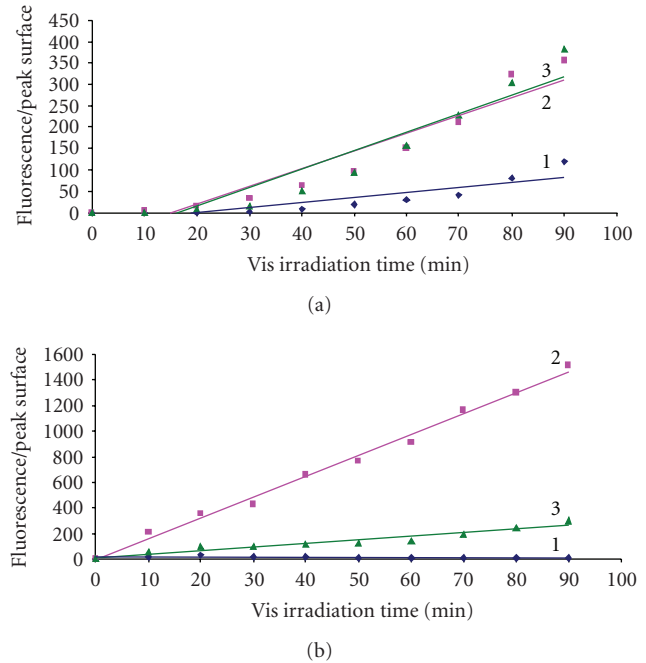


FIGURE 4: OH radicals formation on the photocatalyst surface by the fluorescence measurements of 7-hydroxycoumarine for (a) TiO_2 , (b) $\text{TiO}_2\text{-WO}_3\text{-10\%}$; (1) as received, (2) 400°C -treated, (3) 600°C -treated.

with doping WO_3 from 5%–90%. The highest OH radicals formation under visible light was obtained on the $\text{TiO}_2\text{-WO}_3$ photocatalyst with doping amount of 10% heat treated at 400°C . However this sample did not show significant absorption of light in the visible range; coupling of WO_3 and TiO_2 could occur at small amount of visible light absorption by WO_3 and absorption of UV light by TiO_2 , even although the energy of UV light was insignificant. TiO_2 with 90% of doped WO_3 showed much higher absorption of visible light than the other samples with lower content of WO_3 but had low activity under visible light. It is concluded that TiO_2 activity is much more powerful than WO_3 in generation of OH radicals, and WO_3 can serve as a support in OH radicals formation by transfer electrons to the conductive band of TiO_2 under visible light or can retard the recombination reaction occurring in TiO_2 .

The influence of doping WO_3 to TiO_2 on the particles size of photocatalysts was measured. The results from the measurements of particles size of TiO_2 and $\text{TiO}_2\text{-WO}_3$ samples are listed in Table 1.

In general particles size of WO_3 doped TiO_2 photocatalysts were lower than TiO_2 . Calcination caused growing of crystals, and so some heat-treated samples exhibited higher size of particles than those as received ones.

The structure of photocatalysts and particles size were observed on SEM photos. For comparison SEM of not modified TiO_2 and $\text{TiO}_2\text{-WO}_3\text{-3\%}$ calcinated at 600°C are presented in Figure 5.

Some agglomerates of primary particles of TiO_2 can be seen with size over $1\ \mu\text{m}$ in Figure 5(a) whereas TiO_2 doped with WO_3 comprises of much smaller particles.

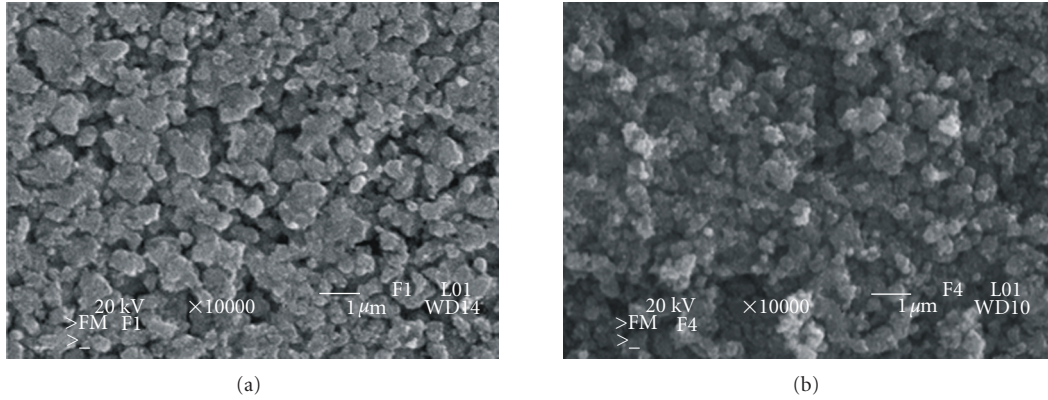
FIGURE 5: SEM of (a) TiO_2 and (b) $\text{TiO}_2\text{-WO}_3\text{-3\%}$ heat treated at 600°C .

TABLE 1: Particles size of photocatalysts measured by DLS method.

Sample	Particles size [nm]							
Amount of doped WO_3 (%)	0	1	3	5	10	30	50	90
As received	365	444	355	365	172	190	174	185
400°C -treated	369	380	367	373	222	178	199	175
600°C -treated	402	369	400	415	201	207	205	192

TABLE 2: Adsorption of AR on the photocatalysts surface.

Photocatalyst	Adsorption of acid red/%					
	Heat treatment temperature/ $^\circ\text{C}$					
	30		400		600	
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
TiO_2	19.8	21.5	14.8	26.9	2.0	14.1
$\text{TiO}_2\text{-WO}_3\text{-1\%}$	28	36.5	16.8	32.5	3.7	14.6
$\text{TiO}_2\text{-WO}_3\text{-3\%}$	15.8	38.4	7.8	16.7	—	—
$\text{TiO}_2\text{-WO}_3\text{-5\%}$	14.1	12.6	15.2	20.5	15.9	21.3
$\text{TiO}_2\text{-WO}_3\text{-10\%}$	0	1	2.8	5.8	0	0
$\text{TiO}_2\text{-WO}_3\text{-30\%}$	0	0	0	0	0	0.5
$\text{TiO}_2\text{-WO}_3\text{-50\%}$	0	0	0	0	0	0
$\text{TiO}_2\text{-WO}_3\text{-90\%}$	0	0	0	0	0	0

Both measurements, DLS and SEM, showed that doping WO_3 to TiO_2 cause, reduction of its particles size, mostly because of reducing tendency of TiO_2 particles to form agglomerates. Smaller particle size of $\text{TiO}_2\text{-WO}_3$ composites in comparison to TiO_2 prepared by the sol-gel method was also reported by Li et al. [7].

From EDS analysis the measured amount of Ti was 93 wt.%, W – 6 wt.%, and S – 1 wt.%. Sulphur came from the production process of TiO_2 .

Photocatalytic activity of prepared samples was tested for Acid Red decomposition under UV and visible light irradiations. Preliminary adsorption of this dye on the photocatalysts surface was performed. The results from the adsorption measurements are presented in Table 2. The

initial concentrations of AR used in case of UV and Vis radiations were 30 and 10 mg/L, respectively.

Noncalcined samples of TiO_2 and TiO_2 doped with low amount of WO_3 up to 5% showed quantitatively adsorption of AR on their surface, which generally was decreasing with heat treatment temperature; only $\text{TiO}_2\text{-WO}_3$ photocatalyst with doping amount of 5% showed opposite tendency, that is increased adsorption of AR after heat treatment.

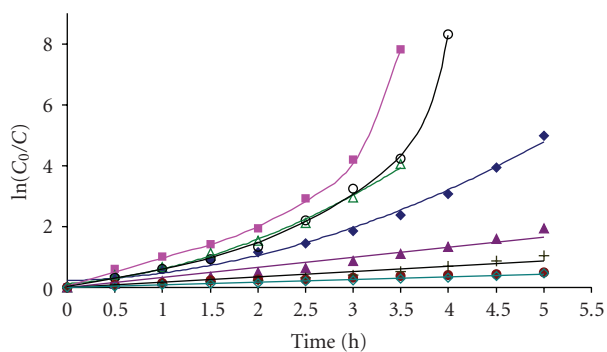
After adsorption, these photocatalysts were submitted to UV and Vis radiations. The results from the measurements are presented in Figures 6 and 7.

Photocatalysts which exhibited high adsorption of AR on their surface showed no linear correlation of $\ln(C_0/C)$ from time of irradiation during AR decomposition. The high acceleration of AR decomposition with time of irradiation on these photocatalysts could be caused by occurring sensitized photocatalysis. Therefore doping WO_3 to TiO_2 , which caused their increased absorption of light to the visible range and high adsorption of AR, appeared to be beneficial for decomposition of AR, as it can be seen especially in case of noncalcined samples used under UV irradiation and $\text{TiO}_2\text{-WO}_3\text{-5\%}$ heat treated at 600°C used under visible light. Although both TiO_2 and $\text{TiO}_2\text{-WO}_3$ photocatalysts were active under visible light irradiation, UV light was more powerful in AR degradation.

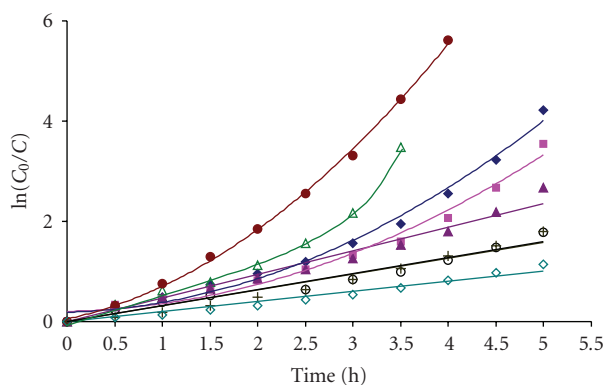
Under visible light irradiation $\text{WO}_3\text{-TiO}_2$ photocatalysts prepared at 400°C were more active for AR decomposition than those prepared at 600°C and noncalcined one.

6. Conclusions

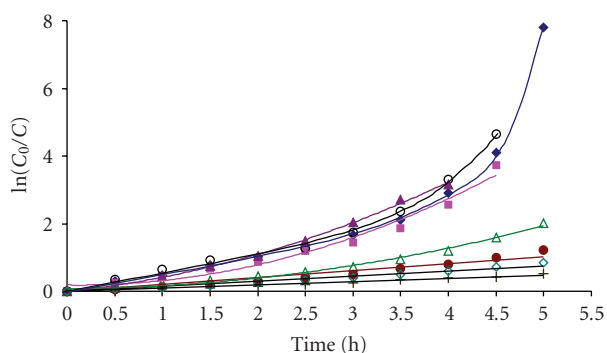
Doping WO_3 to TiO_2 caused increasing its absorption of light to the visible range; however it was observed mostly for noncalcined samples. Although OH radicals formation on prepared $\text{TiO}_2\text{-WO}_3$ photocatalysts was higher than on TiO_2 it was not a key factor affecting the rate of AR decomposition. Both high adsorption of AR on the photocatalyst surface and their ability to absorption of visible light were responsible for the photocatalytic properties of photocatalysts, and therefore the $\text{TiO}_2\text{-WO}_3$ photocatalysts with low amount of WO_3 (1–5 wt.%) were more active than the others. Doping WO_3 to



(a)



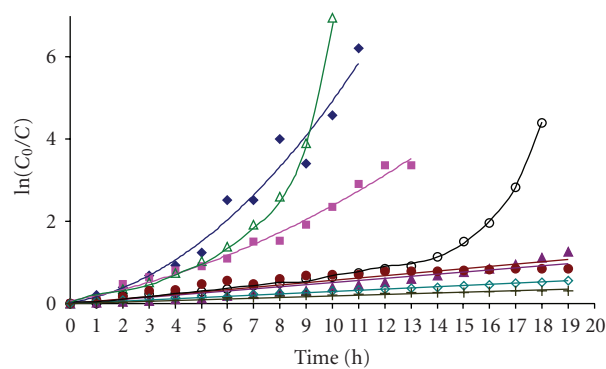
(b)



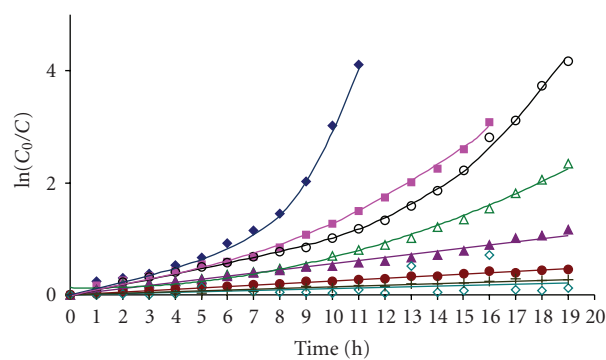
(c)

FIGURE 6: AR decomposition under UV irradiation on TiO_2 and $\text{TiO}_2\text{-WO}_3$ photocatalysts, (a) as received, (b) 400°C -treated, and (c) 600°C -treated.

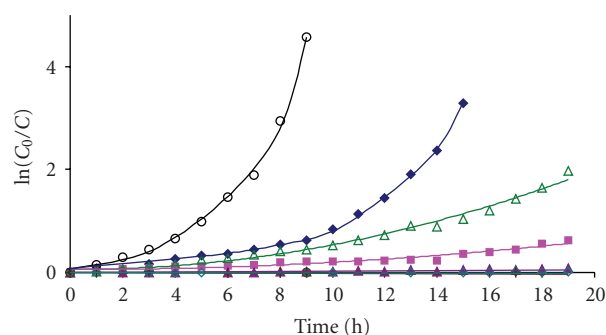
TiO_2 caused also reduction of its particles size, which could improve ability of TiO_2 for dispersion in water and increase the accessible surface for adsorbates. Under visible light irradiation $\text{WO}_3\text{-TiO}_2$ photocatalysts prepared at 400°C were more active for AR decomposition than those prepared at 600°C suggesting that monoclinic phase of WO_3 is more active under visible light than regular WO_3 . Although the photocatalysts were active under both UV and visible light



(a)



(b)



(c)

FIGURE 7: AR decomposition under Vis irradiation on TiO_2 and $\text{TiO}_2\text{-WO}_3$ photocatalysts, (a) as received, (b) 400°C -treated, and (c) 600°C -treated.

irradiations, UV light was more powerful for decomposition of AR than visible light, but the latter had important meaning during occurring sensitized photocatalysis.

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