Synthesis and characterization of SiO_2/Bi_2WO_6 based on biogenic silica synthesized by sol-gel method

Olga D. Arefieva[1,2], *Marina S.* Vasilyeva[1,2], *Praskovya I.* Mitkina[1,2*], *Aleksandra I.* Slavenskaya[1], and *Valery G.* Kuryavy[2]

[1]Far Eastern Federal University, Vladivostok, Russian Federation
[2]Institute of Chemistry, Far-Eastern Branch, Russian Academy of Sciences, Vladivostok, Russian Federation

Abstract. SiO_2/Bi_2WO_6 photocatalyst with Si/Bi/W=1:2:1 molar ratio was obtained by the sol-gel method from bismuth nitrate, sodium tungstate and biogenic silica from rice husk biomass followed by calcination. Bi_2WO_6 was used as a control sample. FT-IR, SEM, XRD, EDXRF, UV-Vis methods were used to systematically characterize the as-obtained materials. Photodegradation of Indigo Carmine in exposure to UV, sunlight and xenon light was studied to evaluate their photocatalytic activities in the presence of SiO_2/Bi_2WO_6 and Bi_2WO_6. It was shown that the degradation degree of Indigo Carmine in the presence of SiO_2/Bi_2WO_6 under the action of UV irradiation and sunlight reaches 36% and 14%, respectively. The SiO_2/Bi_2WO_6 sample is stable during photocatalytic studies.

1 Introduction

Today, heterogeneous photocatalysis is considered a promising method of wastewater treatment from pollutants of various nature [1]. One of the most difficult tasks of heterogeneous photocatalysis is to develop new semiconductor materials sensitive to visible light. Bismuth-based materials, in particular Bi_2WO_6, are attractive study objects due to their structural features and a number of unique properties [2]: narrow band gap, high stability, and low toxicity [3]. It should be noted that many of Bi_2WO_6 physical characteristics (surface area, morphology, particle size, crystallinity) and hence its photoactivity can be improved using porous matrices such as silica. Silica matrices increase the specific surface area, mechanical strength, thermal stability [4], and photocorrosion resistance of photoactive substances. Also, the properties depend on the method of Bi_2WO_6 synthesis. Among the proposed obtainment methods (hydrothermal, solvothermal, microwave, solid-phase, etc.), the sol-gel method is the most accessible, since it does not require high energy costs and the use of additional equipment, while allowing fine control of the physical and chemical parameters of the material [5].

* Corresponding author: mitkina.pi@students.dvfu.ru

At present, the use of organomineral silicon-containing compounds for the synthesis of photocatalysts based on amorphous silicon dioxide has been widely studied [6]. The use of biogenic silicon dioxide is promising, since it is not only environmentally friendly, but also an economically viable alternative precursor for obtaining silica matrix [7]. Main raw material for obtaining biogenic silica is rice production waste (rice husk and straw) [8] due to a high content of silicon dioxide. However, this use of biogenic silica is poorly studied, therefore, the purpose of this work is to obtain SiO_2/Bi_2WO_6 photocatalysts by the sol-gel method using biogenic silica; to study composition, structure, and photocatalytic activity in degradation reaction of Indigo Carmine under various irradiation conditions.

2 Experimental methods

2.1 Chemicals

For preparation of photocatalysts we used $Bi(NO_3)_3 \cdot 5H_2O$, $Na_2WO_4 \cdot 2H_2O$, SiO_2, HNO_3, NaOH; photocatalytic activity was studied using Indigo Carmine (InC) solution prepared from chemicals of an analytical grade.

2.2 Photocatalysts synthesis procedure

In this work, photocatalyst (Si-Bi-W) sample with Si/Bi/W=1:2:1 molar ratio was synthesized by the sol gel using biogenic silica from rice husk, followed by calcination at 500°C for 4 hours.

Biogenic amorphous silicon dioxide was prepared from the rice husk of the Dolinny variety of the Far Eastern selection, created at the A.K. Chaika Federal Research Center of Agrobiotechnologies of the Far East (Ussuriysk, Russia). Biogenic silica (the content of the main substance is ~99%) was obtained from the rice husk according to the method [9].

Husk sample was meshed (~8 mesh) to remove tiny fractions (bran siftings, dust). Then, raw materials were washed in distilled water and air-dried. Raw materials were hydrolyzed by 1 mol L^{-1} hydrochloric acid when heated to 90°C within an hour in laboratory reactor. Temperature was controlled using EKT Hei Con thermocouple (Heidolph, Germany). Mass ratio of solid to liquid was 1:13.

Fixed residue was filtered through synthetic fabric with pore size 15 μm, repeatedly washed with distilled water and air dried at t = 25°C for 48 hours. Then, oxidative roasting was performed in the WiseTherm muffle furnace (DAIHAN, South Korea) at 600°C during 3 h. As the result, amorphous silicon dioxide was obtained. The resulting silica was a white powdery material.

Bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$) was dissolved by heating in a minimum volume of concentrated nitric acid, amorphous silicon dioxide and sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) – in 1 mol L^{-1} sodium hydroxide solution at 60°C to obtain sodium orthosilicate solution. Further, dissolved bismuth nitrate was added into an alkaline solution containing silicon dioxide and sodium tungstate under constant stirring. Sol was formed while stirring, which led to a white gel formation during a pH transition. The resulting gel was left to age in a mother liquor for 24 hours. The solid precipitate was filtered, washed with distilled water until a negative reaction to chloride ions and then dried at a temperature of 25°C for 48 hours. The resulting powder was calcined in the WiseTherm muffle furnace (DAIHAN, South Korea) to 500°C for 4 hours.

For the synthesis of the control sample (Bi-W), the same procedure was performed without adding biogenic silica.

2.3 Characterization of the prepared photocatalysts

Elemental analysis of the photocatalysts samples was performed by energy-dispersive X ray fluorescence analysis (EDXRF) on the EDX 800 HS spectrometer (Shimadzu, Japan).

To determine functional groups in the studied samples, IR absorption spectra was recorded within the range 400-4000 cm^{-1} in potassium bromide on the Vertex 70 Fourier-transform spectrometer (Bruker, Germany).

X-ray powder diffraction analysis (XRD) of the samples was performed in CuK_α radiation on the D8 Advance diffractometer (Bruker, Germany).

Morphology of the surface of catalysts was studied using the scanning electron microscope (SEM) at a high resolution S 5500 (Hitachi, Japan).

The content of bismuth and tungsten in the solution after photocatalytic degradation of Indigo Carmine was determined by atomic absorption spectrometry on the SOLAR M6 double-beam spectrometer (Thermo, USA).

2.4 Procedure for the photocatalytic degradation Indigo Carmine

Photocatalytic properties of the obtained samples were evaluated by example of InC degradation reaction under UV, sunlight (SL), and xenon (Xe) irradiation. InC concentration in in all experiments was 16 $mg \cdot L^{-1}$. Catalyst loading was 1 g per 1 L of dye solution. The solution was irradiated at constant magnetic stirring (625 rpm) for 3 h.

Photocatalytic degradation in UV region was conducted in 100 mL quartz cell filled with 50 mL of InC solution. Radiation source was 100P/F UV lamp (radiation maximum is λ = 365 nm).

The sunlight and xenon degradation of InC solution was carried out in a simple reactor. The reactor was a simple laboratory glass bottle of 100 mL capacity. The sunligh degradation was carried out at the same conditions on sunny days between 9 a.m. and 4 p.m. in April for 3 hours. All experiments were carried out within almost the same days.

The source of xenon light was a lamp of 35 W power and a color temperature of 6000 K.

Absorbtion of InC solution was determined by a photocolorimetric method on the UNICO-1201 spectrophotometer (United Products & Instruments Inc., USA) at a wavelength 610 nm. Degradation degree of InC (χ, %) was determined by a formula:

$$\chi = \frac{A_0 - A}{A_0} \cdot 100\%, \quad (1)$$

where A_0 and A are absorbtions of InC solution before and after photodegradation.

3 Results and discussion

3.1 Sample characteristics

Table 1 presents the results of X-ray fluorescence analysis of the photocatalyst samples converted to oxides. Si-Bi-W sample contains a smaller amount of Bi_2O_3 and WO_3 compared to Bi-W sample due to the introduction of silica into it.

Table 1. Chemical composition of the as-obtained photocatalysts (wt.%)

Sample	SiO_2	Bi_2O_3	WO_3	Fe_2O_3
Bi-W	-	53.50	46.35	0.15
Si-Bi-W	21.77	45.97	32.13	0.12

Absorption band is observed at and 1096 cm^{-1} in the IR spectrum of Si-Bi-W correspond to valence asymmetric vibrations of Si-O-Si siloxane bonds. Both studied samples have an absorption band at 561-571 cm^{-1} which is characteristic of the Bi-O bond, and an absorption band at 743-745 cm^{-1}, corresponding to the W-O bond in Bi_2WO_6 (Fig. 1).

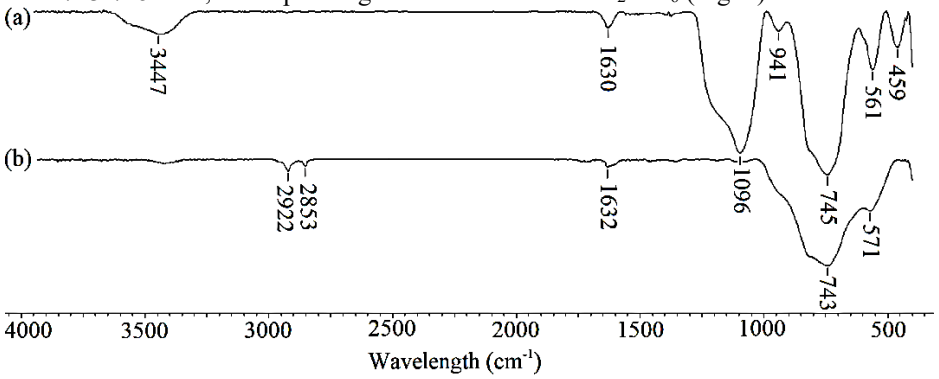

Fig. 1. FT-IR spectra of the as-obtained photocatalysts: a – Bi-W, b – Si-Bi-W

According to the data of X-ray phase analysis, all samples are in the amorphous-crystalline state (Table 2). Bi-W and Si-Bi-W contain photoactive orthorhombic Bi_2WO_6. In addition, the sample synthesized without the addition of silica Bi-W contains monoclinic WO_3.

Table 2. Phase composition of the as-obtained photocatalysts

Sample	Phase state	XRD data
Bi-W	Amorphous-crystalline	Bi_2WO_6 (orthorhombic), WO_3 (monoclinic)
Si-Bi-W	Amorphous-crystalline	Bi_2WO_6 (orthorhombic)

The samples have a porous homogeneous surface, which is presented in the form of many microplates with clear boundaries (Fig. 2).

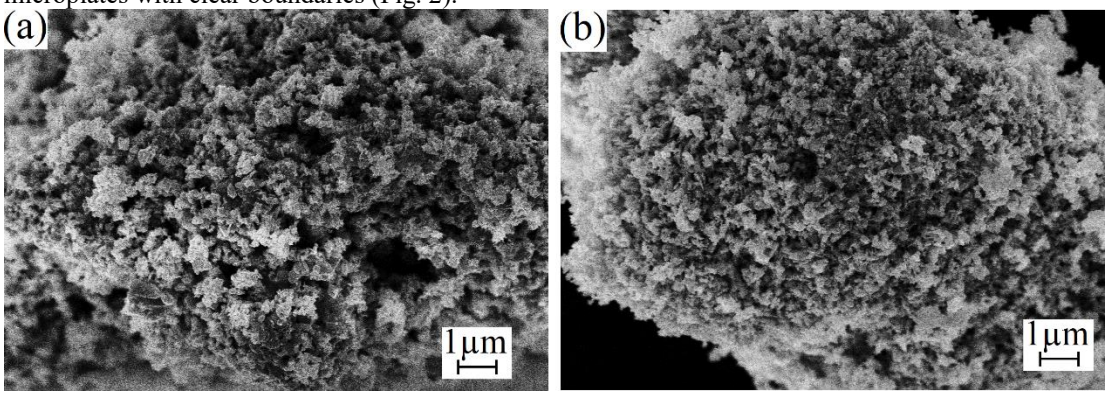

Fig. 2. SEM images of the as-obtained photocatalysts: a – Bi-W, b – Si-Bi-W

3.2 Photodegradation of Indigo Carmine

Photocatalytic activity of the samples was evaluated in the reaction of InC degradation under UV, xenon light, and sunlight irradiation. Experiments carried out without the use of catalysts showed that regardless of the method of irradiation, degradation of the dye does not occur.

The results of photocatalytic tests of the samples exposed to UV light are shown in Fig. 3.

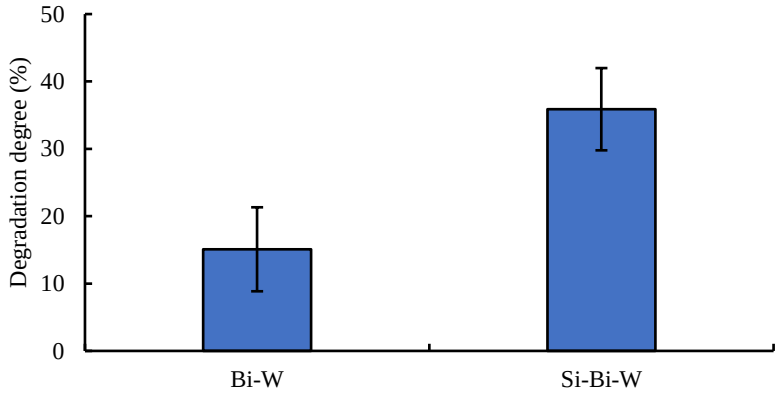

Fig. 3. Indigo Carmine degradation degree in the presence of the as-obtained photocatalysts in exposure to UV light

Fig. 3 shows that the sample Si-Bi-W synthesized with the addition of silica has a higher InC degradation efficiency value (~36%) compared to the control Bi-W sample (15%). Since Si-Bi-W sample showed higher values of χ in the degradation reaction of InC at UV irradiation, its photoactivity was studied under conditions of irradiation with xenon light and sunlight (Fig. 4).

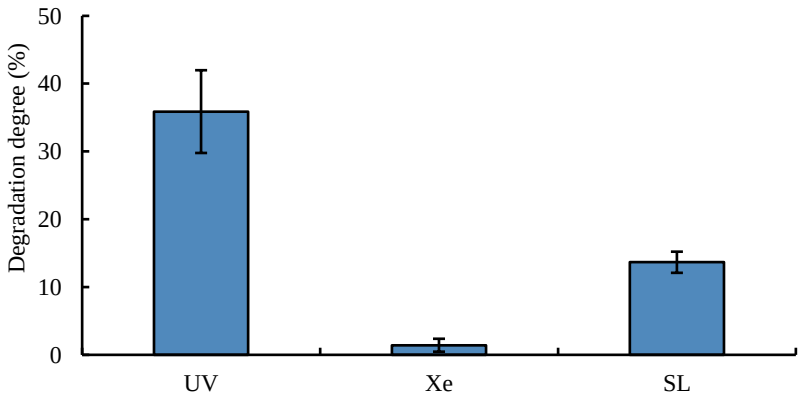

Fig. 4. Indigo Carmine degradation degree in the presence of Si-Bi-W in exposure to UV, sunlight and xenon light

The results of the study showed that in the presence of Si-Bi-W sample, when irradiated with xenon light, the degradation of the dye practically does not occur (~2%), in sunlight the value of χ reaches 14%.

In order to assess the stability of Si-Bi-W sample, the content of bismuth and tungsten in the InC solution after photocatalytic degradation was determined (Table 3).

Table 3. The content of bismuth and tungsten in the solution after photocatalytic degradation of Indigo Carmine in the presence of Si-Bi-W under various types of irradiation

Bismuth(III) content, mg·L^{-1}	**Tungsten(VI) content, mg·L^{-1}**
UV	
4.98	<5
SL	
7.50	12.17
Xe	
1.99	17.24

The content of bismuth(III) in the solutions is in the range from 2 to 7.5 mg·L^{-1}, and tungsten(VI), basically, does not exceed 5 mg·L^{-1} (Table 3).

4 Conclusions

The photocatalytically active material SiO_2/Bi_2WO_6 with the molar ratio Si/Bi/W=1:2:1 was obtained by the sol-gel method. Biogenic amorphous silicon dioxide from rice husk was used as a source of silica. Control Bi_2WO_6 sample was synthesized by a similar method. According to the results of SEM analysis, photocatalysts have a developed porous homogeneous surface.

It was established that the as-obtained samples are a photocatalytically active in the degradation reaction of Indigo Carmine upon irradiation with UV light. The degradation degree of Indigo Carmine in the presence of SiO_2/Bi_2WO_6 and control Bi_2WO_6 under the action of UV irradiation reaches 36% and 15%, respectively. In addition, sample SiO_2/Bi_2WO_6, unlike sample Bi_2WO_6, is photoactive when exposed to sunlight.

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