Mechanochemical synthesis, characterization and photocatalytic properties of Bi_2WO_6/SiO_2 modified biogenic silica

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Introduction

Heterogeneous photocatalysis is considered as a promising technology for industrial wastewater treatment due to its low cost, environmentally friendly process and the absence of secondary pollution [1].

Bi_2WO_6 photocatalyst is actively investigated due to its low toxicity, narrow bandgap (2.8 eV) and simple methods of production [2]. Modification of Bi_2WO_6 with amorphous silicon dioxide makes it possible to change the morphology of the surface, which affects the photocatalytic activity of the sample [3].

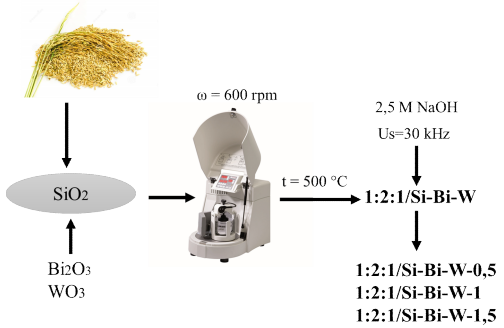
The purpose of this work is to obtain a Bi_2WO_6/SiO_2 photocatalyst modified with biogenic silica by mechanochemical activation and to study its photocatalytic activity.

Experiment

To obtain the Bi_2WO_6/SiO_2 sample, Bi_2O_3 (analytical grade), WO_3 (analytical grade), and SiO2 were mixed in a molar ratio of 1:2:1. Samples of amorphous silicon dioxide were obtained from the husks of "Dolinnyi" rice (Primorsky Krai, Timiryazevsky settlement, Russia), by oxidative firing with pretreatment with 0.1 M hydrochloric acid solution [4].

Photocatalyst Bi_2WO_6/SiO_2 was synthesized by mechanochemical activation followed by firing. Mechanochemical processing was carried out at the planetary mill "Pulverisette 6" (Fritsch, Germany) with 35 balls with a diameter of 8 mm with a rotation speed of 600 rpm for 20 minutes. The activated mixture was calcined for 2 hours at 500°C in a muffle furnace (WiseTherm, South Korea).

The optical density of indigo carmine solution was determined by photocolorimetric method on a UNICO-1201 spectrophotometer (United Products & Instruments Inc., USA) at wavelength 610 nm.



Results and discussions

The results of X-ray fluorescence analysis showed that the Bi_2WO_6/SiO_2 sample contains 75% Bi_2O_3, 15% WO_3 and 9% SiO_2. According to the data of X-ray phase analysis, the photocatalyst is in an amorphous-crystalline state have been identified in the crystalline phase orthorhombic γ-Bi_2WO_6, tetragonal $Bi_{14}W_2O_{27}$, cubic $Bi_{12}W_{0.10}O_{18.3+x}$ and cubic δ-WO_3. It should be noted that, in general, there are reflections of γ-Bi_2WO_6, which has the highest photoactivity.

In the IR spectrum of Bi_2WO_6/SiO_2, the absorption bands at 1101 cm^{-1} and 475 cm^{-1} correspond to asymmetric and bending vibrations of the Si–O–Si bond in amorphous silicon dioxide. Absorption band at 1389cm^{-1}, characteristic of the Bi-O bond in bismuth tungstate. In the spectrum of the sample, the absorption bands at 810 and 733 cm^{-1} correspond to the WO and W-O-W bonds in Bi_2WO_6. There is also an absorption band at about 847 cm^{-1}, which indicates the formation of a Bi-O-Si bond. Bands at 3435 and 1634 cm^{-1} correspond to stretching and bending vibrations of OH groups. This result confirms the formation of Bi_2WO_6.

On fig. 1 shows SEM images of photocatalysts. The Bi_2WO_6/SiO_2 sample has a smooth structure. After etching, the Bi_2WO_6/SiO_2-1 sample becomes looser. Coral branches appear in the structure.

Table 1 shows that after etching of the initial Bi_2WO_6/SiO_2 sample, the photoactivity increases within 5% and ranges from 11.5 to 13.5%. It should be noted that the etching time does not affect the photoactivity of the sample.

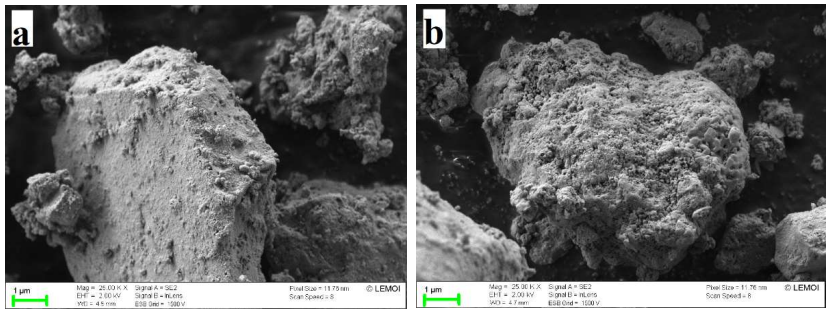


Fig. 1. SEM images of photocatalysts:
a - Bi_2WO_6/SiO_2;
b - Bi_2WO_6/SiO_2-1

The results of photocatalytic tests of the initial Bi_2WO_6/SiO_2 and etched samples under UV light irradiation in the indigocarmine degradation reaction are shown in table 1.

Table 1. The degree of decomposition of indigocarmine under UV light irradiation

Sample	χ, %
Bi_2WO_6/SiO_2	8,5
Bi_2WO_6/SiO_2-0,5	13,0
Bi_2WO_6/SiO_2-1	13,5
$Bi_2WO_6/SiO_2$1,5	11,5

Conclusions

The Bi_2WO_6/SiO_2 photocatalyst modified with biogenic silica from rice husks was obtained by mechanochemical activation. X-ray phase analysis established that the sample contains the photoactive phase γ-Bi_2WO_6. The Bi_2WO_6/SiO_2 was etched with 2.5 M NaOH aqueous solution for 0.5;1;1.5 hours. It is shown that, after sample etching, the photocatalytic activity increases by ~5%.

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