THE MINISTRY OF EDUCATION AND SCIENCE OF THE RUSSIAN FEDERATION
NATIONAL RESEARCH TOMSK STATE UNIVERSITY

CATALYSIS: FROM SCIENCE TO INDUSTRY

Proceedings of
VII International scientific school-conference for young scientists

October 11-15, 2022

Tomsk 2022

Photocatalysts based on $Bi_{12}SiO_{20}$ for water purification from organic pollutants

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Pollution of industrial wastewater with difficult-to-oxidize compounds (phenol derivatives, dyes, antibiotics) has a negative impact on the environmental situation. In recent years, photocatalytic water purification methods have attracted increasing attention due to the ability to decompose organic compounds into harmless H_2O and CO_2 molecules. Bismuth silicates (BSO) [1, 2], in particular bismuth sillenite $Bi_{12}SiO_{20}$ [3], are considered a promising semiconductor photocatalysts. In the main, BSO is obtained by chemical synthesis methods that require the use of high temperatures and pressures during synthesis, as well as additional precursors. In this work, semiconductor nanoparticles (NPs) based on $Bi_{12}SiO_{20}$ with high photocatalytic activity were synthesized via pulsed laser ablation (PLA) in water.

The synthesis of BSO was carried out according to the technique described in [1]. The resulting powders were annealed at temperatures at 400 °C and 600 °C. The initial BSO_ini sample consists of metallic Bi and bismuth carbonate $Bi_2(CO_3)O_2$. Upon annealing at 400°C, the β-Bi_2O_3 and $Bi_{12}SiO_{20}$ phases form in the BSO_ini_400 sample. After laser treatment, the $Bi_{12}SiO_{20}$ phase, as well as $Bi_2(CO_3)O_2$, is formed in the initial sample without annealing BSO_hν. Annealing at 400°C leads to an increase in the percentage of the $Bi_{12}SiO_{20}$ phase from 26 to 77%. The samples after annealing at 600 °C are represented by the $Bi_{12}SiO_{20}$ phase with a small impurity (~2%) of the Bi_2SiO_5 phase. According to UV-vis spectroscopy, all samples (besides for BSO_ini) have the edge of the exciton absorption band in the visible region of the spectrum.

Photocatalytic (PC) activity was measured by the decomposition of Rhodamine B (5 μM), Phenol (50 μM) and Vancomycin (0.17 mM) under irradiation with a LED with λ = 375 nm (51 mW). The reaction rate constant was calculated taking into account the concentration of organic compound in units of [$\mu M \times h^{-1}$]. When evaluating the photodecomposition of Rhodamine B, the rate constants of K_N diethylation (from the decrease in optical density at 553 nm) and K_{app} decomposition (from the decrease in optical density at the absorption maximum) of the dye were calculated. When evaluating the PC activity of Phenol, the reaction rate was estimated from a decrease in the luminescence intensity. The decomposition of the initial Vancomycin molecule was determined by the relative decrease in the absorption band of aromatic fragments of the molecule at 280 nm.

During the decomposition of Rhodamine B, the samples after annealing at 600 °C showed the highest PC activity – K_N was 25.5 and 12.0 $\mu M \times h^{-1}$ for BSO_ini_600 and BSO_hν_600, respectively. In addition, it was found that laser treatment of the colloid leads to stability of the photocatalyst for 10 or more cycles. Samples BSO_ini_600 (K = 36.0 $\mu M \times h^{-1}$) and BSO_hν_400 (K = 30.0 $\mu M \times h^{-1}$) showed the highest PC activity during the decomposition of Phenol. During the decomposition of photostable Vancomycin, the samples after laser treatment with BSO_hν_400 and BSO_hν_600 showed the highest PC activity – the K values were 6.3 and 7.3 $\mu M \times h^{-1}$, respectively.

Thus, in this work, NPs based on bismuth sillenite $Bi_{12}SiO_{20}$ were successfully obtained via PLA method in water. It has been established that the best photocatalytic activity during the decomposition of Rhodamine B, Phenol, and Vancomycin is exhibited by samples with a high percentage of $Bi_{12}SiO_{20}$.

This work was supported by the Russian Science Foundation (Grant No 19-73-30026).

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