IV.p.03

Sol-gel preparation and study photocatalysts ZnS-modified biogenic silica

O.D. Arefieva[1,2], M.S. Vasilyeva[1,2], V.V. Tkachev[1]
[1]Far Eastern Federal University, [2]Institute of Chemistry, FEB RAS, Vladivostok, Russia

Introduction

Heterogeneous photocatalysis is considered to be one of the most promising and innovative types of advanced oxidative processes used for wastewater treatment from persistent organic pollutants. Nanoparticles of metal sulfides are of considerable interest as effective photocatalysts. The introduction of such nanoparticles into the silicon dioxide matrix, which has a high specific surface area, makes it possible to protect sulfides from photocorrosion and improve the adsorption properties of photocatalysts [1-3].
The aim of the work is to obtain sol-gel technology and to investigate the photocatalytic properties of sulfide photocatalysts with a matrix of biogenic silica from rice husk in the degradation reaction of methyl orange.

Experiment

In this work, samples of zinc-containing sulfide photocatalysts with a matrix of biogenic silica obtained from rice husk (RH) were obtained. The synthesis of the photocatalyst included 3 stages. At the first stage, sodium orthosilicate was extracted from the RH. For this purpose, alkaline hydrolysis of RH was carried out when heated to 90ºC for 1 h. Next, a concentrated hydrochloric acid solution was added to the sodium orthosilicate solution to pH 6 and a wet gel was obtained. To obtain xerogel, one of the parts of the wet gel was calcined in a muffle furnace. At the last stage, $Zn(CH_3COO)_2 \cdot 2H_2O$, distilled water, thiourea and concentrated ammonia solution were mixed. Then a wet gel or xerogel of SiO_2 was added to the resulting mixture. The resulting suspensions were dried and calcined in a muffle furnace. The resulting powders were designated as ZnS-SiO_{2wg}, ZnS-SiO_{2xg}.
The photocatalytic activity of the samples was evaluated in the degradation reaction of an organic pollutant - methyl orange (MO) under UV, solar and visible light irradiation. The loading of the catalyst was 1 g/l. The solution was irradiated with constant stirring on a magnetic stirrer (625 rpm) for 3 hours. The source of UV irradiation was a UV lamp of 100P/F (maximum radiation at 365 nm); the visible one was a xenon irradiator with a nominal lamp power of 35 watts and with radiation maxima in the region of 540-675 nm.

Results and discussions

According to the results of X-ray fluorescence analysis, the main element for the photocatalysts ZnS-SiO_{2xg} и ZnS-SiO_{2wg} is silicon. Zinc and sulfur are contained in equal amounts (table 1).

Table I. Chemical composition of sulfide photocatalysts, mass. %

Samples	Si	Na	Zn	S	Cl
ZnS-SiO_{2wg}	35	13	28	8	16
ZnS-SiO_{2xg}	32	19	23	9	18

X-ray phase analysis of samples of sulfide photocatalysts showed that they are in an amorphous-crystalline state. The presence of an amorphous phase is indicated by a blurred peak in the region 2θ = ~ 22-25°. A zinc sulfide semiconductor with a band gap of 3.67 eV has been identified in the crystalline phase. In both cases, the photocatalyst samples are loose irregularly shaped particles with sizes from 1 to 30 and more microns (Fig. 1a). The microstructure of sulfide photocatalysts synthesized using wet gel and xerogel has no significant differences and is a porous SiO2 matrix, which includes faceted crystals of various shapes and sizes, presumably ZnS (Fig. 1b).

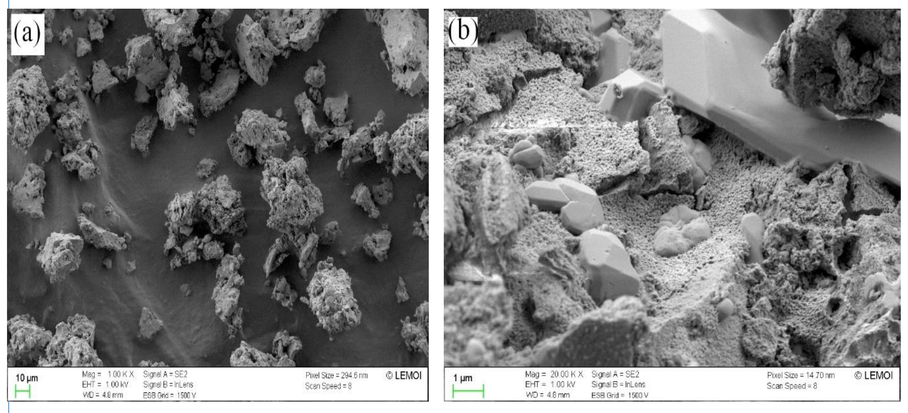

Fig. 1. SEM-image of the photocatalyst ZnS-SiO_{2wg}

The results of photocatalytic tests showed that the studied samples showed photocatalytic activity under various types of irradiation. When exposed to UV and sunlight, the sample had a higher activity, in the process of obtaining which SiO_2 xerogel was used. The ZnS-SiO_{2wg} sample obtained on the basis of a wet SiO_2 gel demonstrated a response when excited by UV, visible and sunlight, while the efficiency of MO degradation ranged from 11 to 35% (Table 2).

Table 2. The degree of decomposition of indigocarmine under UV light irradiation

Photocatalyst	Irradiation conditions			
	Sunlight	UV light	Visible light	In the dark
ZnS-SiO_{2wg}	11± 6	35±7	15±9	1
ZnS-SiO_{2xg}	30±5	88±5	16 ± 5	13

Conclusions

Sulfide SiO_2-ZnS composite photocatalysts with a matrix of biogenic silica sol-gel method were obtained. The immobilization of zinc sulfide in the silica matrix led to the stability and photocatalytic activity of this material under various irradiation conditions. The materials have a response when excited by sunlight in the degradation reaction of the methyl orange dye.

Acknowledgements

The work was carried out within the framework of the state task of the Institute of Chemistry of the FEB RAS 0205-2021-0002. The authors are grateful to the Laboratory of Molecular and Elemental Analysis and the Laboratory for X- ray Structural Analysis (Institute of Chemistry, FEB RAS).

References

[1] Y. Yesu Thangam, R. Anitha. Journal of Research in Nanobiotechnology 1(2012)14.
[2] M. Tan, W. Cai, L. Zhang. Applied Physics Letters 71(1997)3697.
[3] B. Pal, T. Torimoto, K. Iwasaki, T. Shibayama, H. Takahashi, B. Ohtani. Journal of Applied Electrochemistry 35(2005)751.

Arefieva Olga, FEFU,
arefeva.od@dvfu.ru, +7-914-736-92-09