

Brief information about the project

Name of the project	AP14870472 «Technology of green synthesis of structurally modified metal sulfide nanocomposites with high photocatalytic activity and antibacterial properties»
Relevance	<p>The project is dedicated to the environmentally friendly “green” mechanochemical synthesis of nanostructured transition metal sulfide-based nanocomposites and their doped modification to use as photocatalysts for water and air purification from organic pollutants and as an antibacterial agent. Within the framework of the project was planned production of single nanosulfides with inner structural defects MeS, heterostructured binary nanocomposites $^1\text{Me}^2\text{MeS}$, and core/shell structured spherical nanoparticles $^1\text{MeS}@^2\text{MeS}$, where Me = Cu, Zn, Pb, Sn, Cd, Bi, Ag. The influence of noble metal doping of nanocomposites on photocatalytic and antibacterial activity will be studied. The possibility to use different precursors will be investigated, i.e., directly metal and sulfur or various compounds containing these elements will be co-milled. Namely, acetates and nitrates will be used as metal precursors, and sodium sulfide, thiourea, and the eggshell membrane will be used as sulfur precursors. The possibility to dope the sulfides with small amounts of nanoscale silver will be investigated by co-milling of MeS with AgNO_3, or by directly introducing AgNO_3 when synthesizing sulfide in a one-step process. The nanocomposites of more sulfides for specific applications will be also synthesized. Obtaining of MeS, Ag/MeS, and $\text{Me}_1\text{S}/\text{Me}_2\text{S}/\text{Ag}$ will be carried out in planetary ball mills where solid precursors will be introduced, and milling will be carried out in chambers with milling balls of different sizes.</p> <p>Each resulting product system will be studied by all methods available to the research group: X-ray phase analysis using Rietveld refinement, Raman spectroscopy, scanning electron microscopy, transmission electron microscopy, EDX analysis, UV-VIS spectroscopy, photoluminescent spectroscopy, specific surface area measurement (S_{BET}), Fourier-IR spectroscopy, X-ray photoelectron spectroscopy.</p> <p>The intended applications of MeS, $^1\text{Me}^2\text{MeS}$, and $^1\text{MeS}@^2\text{MeS}$ are photocatalysis, hydrogen production, and biomedicine. Depending on the application area, the following will be studied: biological activity (antibacterial properties), photocatalytic activity, and photocatalytic hydrogen production.</p> <p>The methodology described in the project has great potential for commercialization, as it will significantly reduce the cost of production of photocatalysts based on metal sulfide nanostructures due to resource and energy savings, as well as high material productivity. In addition, optimization is aimed at the use of minerals and resources of Kazakhstan, which can lead to the development of the country as a manufacturer of materials for commercial photocatalysts. The scientific group has experience in the synthesis of nanoparticles, and also has all the necessary tools for carrying out all stages of synthesis, as well as physico-chemical analysis.</p>
Purpose	Development of an environmentally friendly and waste-free technology for the synthesis of structurally modified nanocomposites based on transition metal sulfides, which have high photocatalytic activity in the

	decomposition of organic pollutants and the generation of hydrogen, as well as antibacterial properties.
Objectives	<p>1. Development of green technology for mechanochemical synthesis of transition metal sulfide nanoparticles (MeS). Collection of literature sources and study of advantages and disadvantages of existing methods of synthesis of MeS. Determination of environmentally safe precursors and optimal parameters of mechanical activation for the synthesis of MeS nanoparticles.</p> <p>2. Structural, qualitative, and morphological characteristics of the obtained MeS nanoparticles by physico-chemical analysis methods. Determination of the influence of the selected precursors and parameters of mechanochemical synthesis on the structural characteristics of the final nanoparticles.</p> <p>3. Study of the photocatalytic activity of the obtained nanostructures during the decomposition of organic pollutants from aqueous solutions and the photocatalytic generation of hydrogen from aqueous alcohol solutions under visible and solar light. Determination of the dependence of photocatalytic and antibacterial properties of nanoparticles on particle size and morphology.</p> <p>4. Determination of conditions for doping of MeS nanoparticles with noble metals and selection of optimal conditions for the mechanochemical synthesis of structural core/shell bimetallic nanocomposites of $^1\text{Me}^2\text{MeS}$ and $^1\text{Me}^2\text{MeS}@^3\text{MeS}$ metal sulfides. This process will be carried out to improve the photocatalytic properties of the obtained samples. The combination of two different metal sulfides and the doping of metal sulfides can significantly improve the performance of hydrogen during the photocatalysis process.</p> <p>5. Creation of a principal scheme of the production of photocatalysts based on metal sulfides, corresponding to all the principles of green chemistry. This technology will provide for the secondary use of side products. In addition, the technological scheme will be conditioned by the absence of harmful emissions into the environment. The strategy of mechanochemical synthesis will be aimed at improvement, which will be achieved by reducing resource consumption, thereby reducing the cost of the final product.</p>
Expected and achieved results	<p><i>Expected results</i></p> <p>Optimal conditions for the mechanochemical synthesis of MeS, $^1\text{MeS}@^2\text{MeS}$, and $^1\text{Me}^2\text{MeS}@^3\text{MeS}$ nanocomposites will be determined.</p> <p>Detailed characterization of the chemical composition, crystallite size, specific surface area, structure, morphology (size and shape of nanocrystals and nanoparticles), band gap, thermal, spectral and photoluminescent properties of the obtained nanocomposites will be accomplished</p> <p>The green technology for mechanochemical synthesis of transition metal sulfide (MeS) nanoparticles will be developed.</p> <p>The dependence of photocatalytic and antibacterial properties of MeS nanoparticles on particle size and morphology will be determined.</p> <p>The conditions for doping of MeS nanoparticles with noble metals and selection of optimal conditions for the mechanochemical synthesis of</p>

	<p>structural core/shell bimetallic nanocomposites of $^1\text{Me}^2\text{MeS}$ metal sulfides will be determined.</p> <p>The antibacterial properties of the obtained noble metal doped core/shell structured $^1\text{Me}^2\text{MeS}@^3\text{MeS}$ nanocomposites will be investigated using the agar well plate method on bacteria.</p> <p>The schematic diagram of the production of photocatalysts based on metal sulfides, following all the principles of green chemistry will be created.</p> <p><i>Achieved results</i></p> <p>1 article was published in a journal indexed in the Scopus database and 1 article in a journal recommended by the Committee for Quality Assurance in Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan.</p>
<p>Research team members with their identifiers (Scopus Author ID, Researcher ID, ORCID, if available) and links to relevant profiles</p>	<ul style="list-style-type: none"> • PhD – Шалабаев Ж.С. (ORCID: https://orcid.org/0000-0003-3465-8241). Scopus ID: 57203060099. • PhD – Матей Балаж – (ORCID: https://orcid.org/0000-0001-6563-7588). Scopus ID: 55305604900. • PhD – Хан Н.В. (ORCID: https://orcid.org/0000-0003-1794-0018). Scopus ID: 57214114418. • Бурашев Г.Б. (ORCID: https://orcid.org/0000-0002-4812-4112). • Сейсембекова А.Б. - (ORCID: https://orcid.org/0000-0002-7791-3145). Scopus (ID: 57193852937).
<p>List of publications with links to them</p>	<ol style="list-style-type: none"> 1. Baláž P., Achimovičová M., <u>Baláž M.</u>, Chen K., Dobrozhan O., Guilmeau E., Hejtmanek J., Knížek K., Kubíčková L., Levinský P. Thermoelectric Cu–S-based materials synthesized via a scalable mechanochemical process // ACS Sustainable Chemistry & Engineering. – 2021. – T. 9, № 5. – C. 2003-2016. 2. <u>Baláž M.</u>, Dobrozhan O., Tešínský M., Zhang R.-Z., Džunda R., Dutková E., Rajňák M., Chen K., Reece M. J., Baláž P. Scalable and environmentally friendly mechanochemical synthesis of nanocrystalline rhodostannite ($\text{Cu}_2\text{FeSn}_3\text{S}_8$) // Powder Technology. – 2021. – T. 388. – C. 192-200. 3. <u>Baláž M.</u>, Goga M., Hegedus M., Daneu N., Kováčová M. r., Tkáčiková L. u., Balážová L. u., Bačkor M. Biomechanochemical solid-state synthesis of silver nanoparticles with an antibacterial activity using lichens // ACS Sustainable Chemistry & Engineering. – 2020. – T. 8, № 37. – C. 13945-13955. 4. <u>Shalabayev Z.</u>, <u>Baláž M.</u>, Daneu N., Dutková E., Bujňáková Z., Kaňuchová M., Danková Z., Balážová L., Urakaev F., Tkáčiková L., Burkitbayev M. Sulfur-mediated mechanochemical synthesis of spherical and needle-like copper sulfide nanocrystals with antibacterial activity // ACS Sustainable Chemistry and Engineering -2019. - Vol. 7, № 15. - P. 12897-12909. DOI: 10.1021/acssuschemeng.9b01849 (IF: 7.632, Q1). 5. <u>Balaz M.</u>, Zorkovska A., Blazquez J.S., Daneu N., Balaz P. Mechanochemistry of copper sulfides: phase interchanges during milling // Journal of Materials Science. - 2017. - Vol. 52, № 20. - P. 11947-11961. DOI: 10.1007/s10853-017-1189-0 (IF: 3.282, Q2). 6. <u>Baláž M.</u>, Dutková E., Bujňáková Z., Tóthová E., Kostova N.G., Karakirova Y., Briančin J., Kaňuchová M. Mechanochemistry of copper sulfides: Characterization, surface oxidation and photocatalytic activity //

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Patents