ABSTRACT
thesis for the degree of Doctor of Philosophy (PhD)
on specialty «6D072000– Chemical technology of inorganic substances»
Natalya Khan
«Preparation and application of micro-/nano-structures based on sulfur and silver halides»

General description of the work

The thesis is devoted to the production of micro-/nano-structures containing sulfur and silver halides and their testing as photocatalysts and antimicrobial agents. Micro-/nano-structures were obtained using the following percentages of components: 90:10 wt. % (S90:AgX (X=Cl, Br, I) 10) and 70:30 wt.% (S70:AgX30). The materials were obtained via solvothermal synthesis using two methods of sulfur deposition. The physicochemical properties of the obtained micro-/nano-structures were studied and the most effective composition capable of maintaining photocatalytic activity and exhibiting antimicrobial properties was determined.

The relevance of the study

Currently, one of the global issues are environmental and energy problems. To solve them, modern science is trying to find new materials that will have the versatility and potential to treat these problems somehow. More and more research is being devoted to finding new methods for obtaining various materials based on semiconductors and doping or combining them with other materials to improve their functional properties.

In particular, silver halides are widely used semiconductors for photocatalysis and electrochemistry, since these materials have strong optical adsorption, good photoelectric properties, and are sources of elemental silver, the formation of which can lead to improved properties. However, due to the limited (albeit high) absorption of visible light, low oxidation or reduction ability, and high cost, the use of silver halides is limited. The application of non-metallic dopants can solve these problems. The use of α-sulfur can make it possible to achieve suitable photostability and band edges for photocatalytic processes. In addition, sulfur is one of the most common elements with a low cost, having a large number of allotropic modifications and having a number of unique properties – hydrophobic, antibacterial, etc.

Another important environmental problem that poses a threat to the global ecosystem are pathogenic microorganisms. Despite the presence of antibiotics and antifungal drugs, the number of harmful microorganisms is growing, along with their ability to adapt to the effects of drugs. Therefore, the development of new materials that would be efficient against various types of bacterial strains is extremely relevant. It is known that sulfur and silver halides are able to prevent the reproduction of pathogenic microorganisms, and their combination in one multicomponent material can give a synergistic effect.

The above-mentioned point to the need to obtain a material that would be sufficiently effective for both photocatalytic processes and biomedical

applications, and at the same time would be safe for the environment and economically profitable.

Purpose of the work is the preparation of the sulfur and silver halides micro-/nano-structures and the investigation of their physico-chemical properties, photocatalytic activity, antimicrobial and antifungal properties.

The tasks of the thesis:

- preparation of the sulfur and silver halides micro-/nano-structures;
- characterization of the prepared sulfur and silver halides micro-/nano-structures with help of physico-chemical methods of analysis;
- investigation of the photacatalytic activity, antibacterial and antifungal properties of the prepared sulfur and silver halides micro-/nano-structures;
- identification of micro-/nano-structures with the highest photocatalytic and/or antibacterial and antifungal activity;
- development of the principal scheme for producing of the sulfur and silver halides micro-/nano-structures and the calculation of material balance of the process.

Research methods

The following analysis methods were used in the study: X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, Scanning electron microscopy, Transmission electron microscopy (with energy-dispersive X-ray elemental mapping), Brunauer-Emmett-Teller surface area analysis, Differential scanning calorimetry and thermogravimetric analysis, UV-Vis spectroscopy.

The object of the study are sulfur and silver halides micro-/nano-structures.

The subject of the study are the physico-chemical, photocatalytic, antibacterial and antifungal properties of the prepared sulfur and silver halides micro-/nano-structures.

The main provision for the defense:

1) The synthesis of sulfur and silver halides micro-/nano-structures effectively takes place in a DMSO medium at 120° C and, due to the high positive dependence of the solubility of sulfur in DMSO on temperature, excess sulfur precipitates when the reaction mixture is cooled to room temperature, while a highly supersaturated sulfur solution is formed over the precipitate, and it dilution leads to the formation of a heterogeneous system consisting of sulfur microparticles coated with grains of silver halides of smaller sizes.

2) The application of the method of sulfur precipitation by cooling the reaction mixture for 12 hours to room temperature during the synthesis of micro-/nano-structures leads to the formation of irregularly shaped sulfur particles with a size of 20 to 50 μm, and the application of the method of sulfur precipitation from a supersaturated solution by diluting the reaction mixture with water gives irregularly shaped sulfur particles with a size of 10 to 25 μm.

3) Micro-/nano-structures with the 70 wt. % of sulfur and 30 wt. % of silver bromide composition represented by the greatest photodegradation ability of the Orange II organic dye ($C_{16}H_{11}N_2NaO_4S$), decomposing about 90 % of the dye molecules when exposed to visible light ($\lambda \approx$ 380-760 nm, I = 15 mW/cm^2) for 3 hours.

4) Micro-/nano-structures with 70 wt.% of sulfur and 30 wt. % of silver chloride/bromide composition have the greatest ability to suppress pathogenic microorganisms such as *S.aureus* ATCC 6538-P, *C.albicans* ATCC 10231, *E.coli* ATCC 8739, *P.aeruginosa* ATCC 9027, *E.Amylovora*, *S.aureus* ATCC BAA-39, *E.coli* ATCC BAA-196.

The main results of the study

1. Sulfur and silver halides micro-/nano-structures were synthesized in DMSO medium at 120 °C. Two methods of sulfur deposition have been developed: 1) sulfur precipitation by cooling the reaction mixture for 12 hours to room temperature; 2) sulfur precipitation by diluting the solution of the reaction mixture with water at a volume ratio of DMSO:water 1:1.

2. The study of synthesized sulfur and silver halides micro-/nano-structures by physico-chemical characterization methods was carried out. The results of the analyses showed that sulfur and silver halides are present in the micro-/nano-structures, the samples are represented by a heterogeneous system where sulfur grains are covered with silver halide particles. When sulfur is precipitated by cooling the reaction mixture to room temperature, sulfur particles with a size of 20 to 50 μm are formed, while dilution of the reaction mixture solution with water leads to the formation of smaller sulfur particles with a size of 10 to 25 μm. Silver halides, regardless of the method of sulfur deposition method, exhibit the particle size in the range from 1 to 4 μm.

3. SEM, TEM and TEM-elemental mapping showed that dilution of the system of micro-/nano-structures in the DMSO medium with water prevents agglomeration of sulfur particles. The DMSO–water system, due to the DMSO property as a surfactant, forms micelles consisting of stable complexes of these components, and the hydrophobicity of sulfur particles provides protection against aggregation.

4. The photocatalytic, antibacterial and antifungal properties of synthesized micro-/nano-structures were investigated. It was found that synthesized sulfur and micro-/nano-structures based on sulfur and silver iodide do not have significant photocatalytic activity. Sulfur and silver chloride/bromide micro-/nano-structures with a composition of 90:10 wt. % also showed low photodegradation ability of organic dye. Micro-/nano-structures with a content of sulfur:silver halide 70:30 wt. % were more active, and samples based on silver bromide exhibited about 90% degradation of the organic dye. The stability study of samples based on sulfur and silver chloride/bromide with a ratio of 70:30 wt.% showed that these samples remain functional during five cycles of the photocatalytic process.

The study of antimicrobial activity showed that synthesized sulfur and samples based on sulfur and silver iodide are inactive. The remaining samples were able to suppress almost all the test strains studied, and sulfur and silver chloride/bromide micro-/nano-structures with a composition of 70:30 wt.% are able to suppress pathogenic microorganisms at the lowest values of the minimum bactericidal/fungicidal concentration. Samples based on sulfur and silver bromide with a composition of 70:30 wt.% have good prospects of application as functional materials, in photocatalysis and biomedicine.

5. The principal scheme of micro-/nano-structures obtaining was developed. The material balance of the process was calculated.

Substantiation of the novelty and importance of the results obtained

In this work, sulfur and silver halides based micro-/nano-structures in DMSO medium were obtained for the first time using solvothermal synthesis. For the first time, two methods of sulfur deposition from a DMSO medium were proposed: spontaneous deposition at room temperature and precipitation by diluting a DMSO solution with water. A hypothesis was put forward according to which, the dilution of the studied systems of micro-/nano-structures in DMSO with water affects the morphology and size of sulfur grains. The DMSO-water system, due to the properties of DMSO as a surfactant forming micelles that envelop sulfur particles and to some extent prevent its agglomeration, due to the hydrophobic properties of sulfur.

For the first time, the obtained sulfur and silver halides based micro-/nano-structures were tested as photocatalysts, antibacterial and antifungal agents. The 70 wt. % of sulfur and 30 wt. % of silver halides percentage ratio was found to be the optimal composition between the two components of the studied micro-/nano-structures. This percentage ratio makes it possible to exhibit both solid antimicrobial properties and maintain high photocatalytic activity of micro-/nano-structures. Composition 70 wt. % of sulfur and 30 wt. % of silver bromide was determined to be the most effective for micro-/nano-structure, which is capable of displaying the highest degree of photocatalytic and biological activity.

Theoretical significance. The results of the thesis expanded the known knowledge in the field of material science, solvothermal synthesis of materials based on sulfur or silver halides and their application in photocatalysis and microbiology.

Practical significance. The developed micro-/nano-structures have prospects as potential candidates for universal application both for conducting photocatalytic processes and for combating harmful microorganisms.

Relation of the thesis with research and government programs

The dissertation was carried out within the framework of program-targeted funding of the Ministry of Education and Science of the Republic of Kazakhstan (BR05234566), a scientific project of the Ministry of Education and Science of the Republic of Kazakhstan (AP08855868). Also, certain research results were obtained thanks to the Institute of Geotechnics of SAS (Košice, Slovakia) and IGM SB RAS named after V.S. Sobolev (Novosibirsk, Russia).

The personal contribution of the author of the study consists in the analysis of available literature data on the topic of the thesis, performing experiments on the synthesis of sulfur and silver halides micro-/nano-structures, photocatalytic, antibacterial and antifungal properties study of the obtained micro-/nano-structures.

Contribution to scientific publications writing:

1. Khan N. V., Burkitbayev M. M., Urakaev F. K. Development of the synthesis technology of S@ AgCl-Ag_2S nanocomposite in aqua medium // Bulletin

of the Karaganda university. – 2019. – №. 4. – P. 72-76 - investigation, validation, data curation, methodology, writing – original draft, review, editing.

2. Khan N. V., Burkitbayev M. M., Urakaev F. K. Preparation and properties of nanocomposites in the systems S-AgI and S-Ag_2S-AgI in dimethyl sulfoxide //IOP Conference Series: Materials Science and Engineering. – IOP Publishing, 2019. – Vol. 704. – №. 1. – C. 012007 - investigation, validation, data curation, methodology, writing – original draft, review, editing.

3. Burkitbayev M.M., Urakaev F.Kh., Khan N.V., Madikassimova M.S. Oskenbay A.K. Method for producing sulfur-containing nanocomposites / Utility model patent of the Republic of Kazakhstan No. 5241, 2020 - investigation, validation, data curation, methodology, writing – original draft, review, editing.

4. Khan N. V. Synthesis of the S/AgBr nano/micropowder in DMSO-water system //Chemical Bulletin of Kazakh National University. – 2022. – T. 104. – №. 1. – P. 4-10 - investigation, validation, data curation, methodology, writing – original draft, review, editing.

5. Khan N., Baláž M., Burkitbayev M., Tatykayev B., Shalabayev Zh., Nemkayeva R., Jumagaziyeva A., Niyazbayeva A., Rakhimbek I., Beldeubayev A., Uarakaev F. DMSO-mediated solvothermal synthesis of S/AgX (X= Cl, Br) microstructures and study of their photocatalytic and biological activity //Applied Surface Science. – 2022. – Vol. 601. – P. 154122 - visualization, writing – review & editing, writing – original draft, resources, methodology, investigation, conceptualization.

6. Khan N., Baláž M., Burkitbayev M., Tatykayev B., Shalabayev Zh., Niyazbayeva A., Uarakaev F. Solvothermal DMSO-mediated synthesis of the S/AgI micro-/nano-structures and its application as photocatalytic and biological agents //International Journal of Biology and Chemistry. – 2022. – Vol. 15. – №. 1. – P. 79-89 - investigation, validation, data curation, methodology, writing – original draft, review, editing.

7. Abstracts at international conferences - investigation, validation, data curation, methodology, writing – original draft.

Volume and the structure of the thesis

The thesis is consisting of introduction, four sections, conclusions and a list of references. The work is presented on 110 pages, contains 43 figures, 15 tables, and 304 bibliographical references.