Review of the official reviewer
for the dissertation work by Natalya Khan «Preparation and application of micro-/nano-structures based on sulfur and silver halides», submitted for the degree of Philosophy Doctor by specialty «6D072000 - Chemical technology of inorganic substances»

№	Criteria	Criteria eligibility (it is necessary to mark one of the answer options)	Justification of the position of the official reviewer
1.	The topic of the thesis (as of the date of its approval) corresponds to the development of science and/or government programs	1.1 Compliance with priority areas of science development or government programs:	
		1) **The thesis was completed within the framework of a project or target program financed from the government budget (indicate the name and number of the project or program)** 2) The thesis was completed within the framework of another government program (indicate the name of the program) 3) The dissertation corresponds to the priority area of the development of science, approved by the Higher Scientific and Technical Commission under the Government of the Republic of Kazakhstan (indicate the direction)	The thesis was performed within the framework of target program financed from the government budget BR05234566 «Development and testing of technologies for the production of new sulfur-containing nanocomposites and preparations», and within the framework of scientific project of the Ministry of Education and Science of the Republic of Kazakhstan AP08855868 «Sulfur solutions in dimethyl sulfoxide – precursors for the production of sulfur nanoparticles and nanocomposites based on them».
2.	Importance for science	The work **makes**/does not make **a significant contribution to science, and its importance is well disclosed** / not disclosed	The work makes a significant contribution to the development to science, namely, to the material science and understanding of the synthesis of new materials based on sulfur and silver halides, and their application as photocatalysts for the absorption of organic dyes (azo dyes) and for the suppression of pathogenic strains such as *S.aureus*, *C.albicans*, *E.coli*, *P.aeruginosa*, *E.Amylovora*.
3.	The principle of independence	Self-reliance level:	The level of independence in conducting research is

		1) **High;** 2) Medium; 3) Low; 4) No independence	assessed as high. The author independently carried out the entire experimental part on the synthesis of micro-/nano-structures based on sulfur and silver halides, performed all tests on the use of the obtained samples as photocatalysts, anti-bacterial and fungicidal agents. The author independently described the results of the experimental work and, based on them, formulated conclusions. Moreover, according to the analysis of publications made as part of the study, the author made a significant contribution to their writing.
4.	The principle of internal unity	4.1 Justification of the relevance of the thesis: 1) **Justified;** 2) Partially justified; 3) Not justified.	The relevance of the thesis is justified. Indeed, obtaining new substances that can be used in various fields of science and technology is an urgent task. Photocatalysis is currently one of the most promising areas, since it helps to solve many problems. This can be wastewater treatment, air treatment, hydrogen production, etc. Despite the large number of already developed materials, there is a need to develop new ones that would be beneficial in terms of application, economy and environmental friendliness. The fight against microorganisms is also important in the modern world, since practice shows that in most cases pathogenic strains are able to adapt to the effects of various drugs and their mutation leads to serious consequences. Despite the large number of already existing drugs, scientists around the world are working daily to develop such materials. Especially if we are talking about agriculture and biomedicine in general, economy, versatility and efficiency are also vital here.
		4.2 The content of the thesis reflects the topic of the	The content of the thesis reflects the topic of the thesis. The

	thesis: 1) **Reflects;** 2) Partially reflects; 3) Does not reflect	thesis uses a logical approach to solving the tasks set, which consists in obtaining micro-/nano-structures for use in photocatalysis and microbiology, and studying their physicochemical properties. Such a systematic approach indicates the internal unity of the results obtained in the work.
	4.3. The purpose and objectives correspond to the topic of the thesis: 1) **correspond;** 2) partially comply; 3) do not match.	The purpose and objectives fully correspond to the topic of the thesis.
	4.4 All sections and provisions of the thesis are logically interconnected: 1) **fully interconnected;** 2) the connection is partial; 3) there is no connection	All sections and provisions of the thesis are fully interconnected. The section of the literature review consists of a description of methods for obtaining sulfur and silver halides based materials, a description of the use of these materials in photocatalysis and microbiology and the use of DMSO and its properties. The author of the thesis conducted an in-depth analysis of the literature data and critically assessed the need to obtain sulfur and silver halides based materials. The next section of the thesis is devoted to the description of methodology. The "Results and discussion" section reflects the study of physico-chemical characteristics of micro-/nano-structures and their application in photocatalysis and microbiology.
	4.5 The new solutions (principles, methods) proposed by the author are reasoned and evaluated in comparison with the known solutions: 1) **there is a critical analysis;**	The new solutions (principles, methods) proposed by the author are reasoned and evaluated in comparison with the known solutions. The author of the thesis, relying on already known knowledge, proposes a new approach to

		2) partial analysis; 3) the analysis does not represent one's own opinions, but quotes from other authors	obtaining materials based on sulfur and silver halides. The author also makes a critical analysis of the developed methods and reasoning about the influence of the DMSO environment on the synthesis process.
5.	Scientific novelty principle	5.1 Are the scientific results and provisions new? 1) **completely new;** 2) partially new (25-75 % are new); 3) not new (less than 25 % are new)	All scientific results of the dissertation are completely new, since materials based on sulfur and silver halides have not yet been synthesized and investigated.
		5.2 Are the dissertation conclusions new? 1) **completely new;** 2) partially new (25-75 % are new); 3) not new (less than 25 % are new)	All conclusions of the thesis are completely new. The conclusions put forward specifically reflect the results of the study, there is novelty in each scientific result, since the studied research objects were obtained for the first time. The author independently conducted a large-scale study and was able to substantiate the results and conclusions. Thus, the work contains a sufficient degree of novelty of the main results and conclusions, which are fully reflected in the thesis. The conclusions are proven in an article of Q1 journal **"Applied Surface Science"** and **International Journal of Biology and Chemistry** (scientific journals recommended by the Committee for Quality Assurance in the Field of education and Science of the Ministry of Education and Science of the Republic of Kazakhstan)
		5.3 Technical, technological, economic or management solutions are new and reasonable: 1) **completely new;** 2) partially new (25-75 % are new); 3) not new (less than 25 % are new)	The technical and technological solutions proposed in the thesis are completely new and reasonable. The author proposes for consideration a solvothermal method for obtaining materials based on sulfur and silver halides in DMSO at 120°C. Also, author compares two methods of sulfur precipitation and their effect on the physicochemical

			properties of the samples. According to scientific publications, it is possible to trace how the author developed and selected suitable approaches for the synthesis of micro-/nano-structures (Q1 journal **"Applied Surface Science", patent on utility model** and articles in scientific journals recommended by the Committee for Quality Assurance in the Field of education and Science of the Ministry of Education and Science of the Republic of Kazakhstan (**Bulletin of the Karaganda University, Chemical Bulletin of Kazakh National University and International Journal of Biology and Chemistry**)).
6.	Validity of key findings	All the main **conclusions are**/are not **based on scientifically significant evidence** or reasonably well substantiated	All the main conclusions are based on scientifically significant evidence.
7.	The main provisions for the defence	It is necessary to answer the following questions for each provision separately: 7.1 Is the provision proven? 1) **proven;** 2) rather proven; 3) rather unproven; 4) unproven. 7.2 Is it trivial? 1) yes; 2) **no.** 7.3 Is it new? 1) **yes;** 2) no.	Provision 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. The provision 1 is proved by the author and it is not trivial. This data expands already known knowledge in synthesis of new materials. The provision is new because it has not been previously described in the scientific literature. The

		7.4 Application level: 1) narrow; 2) **average;** 3) wide. 7.5 Is it proven in the article? 1) **yes;** 2) no.	application level of the provision is wide since it can be useful for subsequent research devoted to the obtaining of various materials. The provision 1 is proven in an article of Q1 journal "Applied Surface Science". Moreover, author has developed and improved the synthesis by different ways and it is reflected in such scientific publications as patent on utility model and three articles in scientific journals recommended by the Committee for Quality Assurance in the Field of education and Science of the Ministry of Education and Science of the Republic of Kazakhstan (**Bulletin of the Karaganda University, Chemical Bulletin of Kazakh National University and International Journal of Biology and Chemistry**).
		7.1 Is the provision proven? 1) **proven;** 2) rather proven; 3) rather unproven; 4) unproven. 7.2 Is it trivial? 1) yes; 2) **no.** 7.3 Is it new? 1) **yes;** 2) no. 7.4 Application level: 1) narrow; 2) **average;** 3) wide.	Provision 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. The provision 2 is completely proved by author with help of morphology and size study by means of SEM and TEM (EDS elemental mapping). The role of DMSO in this process is also discussed by author. The provision 2 is not trivial and completely new. The provision's usage is rated as average. The provision 2 is discussed and proven in an

		7.5 Is it proven in the article? 1) **yes;** 2) no.	article of the Q1 journal **"Applied Surface Science".**
		7.1 Is the provision proven? 1) **proven;** 2) rather proven; 3) rather unproven; 4) unproven. 7.2 Is it trivial? 1) yes; 2) **no.** 7.3 Is it new? 1) **yes;** 2) no. 7.4 Application level: 1) narrow; 2) **average;** 3) wide. 7.5 Is it proven in the article? 1) **yes;** 2) no.	Provision 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/cm2) for 3 hours. The provision 3 is completely proved by the results of photocatalytic experiments. The provision is not trivial and it is completely new. The provision is new as it has not been previously described in any scientific sources. The provision's usage is rated as average. The provision 2 is discussed and proven in an article of the Q1 journal **"Applied Surface Science".**
		7.1 Is the provision proven? 1) **proven;** 2) rather proven; 3) rather unproven; 4) unproven.	Provision 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

		7.2 Is it trivial? 1) yes; 2) **no.** 7.3 Is it new? 1) **yes;** 2) no. 7.4 Application level: 1) narrow; 2) **average;** 3) wide. 7.5 Is it proven in the article? 1) **yes;** 2) no.	BAA-39, *E.coli* ATCC BAA-196. The provision 4 is completely proved by the results of experiments on suppression of pathogenic microorganisms by synthesized samples. The provision is not trivial, since it does not explicitly follow the available knowledge in the field material science and application of various materials in microbiology. The provision is new because it has not been previously described in the scientific literature. The level of applicability of the provision is assessed as average. The provision 1 is discussed and proven in an article of Q1 journal **"Applied Surface Science"**. And in scientific journal recommended by the Committee for Quality Assurance in the Field of education and Science of the Ministry of Education and Science of the Republic of Kazakhstan (**International Journal of Biology and Chemistry**).
8.	8.1 The principle of reliability Reliability of sources and information provided	8.1 Choice of methodology - is justified or the methodology is described in sufficient detail 1) **yes;** 2) no.	The choice of methodology is completely justified. All approaches used in the thesis are generally recognized for research in the field of materials science, photocatalysis and microbiology.
		8.2 The results of the dissertation work were obtained using modern methods of scientific research and methods of processing and interpreting data using computer technologies: 1) **yes;** 2) no.	The results of the thesis were obtained using modern methods of scientific research. The prepared samples were characterized by means of XRD, XPS, Raman spectroscopy, SEM, TEM, specific surface area analysis by method BET, TGA-DSC, UV-Vis spectroscopy.
		8.3 Theoretical conclusions, models, identified	All conclusions, models, identified relationships and

		relationships and patterns have been proven and confirmed by experimental research: 1) **yes;** 2) no.	patterns have been proven and confirmed by experimental research.
		8.4 Important statements **are confirmed** / partially confirmed / not confirmed **by references to the current and reliable scientific literature**	All important statements are confirmed by references to the current and reliable scientific literature.
		8.5 **Used literature sources are sufficient** / not sufficient for a literature review	All sources used are sufficient. The list of references of the thesis includes 304 sources; most of the sources are articles from the last few years published in the Q1 and Q2 journals.
9	Practical value principle	9.1 The thesis has theoretical value: 1) **yes;** 2) no.	The thesis has theoretical value. The results of the work expand the existing knowledge in the field of material science, microbiology and photocatalysis.
		9.2 The thesis is of practical importance and there is a high probability of applying the results obtained in practice: 1) **yes;** 2) no.	The thesis is of practical importance and there is a high probability of applying the results obtained in practice. Results of this study can help in the conducting of experiments on the synthesis of new materials and their characterization and application. The practical importance is reflected in an article of Q1 journal **"Applied Surface Science".** Moreover, author has developed and improved the synthesis by different ways and it is reflected in such scientific publications **as patent on utility model** and three articles in scientific journals recommended by the Committee for Quality Assurance in the Field of education and Science of the Ministry of Education and Science of the Republic of Kazakhstan (**Bulletin of the Karaganda University, Chemical Bulletin of Kazakh National**

			University and International Journal of Biology and Chemistry).
		9.3 Are the practice suggestions new? 1) **completely new;** 2) partly new (25-75% are new); 3) not new (less than 25% are new).	The practical proposals are new and have not been previously put forward or published.
10.	The quality of writing and design	Academic writing quality: 1) high; 2) **average;** 3) below average; 4) low.	The dissertation work is written in a traditional scientific style in accordance with the requirements of the standards. My comments for the PhD dissertation: • *In the table 9, it is worth correcting the name of the last column to "Average particle size".* • *It is worth considering and explaining the reasons for the low specific surface area of the studied samples* • *It is recommended to pay attention to a more detailed explanation of the presence of nanoscale particles.*

Decision: *I support the award of the PhD degree by specialty «6D072000 - Chemical technology of inorganic substances» to Natalya Khan.*

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signature

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