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 dissertation work was carried out 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 a 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 of material science, in particular, to understanding the processes of obtaining of materials based on sulfur and silver halides and its behavior in photocatalytic degradation of organic dyes and suppressing of pathogenic microorganisms.
3.	The principle of independence	Self-reliance level:	The level of independence in the performance of research is

		1) **High;** 2) Medium; 3) Low; 4) No independence	rated as high. The PhD candidate independently performed all experimental work on synthesis of micro-/nano-structures based on sulfur and silver halides and their application in photocatalysis and microbiology. The author independently interpreted the results of the experimental work and formulated conclusions from the dissertation work. Moreover, PhD candidate has made a significant contribution to the writing of scientific publications.
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 is justified by the current environmental situation in the world, as well as the need to develop new materials applicable in various fields of science and technology. The author gave weighty arguments in favor of choosing the topic of the dissertation.
		4.2 The content of the thesis reflects the topic of the thesis: 1) **Reflects;** 2) Partially reflects; 3) Does not reflect	The content of the thesis fully reflects its topic. The literature review provides information about the main object of research (that is, sulfur and silver halides based materials), a critical analysis of the existing ways of synthesis of materials based on sulfur or silver halides and their application in photocatalysis and microbioligy. There is also given information in literature review and experimental part about the role of DMSO in the synthesis.
		4.3. The purpose and objectives correspond to the topic of the thesis: 1) **correspond;** 2) partially comply; 3) do not match.	The goal and objectives are fully consistent with the topic of the dissertation. All tasks are aimed at achieving this goal.
		4.4 All sections and provisions of the thesis are logically interconnected:	All sections and provisions of the thesis are fully interconnected. The literature review identifies the most

		1) **fully interconnected;** 2) the connection is partial; 3) there is no connection	commonly used methods for the synthesis of materials based on sulfur and silver halides, their advantages and disadvantages; also provides behavioral features and conditional details of photocatalysis and suppression of microorganisms. In the "Experimental Part" the PhD candidate indicated the methodology for conducting experiments, as well as the methods used to characterize synthesized materials. The "Results and Discussion" section is devoted to the description of the photocatalytic and antibacterial and antifungal properties of the synthesized materials.
		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;** 2) partial analysis; 3) the analysis does not represent one's own opinions, but quotes from other authors	New solutions for the synthesis of micro-/nano-structures are argued and critically evaluated in comparison with the known ones. PhD candidate compares two methods of sulfur precipitation, which are the final step of the synthesis of investigated samples. The role of DMSO in the process of synthesis is also explained.
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 and provisions in the thesis are completely new. The materials based on sulfur and silver halides were not synthesized and studied yet.
		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 dissertation work have not been previously formulated and are completely new.
		5.3 Technical, technological, economic or management solutions are new and reasonable:	The technical and technological solutions proposed in the dissertation are completely new and reasonable. For the

		1) **completely new;** 2) partially new (25-75 % are new); 3) not new (less than 25 % are new)	first time, for the obtaining of micro-/nano-structures based on sulfur and silver halides was proposed to carry out the solvothermal synthesis in DMSO media, followed by two approaches of sulfur deposition: cooling of reaction mixture for 12 hours at room temperature and diluting of hot reaction mixture by water with volume ratio 1:1.
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 in the dissertation are based on the results of the experiments and their competent interpretation. The conclusions of the thesis work are consistent with modern views in the field of material science, photocatalysis and microbiology.
7.	The main provisions for the defence	It is necessary to answer the following questions for each provision separately: 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. 7.1 Is the provision proven? 1) **proven;** 2) rather proven; 3) rather unproven;	This provision is fully proved by the results of experiments on synthesis of micro-/nano-structures based on sulfur and silver halides. The provision is not trivial, since it does not explicitly follow the known knowledge in the field of material science, namely in the production of new materials based on sulfur and silver halides. The provision is new because it has not been previously described in the scientific literature. The level of application of the provision is average since it can be used to subsequent experiments devoted to the obtaining of sulfur and silver halides based materials. The provision is fully proven in an article in the journal of the first quartile (Q1) on Web of Science *"Applied Surface Science"*.

		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 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. 7.1 Is the provision proven? 1) **proven;** 2) rather proven; 3) rather unproven;	This provision is fully proved by the results of physicochemical study of the synthesized materials. Moreover, the nature of this phenomena is explained by the fact that DMSO plays a key role in this process and at the same time behaves as solvent and surfactant. Indeed, it is clearly seen from the study of the size and morphology of the micro-/nano-structures, that the size of the sulfur particles is differ and depends on the method of sulfur precipitation. The provision's usage is rated as average. The provision is fully proven in an article in the journal of the first quartile (Q1) on Web of Science *"Applied Surface Science"*.

		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 (λ≈ 380-760 nm, I = 15 mW/cm2) for 3 hours. 7.1 Is the provision proven? 1) **proven;** 2) rather proven; 3) rather unproven; 4) unproven. 7.2 Is it trivial? 1) yes;	The provision has been fully proved experimentally: the mentioned in the provision compositions showed the highest activity in comparison with others. The provision is not trivial, since it does not explicitly follow the available knowledge in the field material science and photocatalysis. 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 is fully proven in an article in the journal of the first quartile (Q1) on Web of Science " *Applied Surface Science"*. Moreover, the investigation of the photocatalytic activity of silver iodide based materials is given in the article *(scientific journals recommended by the Committee for Quality Assurance in the Field of education and Science of the Ministry of Education and*

		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.	*Science of the Republic of Kazakhstan) of International Journal of Biology and Chemistry.*
		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 BAA-39, *E.coli* ATCC BAA-196. 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;**	The provision has been fully proved experimentally: the mentioned in the provision compositions showed the highest to suppress pathogenic microorganisms in comparison with others. 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 is fully proven in an article in the journal of the first quartile (Q1) on Web of Science " *Applied Surface Science"*. Moreover the investigation of the photocatalytic activity of silver iodide based materials is given in the article (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) *of International Journal of Biology and Chemistry.*

		2) no. 7.4 Application level: 1) narrow; 2) **average;** 3) wide. 7.5 Is it proven in the article? 1) **yes;** 2) no.	
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 fully justified. All approaches used in the dissertation work are generally recognized for research in the field of material 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.	All results of the dissertation work were obtained using modern methods. Materials were characterized by X-ray diffraction analysis, X-ray photoelectron spectroscopy, Raman spectroscopy, scanning electron microscopy, high resolution transmission electron microscopy with energy dispersive X-ray spectroscopy (elemental mapping), specific surface area analysis by method BET, Thermogravimetric analysis and differential scanning calorimetry, UV-Vis spectroscopy.
		8.3 Theoretical conclusions, models, identified relationships and patterns have been proven and confirmed by experimental research: 1) **yes;** 2) no.	All theoretical conclusions, models, identified relationships and patterns are confirmed experimentally.
		8.4 Important statements **are confirmed** / partially confirmed / not confirmed **by references to the**	All important statements are consistent with modern views in the field of material science, photocatalysis and

		current and reliable scientific literature	microbiology and are also confirmed by references to articles in high-reputable journals, books and handbooks of high-reputable publishers.
		8.5 **Used literature sources are sufficient** / not sufficient for a literature review	All sources used are sufficient for literature review. The list of references includes 304 sources; most of the sources are articles from the last few years published in the Q1 and Q2 Web of Science journals.
9	Practical value principle	9.1 The thesis has theoretical value: 1) **yes;** 2) no.	The dissertation has theoretical value. The results of the work expand the existing knowledge in the field of synthesis of materials applicable in the photocatalysis and microbiology.
		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 dissertation is of practical importance. Results of this work will allow research aimed at obtaining new materials and their application in various fields of science and technology to advance even further. The practical importance is also reflected in the scientific publications: in an article in the journal of the first quartile (Q1) on Web of Science " *Applied Surface Science"* and 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*) and utility model patent N5241.
		9.3 Are the practice suggestions new? 1) **completely new;** 2) partly new (25-75% are new);	The author proposed a new concept for the obtaining of micro-/nano-structures based on sulfur and silver halides, in DMSO media at 120°C. Such kind of materials were

		3) not new (less than 25% are new).	obtained and investigated on photocatalytic activity and ability to suppress pathogenic microorganisms for the first time. Novelty of practice suggestions is proven by utility model patent N5241, 2020.
10.	The quality of writing and design	Academic writing quality: 1) high; 2) **average;** 3) below average; 4) low.	In general, the quality of writing a dissertation is assessed as quite acceptable. The existing individual inaccuracies are because English is not native to the author.

My comments for the PhD dissertation:

- In Paragraph 1.5 a more detailed description of photocatalytic properties of sulfur and sulfur based materials would be required since for AgX and AgX based materials the more detailed description of the photocatalytic properties was given.
- The author should justify the choice of a combination of sulfur and silver halides.
- The designation of synthesized samples should be revised, since the perception of the results is sometimes difficult.
- The statement of the presence of nanoparticles is doubtful. More attention should be paid to substantiating this statement.
- In Figure 12 g a peak of sulfur at ~169 eV is determined as bond of sulfur with other elements. With which exact elements sulfur forms this peak?

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

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Подпись
УДОСТОВЕРЯЮ
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МИНИСТЕРСТВО НАУКИ И ВЫСШЕГО ОБРАЗОВАНИЯ РОССИЙСКОЙ ФЕДЕРАЦИИ