NAZARBAYEV UNIVERSITY
SCHOOL OF ENGINEERING AND DIGITAL SCIENCES

December 3, 2019

Review

of the Official Reviewer, Professor Zhumabay Bakenov, Ph.D. of the thesis of Mr. Shalabayev Zhandos Smagulovich titled "Solid-phase and liquid-phase preparation of sulfur nanoparticles and their composites: properties study and application fields" submitted for the degree of Doctor of Philosophy (Ph.D.) in the specialty 6D072000 – «Chemical technology of inorganic substances»

1. The relevance of the research topic and its relationship with general scientific and national programs

The use of functional materials based on semiconductor nanoparticles is actively expanding in advanced science-intensive fields. Recently, semiconductor copper sulfide nanoparticles have been the focus of the attention of researchers around the world. They are used for various purposes (e.g. in solar cells, cathode material in lithium batteries, optical filters, thermoelectric materials, biomedicine, and photocatalysis). In such materials, a quantum-size effect was discovered, consisting in the fact that the bandgap of nanoparticles and the energy of electronic transitions can vary significantly with a slight change in the size of the same nanoparticles.

Sulfur nanoparticles are suitable for similar applications like semiconductor CuS nanoparticles, namely their use in lithium battery and pharmaceutical technologies are of importance. This comes from its anti-cancer, antibacterial and antifungal activities.

Nowadays, in addition to the synthesis of sulfur and semiconductor copper sulfide nanoparticles, which are used for various abovementioned purposes, the synthesis of binary, ternary, and quaternary nanocomposites based on them is intensively studied. This is explained by the fact that nanocomposites, unlike nanoparticles, have a wider range of application fields and improved properties.

The traditional methods for producing sulfur and copper sulfide nanoparticles, as well as sulfur-containing nanocomposites are characterized by a number of disadvantages, among which the need to use expensive and toxic precursors, the duration of the process, the difficulty of isolating nanoparticles in free form, and also obtaining them in relatively large quantities should be noted. All of these are factors that limit the scope of the practical application of the abovementioned nanoparticles and nanocomposites.

Thus, the research topic aimed at developing a method for producing sulfur, copper sulfide nanoparticles, and composites based on them, providing the possibility of its scaling, not involving the use of expensive and toxic precursors, with the possibility of isolating the nanoparticles in free form, is very relevant.

2. Scientific results and their validity

The scientific statements of the thesis comply with the requirements for such works. The tasks set by the applicant are consistently solved in the work. The main scientific results are as follows:

Result 1. The chemical reaction with the formation of sulfur nanoparticles and calcium carbonates under the action of carbon dioxide on alkaline earth metal polysulfide was established. It was found that sulfur particles are first synthesized from the corresponding carbonate with sizes of about 20–25 nm, which are subsequently enlarged (aggregated) with the deposition of a composite ($S/CaCO_3$) consisting of hydrophobic particles of sulfur and carbonate. As obtained sulfur nanoparticles and sulfur-containing composite showed hydrophobic properties and biological properties.

Result 2. Sulfur-containing nanocomposite CuS/S have been synthesized via liquid-phase (hydrothermal) synthesis method reacting step-by-step copper acetate, copper chloride, and thiourea in an aqua media at 80 °C. Results of SEM analysis revealed that CuS nanoparticles had an elongated parallelepipedal shape.

Result 3. It is shown that sulfur-containing composite CuS/S has been synthesized via the mechanochemical method from elemental precursors (Cu and S powders). After 12.5 min of milling, elemental copper was not identified in the sample, forming pure CuS and S phases. Also, the possibility of detecting iron wear which comes from stainless steel chamber using magnetometry is shown.

Result 4. Elongated needle-like copper sulfide (nCuS) nanocrystals with a thickness in the range between 6 and 8 nm and lengths up to 60 nm (aspect ratio up to 1:10) have been synthesized via the mechanochemical method. The synthesis is completed in just 5 min. It was found that nCuS is a less selective antibacterial agent, as it possessed activity against both *E. coli* and *S. aureus* bacteria, whereas the spherical CuS sample showed activity only against *E. coli*.

3. The degree of validity and reliability of each result (scientific position) and conclusions formulated in the thesis

All tasks assigned to the work are solved in full. The reliability and validity of the research results are ensured by the involvement of a whole complex of modern physical and chemical methods and devices, a good correlation with the literature. All objects of research, as well as synthesized nanocomposites, are carefully characterized, and the results of the research are interpreted in detail.

4. The degree of novelty of each scientific result (provision), the conclusion of the applicant formulated in the thesis

Result 1 is new since, for the first time, the chemical reaction with the formation of sulfur nanoparticles and calcium carbonate under the action of carbon dioxide on alkaline earth metal polysulfide was established.

Result 2 is new since, for the first time, sulfur-containing nanocomposite CuS/S has been synthesized via liquid-phase (hydrothermal) synthesis method reacting step-by-step copper acetate, copper chloride, and thiourea in an aqua media at 80 °C.

Result 3 is new since, for the first time, sulfur-containing CuS/S composites have been synthesized via the mechanochemical method from elemental precursors. Moreover, the possibility of detecting iron wear which comes from the stainless steel chamber using magnetometry is presented.

Result 3 is new since, for the first time, elongated needle-like copper sulfide (nCuS) nanocrystals with a thickness in the range between 6 and 8 nm and lengths up to 60 nm (aspect ratio up to 1:10) have been synthesized via the mechanochemical method. The synthesis is completed in just 5 min. It was found that nCuS is a less selective antibacterial agent, as it possessed activity against both *E. coli* and *S. aureus* bacteria, whereas the spherical CuS sample showed activity only against *E. coli*.

5. The practical and theoretical significance of scientific results

The results obtained in the framework of the thesis can form the basis of the technology for producing sulfur nanopowders and sulfur-containing nanocomposites in large quantities. The conditions that were determined during the experiments to obtain needle-like nanocrystals of copper sulfide mechanochemically can also be actively used in the production of functional nanoparticles. The developed method of the solid-phase and liquid-phase method for the synthesis of sulfur, copper sulfide nanoparticles, as well as sulfur-containing nanocomposites, can be used by enterprises producing functional nanopowders, due to its simplicity and efficiency.

The thesis research makes a great contribution to the development of the fundamental and applied problems of nanomaterials science and technology of new materials. The parameters found for carrying out liquid-phase and solid-phase synthesis (mechanochemical) of sulfur nanoparticles, copper sulfide, and also sulfur-containing nanocomposites are of great importance for the theoretical foundations of chemical technology and technology for producing nanosized particles. The new knowledge gained in the field of mechanochemical synthesis of semiconductor copper sulfide nanoparticles will find application in the nanopowder industry. The developed chemical method for separating sulfur nanoparticles from a nanocomposite has high theoretical significance in the field of synthesis and separation of nanoparticles in free form

6. Comments and suggestions on the thesis

The thesis is well-written although needs some improvement of English. The materials synthesized could be interesting to test in rechargeable batteries.

7. Compliance of the content of the dissertation with the requirements of the Rules for awarding degrees.

The dissertation work by Zhaldos Smagulovich Shalabaev makes a certain contribution to the development of new functionally and cost-effective technologies for producing anti biological materials designed to treat cultivated plants from harmful bacteria and fungi. The work performed can be characterized as a study, which has scientific and practical significance, that meets all the requirements of the "Rules for the awarding of degrees" of the Committee for Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan and fully complies the requirements for theses for the academic degree of doctor of philosophy (Ph.D.) in the specialty "6D072000- Chemical technology of inorganic substances", and maybe submitted for defense to the appropriate Dissertation Council.

Official Reviewer,

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