REVIEW

of the official reviewer, Doctor of Chemical Sciences, Professor, Kudaibergenov Sarkyt Elekenovich for the Thesis of Shalabayev Zhandos Smagulovich entitled "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 (PhD) 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

Currently modern advances in chemical technology of inorganic substances and rapid development of nanotechnology and nanomaterials initiate the development of new approaches for their synthesis. One of them is mechanochemical synthesis, which is used for synthesis of novel nanomaterials with unique properties. The Thesis of the applicant is devoted to synthesis of nanosized sulfur, nanoparticles of semiconducting copper sulfide (CuS), and nanocomposites of sulfur-containing substances. Recently, synthesis of binary and ternary nanocomposites became a hot topic among researchers who are engaged in the field of materials science due to advanced physicochemical properties. Nanosized sulfur, CuS nanoparticles, as well as sulfur-containing nanocomposites are widely used in various fields of science and technology. They are used as semiconductors, antibacterial and anti-fungicidal materials, cathode materials in Li-ion batteries, and photocatalysts. In this connection, designing of nanocomposites based on sulfur and its derivatives is very relevant. Nowadays, there are many ways to produce nanoparticles, however only several of them can afford to produce nanoparticles in large quantities. Therefore, the main advantage of this research is production of nanosized sulfur, CuS nanoparticles, and sulfur-containing nanocomposites by liquid-phase and solid-phase synthetic methods in large scale.

In this work, the needle-like copper sulfide nanocrystals were obtained for the first time by mechanochemical synthesis. The proposed technology is simple and efficient, the synthetic procedure takes comparatively short time with high yield of the final product.

In this regard, the topic of the PhD Thesis of Shalabayev Zhandos Smagulovich devoted to the development of mechanochemical method of preparation of nanosized sulfur, CuS nanoparticles, and sulfur-containing nanocomposites are relevant.

2. Research results and their validity

At first, the applicant surveyed the literature data. He analyzed and discussed in detail a various methods of preparation the sulfur nanoparticles and copper sulfide nanocrystals, as well as sulfur-containing nanocomposites. However, it would be useful to add a brief conclusion at the end of the literature survey that describes the advantages and drawbacks of used methods for preparation of nanosized sulfur, CuS nanoparticles, and sulfur-containing nanocomposites. Unfortunately, such information is lacking in PhD dissertation.

The experimental part includes the used chemical reagents, equipment for solid-phase and liquid-phase synthesis, and characterization methods.

The results and discussion part contains the liquid-phase, hydrothermal and mechanochemical synthetic methods of key products.

As a result, the following novel results were obtained:

1. For the first time, the formation of sulfur nanoparticles and calcium carbonate under the action of carbon dioxide on alkaline earth metal polysulfides was established. It was found that the sulfur particles synthesized in the presence of calcium carbonate have the sizes about 20–25 nm.

2. For the first time, the sulfur-containing nanocomposite CuS/S was synthesized *via* liquid-phase (hydrothermal) synthetic method by step-by-step reacting of copper acetate, copper chloride, and thiourea in aqueous medium at 80 °C.

3. For the first time, sulfur-containing CuS/S composites were synthesized *via* mechano-chemical synthesis from elemental precursors. Also, some content of iron wear coming from a stainless steel chamber in the course of milling was detected. However, the presence of iron wear may be excluded, if agate balls instead of iron ones would be used.

4. For the first time, the 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) were synthesized *via* the mechanochemical method. The synthesis was completed during 5 min. It was found that nCuS possesses some activity against both *E. coli* and *S. aureus* bacteria, whereas the spherical CuS sample showed activity only against *E. coli*.

Thus, the results obtained in the frame of this Thesis substantially cover and clarify the synthesis of sulfur, copper sulfide nanoparticles, and sulfur-containing nanocomposites, as well as evaluation of their physicochemical and biological properties.

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

High degree of validity and reliability of each scientific result, proposition, and conclusions formulated in the dissertation is determined, at first, by the competence of dissertation subject, selection of tasks, solution of the goal of the dissertation "Solid-phase and liquid-phase preparation of sulfur nanoparticles and their composites: properties study and application fields". Secondly, the author adequately selected the modern research methods aimed solving the problems put in dissertation. In addition, the author carefully planned and implemented the experiments on mechanochemical synthesis of sulfur, CuS nanoparticles, as well as sulfur-containing nanocomposites.

All above-mentioned, coupled with an adequate interpretation of the results based on modern views in the field of chemistry, chemical technology, and nanotechnology, allows to judge the high degree of validity of main conclusions of the dissertation.

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

All scientific results and conclusions formulated in the thesis are characterized by a high degree of novelty. The author of this PhD dissertation for the first time synthesized the elongated needle-like copper sulfide nanocrystals by mechanochemical method. The optimal conditions for separation of sulfur nanoparticles were found. In addition, the ability to scale the process to produce the nanosized sulfur, CuS nanoparticles, as well as sulfur-containing nanocomposites is justified.

5. The practical and theoretical significance of scientific results

The results of Zh. S. Shalabaev's dissertation contribute to development of fundamental and applied aspects of nanomaterials and nanotechnology in concrete selected fields. The parameters found for liquid-phase and solid-phase (mechanochemical) synthesis of nanosized sulfur, copper sulfide nanoparticles, and sulfur-containing nanocomposites are important from theoretical and practical points of view. The new knowledge gained in the field of mechanochemical synthesis of nanoparticles of semiconductor copper sulfide can considerably expand our fundamental representations on this subject and find a wide application in nanopowder industry. The developed chemical method of separation of sulfur nanoparticles from nanocomposite is has a valuble importance for synthesis and separation of nanoparticles in separate forms.

The results obtained in the framework of the Thesis can serve as the basis for the technology of obtaining sulfur nanopowders and sulfur-containing nanocomposites in large quantities. The conditions that were developed in the course of experiments for production of needle-like copper sulfide nanocrystals *via* mechanochemical synthesis can be actively used in the production of functional nanoparticles. The developed methods of solid-phase and liquid-phase synthesis of nanosized sulfur, copper sulfide nanoparticles, and sulfur-containing nanocomposites can potentially be used by enterprises for production of functional nanopowders, due to its simplicity and efficiency.

6. Comments, suggestions on the dissertation

There are some major and minor comments and propositions concerning this PhD thesis:

i) It would be useful to add a brief conclusion at the end of the literature survey that describes the advantages and drawbacks of used methods for preparation of nanosized sulfur, CuS nanoparticles, and sulfur-containing nanocomposites. Unfortunately, such information is lacking in PhD dissertation.

ii) The presence of iron wear may be excluded, if agate balls instead of iron ones would be used.

iii) The dissertation contains many repetitions. For example, in Results and Discussion part it is not necessary to give the biological activity of $S/CaCO_3$ nanocomposies separately, because it is given in Section 4 "Applied aspects of the developed methods for producing of sulfur, copper sulfide nanoparticles and sulfur-contaning nanocomposites".

iv) Many methods, such as XRD, AFM, DSC-TG, etc are also repeated for each sections of Results and Discussion.

v) The English of the dissertation should considerably be improved attracting the native English specialist (for example, co-advisor).

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

Based on the abovementioned, I believe that Zh. S. Shalabaev's dissertation entitled «Solid-phase and liquid-phase preparation of sulfur nanoparticles and their composites: properties study and application fields» submitted for the PhD degree, according to theoretical and practical significance of the obtained results meets the requirements of the «Rules for the award of academic degrees» of the Committee for Control in the field of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, and its author deserves the award of a Ph.D. in the specialty 6D072000 – «Chemical Technology of Inorganic Substances».

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