ABSTRACT

of dissertation work for the doctor of philosophy degree (Ph.D.)
«6D072000 – Chemical technology of inorganic substances»

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Solid-phase and liquid-phase preparation of sulfur nanoparticles and their composites: properties study and application fields

General description of work

The thesis is devoted to obtaining and studying properties of sulfur, copper sulfide (CuS) nanostructures, and sulfur-containing nanocomposites by the liquid-phase and solid-phase preparation methods. Since all nanomaterials in inorganic and/or organic chemistry are synthesized either in a liquid medium or in a solid medium, the abovementioned liquid-phase and solid-phase methods for the synthesis of nanomaterials include almost all methods of synthesis of the abovementioned nanoparticles and nanocomposites. In this regard, sulfur and CuS nanoparticles, as well as sulfur-containing nanocomposites were synthesized by methods that are fast, facile, energy-efficient, and low-cost. In a literature review, analyzing all types of methods for the synthesis of inorganic nanomaterials, mechanochemical and hydrothermal synthesis methods were selected for the synthesis of the abovementioned nanostructures.

In this work, the possibilities of using mechanochemical synthesis to obtain needle-like copper sulfide (nCuS) nanocrystals, liquid-phase production of sulfur-containing nanocomposites, as well as sulfur separation from the obtained nanocomposite are shown for the first time.

The relevance of the study

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.

The purposes of the thesis are the synthesis of sulfur, CuS nanostructures, and sulfur-containing nanocomposites using simple, quick, environmentally friendly and cost-effective method, and investigation their physicochemical, biological, and anti-biological properties against bacteria and fungi.

The tasks of the thesis:

- determination of conditions for the liquid-phase and solid-phase synthesis of target sulfur, semiconductor CuS, and sulfur-containing nanocomposites;
- characterization of as-obtained sulfur, CuS nanoparticles, and sulfur-containing nanocomposites with modern physicochemical methods and techniques;
- determination of physicochemical, biological, and anti-biological properties of as-obtained sulfur, CuS nanoparticles, and sulfur-containing nanocomposites;
- development of a principal scheme of preparation sulfur, CuS nanostructures, and sulfur-containing nanocomposites;
- preliminary assessment of the economic efficiency of using the developed method for producing sulfur, CuS nanostructures, and sulfur-containing nanocomposites in comparison with known methods.

The object of the thesis is sulfur, CuS nanostructures (nanoparticles and nanocrystals), and sulfur-containing nanocomposites.

The subject of the research is the composition, structure, morphology, and physicochemical, biological, and anti-biological (antibacterial and anti-fungicidal) properties of sulfur, CuS nanostructures, and sulfur-containing nanocomposites.

The methodological framework of the research

Solid-phase (mechanochemical) and liquid-phase synthesis methods; separation of solids from liquid in a centrifuge and by filtration; precipitation; Soxhlet extraction; agar well plate method; physicochemical and analytical methods.

The scientific novelty of the thesis

1. 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. 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.

2. For the first time, 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 ºC.

3. For the first time, sulfur-containing CuS/S nanocomposites have been synthesized via mechanochemical method from elemental precursors. Also, the possibility of detecting iron wear which comes from a stainless steel chamber using magnetometry is shown.

4. 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 agent, as it possessed activity against both *E. coli* and *S. aureus* bacteria, whereas the spherical CuS sample showed activity only against *E. coli*.

The scientific and practical significance of the study

The results obtained in the framework of the thesis can form the basis of the technology for the production of sulfur nanopowders, semiconductor needle-like CuS nanocrystals, and sulfur-containing nanocomposites in large quantities. The new knowledge gained in the field of solid-phase (mechanochemical) and liquid-phase synthesis of sulfur nanoparticles, semiconductor copper sulfides nanocrystals, and sulfur-containing nanocomposites will find application in the nanotechnology industry. The developed "Method for producing sulfur nanoparticles, semiconductor needle-like copper sulfide nanocrystals, and sulfur-containing nanocomposites" can be used by enterprises producing sulfur, needle-like copper sulfide (nCuS), and sulfur-containing nanostructures due to its simplicity and cost-effectiveness.

The main provisions for the defense of the thesis

1. Among the sulfur, calcium carbonates nanoparticles, and sulfur-containing $S/CaCO_3$ nanocomposites, $S/CaCO_3$ nanocomposite has the strongest effect on wheat-seed germination by accelerating the growth of shoots and roots by 55 and 45%, respectively.

2. In the mechanochemical synthesis of CuS/S composites from elemental precursors in stoichiometric amount, after 12.5 min of milling elemental copper completely reacts with elemental sulfur. By the increasing time of milling, the trace amount of iron wear released from steel chamber also increases.

3. Introducing *in situ* prepared sulfur nanoparticles to the reaction media of acetate route synthesis of copper sulfide (CuS) nanoparticles promotes the formation of needle-like copper sulfide (nCuS) nanocrystals. Elongated needle-like copper sulfide (nCuS) nanocrystals are less-selective antibacterial agent in comparison with spherical ones.

Experimental and theoretical methods

The composition, structure, and morphology of as-prepared sulfur, needle-like copper sulfide (nCuS) nanostructures, and sulfur-containing nanocomposites were studied by XRD, Raman spectroscopy, TG-DSC, PCCS, FTIR, elemental analysis, XPS, AFM, SEM and EDAX, TEM and SAED, UV-Vis, and PL spectroscopy.

The personal contribution of the author

The author has reviewed and analyzed the literature on the topic under study, studied the methods of experiments on the solid-phase (mechanochemical) and liquid-phase synthesis of nanoparticles and nanocrystals, their isolation in free form, as well as the characterization of the isolated nanoparticles and nanocrystals. In addition, the contribution of the doctoral candidate is to process and interpret the results, as well as approbation at conferences and registration in the form of scientific papers.

Publications

Based on the results of the thesis 9 scientific papers were published, including:

- in two articles (*ACS Sustainable Chemistry and Engineering* (IF ≈ 7) and *Colloid Journal* (IF ≈ 1)) published in international scientific journals having, according to the information base of the company Clarivate Analytics (ISI Web of Knowledge, Clarivate Analytics) a non-zero impact factor;
- in one article published in scientific journals recommended by the Committee for the Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan;
- in four abstracts at international and national conferences and symposia.

In addition, a conclusion was received on the issuance of two patents for the invention “Method for obtaining of sulfur nanoparticles”, application №2017/0532.1 dated 20.06.2017 of RSE “National institute of intellectual property” (Republic of Kazakhstan) and “Method for producing sulfur nanoparticles from solutions in dimethyl sulfoxide” application №201700540 dated 2017.11.29 of “Eurasian patent organization” (Russian Federation). All of these publications were made during the Ph.D. program.

Relation of the thesis with research and government programs

The dissertation work was performed within the framework of the program of targeted financing for 0130/PCF-14 “Development of new methods for obtaining sulfur nanoparticles to create technologies for the production of drugs for various functional purposes” (2015-2017 yy.) and BR 05234566 “Development and approbation of technologies for obtaining new sulfur-containing nanocomposites and drugs” (2018-2020 yy.). Also, this dissertation work was performed and supported within the framework of the grant funding project of MES of Republic of Kazakhstan AP 05133115 “Mechanochemical and solution synthesis of metal sulfide and sulfur nanocomposites (MeS@S; Me = Cd, Cu, Pb, Zn): properties and application prospects” (2018-2020 yy.).

Conclusions

1. The optimal conditions for solid-phase (mechanochemical) and liquid-phase preparation of sulfur, semiconductor spherical and needle-like copper sulfide (nCuS), and sulfur-containing nanocomposites ($S/CaCO_3$ and CuS/S) were found.

2. All as-obtained products have been characterized using vast of modern methods of physicochemical analysis.

3. The physicochemical, biological, and anti-biological properties of as-obtained sulfur, CuS nanoparticles, and sulfur-containing nanocomposites are determined.

The hydrophobic properties of sulfur, calcium carbonate nanoparticles, as well as sulfur-containing $S/CaCO_3$ nanocomposites are evaluated. The measurements of the contact angles of water droplets yielded the following results: $140^{\circ}\pm3^{\circ}$, $147^{\circ}\pm3^{\circ}$, and $133^{\circ}\pm3^{\circ}$ for the densified surface of sulfur, calcium carbonate nanoparticles, and $S/CaCO_3$ nanocomposites, respectively.

The biological activity of sulfur, calcium carbonate nanoparticles, and $S/CaCO_3$ nanocomposites on wheat-seed germination are tested. It was found that calcium carbonate nanoparticles have the weakest effect on seed germination. Sulfur nanoparticles have a moderate effect, while $S/CaCO_3$ composite has the strongest action and accelerates the growth of the shoots and roots by 55 and 45%, respectively.

The antibacterial properties of mechanochemically synthesized sulfur microparticles, spherical, and needle-like copper sulfide (nCuS) nanocrystals are studied. It was found that nCuS is a less selective agent, as it possessed activity against both *E. coli* and *S. aureus* bacteria, whereas the spherical CuS sample showed activity only against *E. coli*. Sulfur microparticles did not show any antibacterial activity against both of bacteria.

4. The principal technological scheme for production of sulfur, nCuS nanocrystals, and sulfur-containing ($S/CaCO_3$) nanocomposites are developed. Facile, quick, low-cost, and environmentally-friendly methods for production abovementioned nanostructures are developed.

5. The economic efficiency of using the developed method for producing sulfur, CuS nanostructures, and sulfur-containing nanocomposites in comparison with known methods is preliminary assessed. Based on data from open sources, it was calculated that

the cost of sulfur nanoparticles obtained by the developed method is three times cheaper than the selling price of commercial sulfur nanoparticles (SkySpring Nanomaterials Inc, USA). Also, on the website of US Research Nanomaterials Inc, we found copper monosulfide microparticles with average particle size of 15 μm which cost more than 300 thousand tenges for 100 g. Typically, copper sulfide nanoparticles are one or two orders of magnitude more expensive than copper sulfide microparticles. Thus, in both case, upon realizing the production of the above nanoparticles will be very rentable.

Volume and structure of the thesis

The thesis consists of an introduction, four sections, a conclusion, and list of references. The work is presented on 106 pages, contains 40 figures, 8 tables, and 159 bibliographical references.