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# SYNTHESIS OF MULTILEVEL ZnS/ZnO NANOSTRUCTURES BY ELECTROSPARK EROSION

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ZnO/ZnS multilevel nanostructures were prepared using the electrospark erosion (ESE)technique. ZnS nanoparticles were produced via self-propagating high-temperature synthesis using stoichiometric mixtures of pure elementary sulfur and Zn nanopowder prepared by the ESE method. According to the XRD analysis data, the phases of ZnO, ZnS were found in the final synthesis products. The SEM observations show that the obtained products are multilevel structures consisting of ZnO spherical particles covered with ZnS nanorods.

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*Keywords:* Electrospark erosion, Self-propagating high-temperature synthesis, Multi-level nanostructures

## 1. Introduction

These latest decades a tendency for fabrication of multilevel sulfide-oxide heterostructures has been developed in materials science. Amongst them, ZnS/ZnO nanostructures have attracted great interest and have been used in various applications [1-5]. These materials represent a semiconductor modified with a semiconductor of wider band-gap and it relates to enhanced luminescence characteristics. ZnS is a wide band gap semiconductor with band gap of 3.7eV whereas ZnO is characterized with that of 3.3 eV. One of the main questions asked by materials scientists consists of organization of multilevel systems using chemical, physical methods and their combinations. Surface modification seems to be one of the most interesting approaches methods to prepare such nanostructured materials. In this paper we consider a possibility of modification of as-prepared zinc oxide nanoparticles with zinc sulfide nanorods because of technological features of electrospark erosion. Electrospark erosion is an efficient technique for fabrication of ultrafine particles of different metals and compounds [6]. This technique provides a possibility to use electrical discharges for activation of physicochemical processes, including chemical modification of as-formed surfaces [7-10]. Besides, it is a good approach to provide viable conditions for the formation of elongated nanostructured 1D-materials like nanorods, nanowires and nanowhiskers. The main advantages of the electrospark erosion technique and properties of the produced nanomaterials are comparable with those of electrical explosion of wires [11-13].

In this work, electrospark erosion (ESE) is considered as a promising method for the fabrication of multilevel ZnS/ZnO nanostructures. This technique is essentially related to electrical discharge activation of physicochemical processes: high energy and high rates of the processes allow generation of nanosized rod- or wire-like crystallites of as-produced materials. As described below, we tried to combine the processes of zinc oxidation and simultaneous growth of zinc

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sulfide elongated nanostructures when electrically eroding zinc granules in a hydrogen peroxide water solution.

## 2. Experimental method

The experimental setup of electrical spark erosion is presented in Fig.1. The setup consists of a reactor and a pulsed power supply. A layer of metal granules is placed on the bottom of the reactor made of dielectric material. External electrodes supplying energy to the granule layer are at opposite walls of the reactor and slightly press the granules in the contact points. A pulse voltage with amplitude of 500-1000 V and pulse duration of 15-20 μs is applied to the external electrodes. The maximal single pulse can vary in the range of 250-500 A. The single pulse energy can change in the range of 0.5-2 J. It is worth to be noted that one voltage pulse leads to the formation of numerous microdischarges having a duration of 5 μs and an energy of ~ $10^{-2}$ - $10^{-4}$ J [6,7,14].

More simply, the mechanism of formation of nanosized particles under pulsed electrical discharge can be presented consisting of 2 parallel processes: (1) melting of metal granule material and electrodes when applying voltage pulses with further release of the material in the form of molten metal droplets with an initial temperature of approximately 2200 K [6, 7] and (2) evaporation of the materials of the medium and electrodes with plasma formation. Thereupon, surface interaction of the molten metal with the liquid medium and its components occurs during fast cooling of the particles (cooling rate is $10^9$ K/s). On completing the process, this interaction results in particles consisting of a metal core coated with a film of interaction products of the metal with the dispersion medium, as well as single particles formed due to radiation-chemical and thermal decomposition of the dispersion medium. The effect of plasma leads to atomization of the medium with consequent recombination and formation of decomposition products which interact with products of the first process forming a highly dispersed composite material. By varying the nature of the liquid dispersion medium, we can impact on the composition and properties of obtained nanoparticles of liquid phase [7]. The use of short electrical pulses (< 20 μs) supports fabrication of nanoparticles [6, 15,16]. Besides, it should be noted that when applying current pulses a hydromechanical effect is observed and accompanied by strong cavitation. Due to this effect, the formed particles are uniformly distributed in all volume of the dispersion medium. Taking into account that the formed primary particles are in a medium with high viscosity, they weakly aggregate and agglomerate up to a certain limit concentration. Thus, process behavior under highly non-equilibrium conditions leads to formation of nanocomposites with a high volume and surface deficiency of the structure and, as consequence, a high chemical activity in various processes.

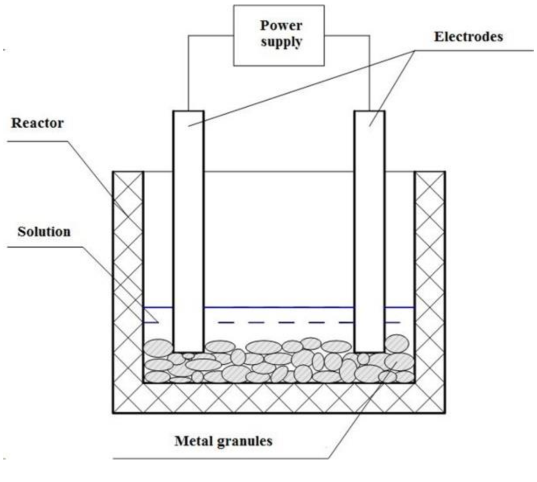

*Fig. 1. Scheme of the experimental setup of electrical spark erosion*

To obtain ZnS/ZnO multilevel hetero-nanostructures the above-described experimental setup was used. For this purpose, chemically pure zinc granules and a 40% $H_2O_2$ water solution were employed. The zinc granules were placed on the bottom of the experiment setup reactor. Then the hydrogen peroxide water solution (200 ml) was poured into the reactor. The ZnS nanostructured powder was added to the as-prepared reaction mixture (Zn granules + $H_2O_2$ water solution) in amounts of 30 wt. % of the Zn granules. ZnS was thoroughly mixed with the reaction mixture before the ESE experiment. After preparing the stable reaction, the voltage was applied to it as described and shown above.

For X-ray diffraction (XRD) measurements of as-prepared materials, a Shimadzu 7000S X-ray diffractometer with $CuK_\alpha$ radiation ($\lambda = 1.54$ Å) was used. The morphology and structure of the synthesized nanostructures were examined using a scanning electron microscope JSM-7500FA (JEOL, Japan), a transmission electron microscope JEM-2100F (JEOL, Japan).

## 3. Results and discussion

Fabrication of multi-level ZnO/ZnS nanostructures in this work is connected to the use of two different methods: self-propagating high-temperature synthesis (SHS) and electrospark erosion (ESE). The employment of these two methods allowed us to combine preparation of zinc oxide nanoparticles and growth of zinc sulfide nanorods on their surface. ZnS nanoparticles were prepared using the self-propagating high-temperature technique described in [17]. In order to produce ZnS nanoparticles by SHS, we used pellets manufactured from stoichiometric mixtures of pure elementary sulfur and zinc nanoparticles prepared by electrospark erosion of zinc granules in hexane. The ESE method allows fabrication of zinc nanoparticles with an average diameter in the range of 5-50 nm. Figure 2suggests TEM observations of the ultrafine particles of zinc sulfide prepared by self-propagating high-temperature synthesis as described in [17]. The zinc sulfide powder presents layered agglomerations of faceted particles of 50-100 nm in length.

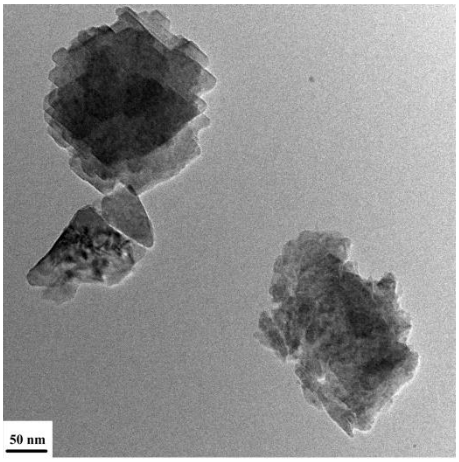

*Fig. 2. TEM micrograph of the ZnS nanopowder produced by self-propagating high-temperature synthesis*

The X-ray diffraction measurements show (Fig. 3) that the main phase of the SHS process is hexagonal zinc sulfide ZnS (Wurtzite-H, JCPDS 05-0492). This XRD data is in a good agreement with the TEM observations. The intensity and the width of the ZnS diffraction peaks illustrate that the zinc sulfide crystallites have the ratio between the horizontal and vertical dimensions which witness their elongated and layered shape.

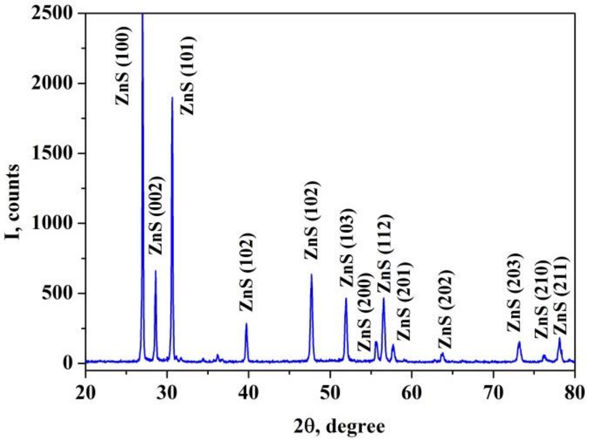

*Fig. 3. X-ray pattern of the ZnS nanopowder produced by self-propagating high-temperature synthesis*

Fig.4 depicts a TEM image of ZnO nanoparticles usually prepared by ESE of zinc granules in a hydrogen peroxide water solution. The products of electrospark erosion of zinc granules are aggregates and agglomerates of nanoparticles having a diameter from 5 to 50 nm. The particle shape is not uniformly spherical but can be slightly faceted. For electrical discharge methods like ESE, it is often connected to oxide formation and the particle surface can include amorphous forms of metal oxides. In a typical ESE experiment, we applied electrospark dispersion of zinc granules in the hydrogen peroxide solution within 20-40 seconds. This period is enough for the formation of ZnO nanoparticles characterized by a rather narrow particle size distribution.

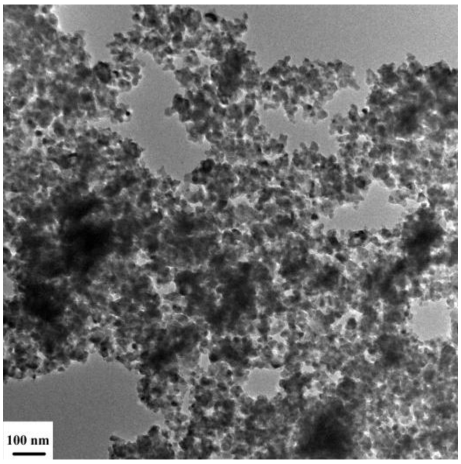

*Fig. 4. TEM micrograph of the ZnO nanoparticles produced by electrospark erosion in a hydrogen peroxide water solution*

Figure 4 describes the ZnO particles generated by the ESE in a hydrogen peroxide water solution in the absence of any additives. Under these conditions, rather uniform particles with a narrow size distribution are formed. We can therefore state that the normal process of ZnO formation under electrospark erosion of zinc granules in a $H_2O_2$ solution in the absence of any additive does not result in elongated particles like nanorods or nanowires. In contrast, it is supposed that the presence of any active additive can lead to the formation of certain elongated structures. In this work we tried to modify this process by adding ZnS nanostructure powder to the reaction zone.

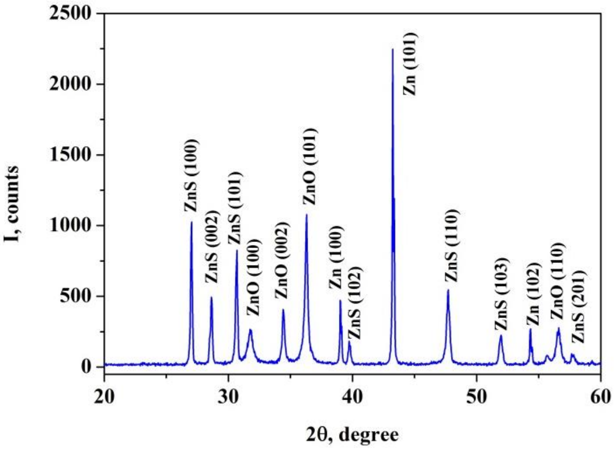

*Fig. 5. X-ray pattern of the multilevel Zn/ZnO/ZnS nanostructures prepared by electrical spark erosion*

Fig. 6 presents an SEM micrograph of the ZnS/ZnO multilevel nanostructures produced by electrospark erosion of zinc granules in a hydrogen peroxide water solution when adding ZnS nanostructured powder. The SEM observations show two types of ZnS-ZnO structures: vertically aligned and urchin-like nanorods on the ZnO particles. Such shape of multilevel structures can be related to strong non-equilibrium conditions of electrospark erosion synthesis. Taking into account the possibility for the formation of radicals under ESE conditions, we can assume that the following reaction can occur:

$$Zn + 2H_2O_2 = ZnO + 2H_2O + O_2$$
$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot}$$
$$2Zn + O_2 = 2ZnO$$

Probably, some $Zn^{\cdot}$ radicals can also form during the electrospark processes. The presence of radicals in the reaction zone can provoke generation of active center on the ZnO particle surface on which ZnS particles can be grafted.

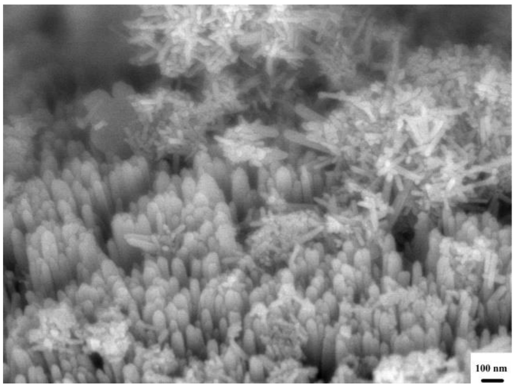

*Fig. 6. SEM micrographof theZnS/ZnO multilevel nanostructures prepared by electrospark erosion*

In our point of view, the formation mechanism of such structures can be described using the following consequence. On the first stage, dispersion of zinc granules occurs according to the mechanism of electrospark erosion with the formation of ultrafine and ultra-active zinc nanoparticles. At this moment particles represent ultrafine products of zinc granule erosion. These as-prepared Zn nanoparticles start to react with hydrogen peroxide immediately with the formation of ZnO nanoparticles. The presence of radicals can provide of active centers on the ZnO particle surface which can lead to the formation of ZnS nuclei and the growth of zinc sulfide nanorods and urchin-like particles.

## 4. Conclusions

Multilevel ZnS/ZnO nanostructures were prepared using the electrospark erosion technique. Synthesis of ZnO nanoparticles was accompanied by the growth of ZnS nanorods on the surface of as-formed ZnO particles when electrical eroding Zn granules in the $H_2O_2$ water solution. Two types of ZnS-ZnO structures were found: vertically aligned and urchin-like nanorods on the ZnO particles. Such shape of multilevel structures can be related to strong non-equilibrium conditions of electrospark erosion synthesis.

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